STUDY ON WASTE WATER TREATMENT PROCESS AND ASSESSMENT OF HEAVY METAL CONCENTRATION IN DIFFERENT TYPES OF ETP AND STP IN SOME INDUSTRIES AT CHATTOGRAM REGION

By

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A thesis submitted in partial fulfilment of the requirements for the degree of Master of Philosophy in Chemistry

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CHITTAGONG UNIVERSITY OF ENGINEERING & TECHNOLOGY

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DECLARATION

I hereby declare that the work contained in this Thesis has not been previously submitted to meet requirements for awarding of any degree at this or any other higher education institution. To the best of my knowledge and belief, the Thesis contains no material previously published or written by another person except where due reference is cited. Furthermore, the Thesis complies with the PLAGIARISM and ACADEMIC INTEGRITY regulations of CUET.

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DEDICATION

Dedicated

To

My Beloved Parents

APPROVAL/DECLARATION BY THE SUPERVISOR

This is to certify that Md. Kamrul Hassan has carried out this research work under my supervision, and he has fulfilled the relevant requirements of the Academic Ordinance of the Chittagong University of Engineering and Technology so that he is qualified to submit the following Thesis in the application for the degree of Master of Philosophy in Chemistry. Furthermore, the Thesis complies with the PLAGIARISM and ACADEMIC INTEGRITY regulations of CUET.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometer
APHA	American Public Health Association
BBS	Bangladesh Bureau of Statistics
BCAS	Bangladesh Center for Advanced Studies
BCIC	Bangladesh Chemical Industries Corporation
BOD_5	Biological Oxygen Demand
BSIE	Bangladesh Standard for Industrial Effluent
DO	Dissolved oxygen
D.S.	Dry Season (January–February)
COD	Chemical Oxygen Demand
DoE	Department of Environment
EPA	Environmental Protection Agency
ETP	Effluent Treatment Plant
EU-DIR	Directives of the European Union
KAFCO	Karnaphuli Fertilizer Company Limited
LDC	Least Developed Country
M.S.	Monsoon Season (July–August)
STPs	Sewerage Treatment Plants
TDS	Total Dissolved Solids
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

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Md. Kamrul Hassan, M. Mehedi Hasan Rocky & M. K. Mohammad Ziaul Hyder

Abstract

This study aims to investigate the wastewater treatment process and assess the industrial wastewater quality before and after being treated by effluent treatment plants (ETPs) of steel-galvanizing industries located in Mirsharai, Sitakunda, Karnaphuli, and Kalurghat industrial areas of Chattogram, Bangladesh. Wastewater samples were collected from six steel-galvanizing industries during the dry season and monsoon season. The water quality was evaluated based on five physicochemical parameters, namely pH, dissolved oxygen (DO), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total dissolved solids (TDS), as well as the concentration of heavy metals including Fe, Cu, Cr, Ni, and Cd. The measured data were compared with the national and international standards established for ensuring water safety. It was observed that steel plants generate complex wastewater rich in highly dissolved solids and heavy metal ions. Although pH, BOD_5, and COD values were within acceptable ranges in these industries, high TDS values were observed. The Fe concentration of discharged stream areas ranged from 0.992 to 16.89 mg/L, exceeding the guideline limits. Additionally, the Cr concentration in both the inlet and outlet exhibited high concentrations, surpassing the standard limits, particularly those set by the United States Environmental Protection Agency (US EPA). Thus, steel-galvanizing industries are likely contributing to water pollution through the discharge of wastewater, particularly in terms of Fe and Cr. The efficiency of ETPs varied for different metals. Furthermore, this study highlighted the importance of the effective design of ETPs to mitigate potential pollution and promote sustainable practices.

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<u>Title & Abstract</u>

Evaluation of the capability of wastewater treatment in steel galvanizing industries in Chattogram, Bangladesh

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Abstract: This study aims to investigate the wastewater treatment process and assess the industrial wastewater quality before and after being treated by effluent treatment plant (ETP) of steel industries situated in Mirsharai,Sitakunda, Karnaphuli, and Kalurghat industrial areas of Chattogram, Bangladesh. This study collected wastewater samples from six steel industries during the dry and monsoon seasons. The water quality was evaluated based on five physio-chemical parameters, namely pH, dissolved oxygen (DO), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total dissolved solids (TDS), and concentration heavy metals Fe, Cu, Cr, Ni, and Cd. The collected data were compared with the World Health Organization (WHO) and Bangladesh Standard for Industrial Effluent (BSIE) standards. We found that steel plants generate complex liquid waste or wastewater rich in highly dissolved solids, suspended particles, and heavy metal ions. It was observed that although pH, BOD_5, and COD values were within acceptable ranges in the steel industry, high TDS values were observed. The Fe concentration of discharged stream areas ranged from 0.992 mg/L to 16.89mg/L, exceeding the WHO guideline limits, indicating probable Fe pollution. The Cr concentration of the inlet aries from 0.0799 mg/L to 1.326 mg/L, exceeding the range of WHO and BSIE standards and suggesting that such industries are a probable source of Cr contamination. The ETP plants maintained well for other metals Cu, Ni, and Cd. The study concludes that the findings could help industries pick up best practices and inform policymakers in developing new frameworks for improving industrial sustainability.

ABSTRACT

This study delves into a comprehensive assessment of Wastewater Treatment Plants including Effluent Treatment Plants (ETPs) and Sewerage Treatment Plants (STPs) within diverse industries in Chattogram Division, Bangladesh. The investigation was mainly focused on the analysis of ETP samples obtained from the steel and paint industries located in Mirsharai, Sitakunda, Karnaphuli, and Kalurghat industrial areas of Chattogram, as well as STP samples collected from hotels in Cox's Bazar of Chattogram Division. These industries release complex liquid waste rich in dissolved solids, suspended particles, and heavy metal ions. Considering the economic and environmental significance of Chattogram and the detrimental effects of water pollution on ecosystems, the assessment of the discharge of effluents from those industries into water bodies becomes imperative. Thus, this study aims to find out the operational maintenance practices in wastewater treatment plants and to analyze the water quality in ETP samples and STP samples from the industries mentioned above in terms of studying various physio-chemical parameters before and after discharge from the treatment plants. Effluent samples were collected from the ETPs and STPs bi-annually during the dry season (D.S., January- February) and monsoon season (M.S., July- August) using systematic and standardized analytical methods. Sampling procedures involved collecting effluent samples from both the inlet and outlet points of the industrial ETPs and STPs. The water quality was evaluated based on five physio-chemical parameters, namely pH, dissolved oxygen (DO), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total dissolved solids (TDS), as well as the concentration of heavy metals including Fe, Cu, Cr, Ni, and Cd. The results were compared to national and international regulations, such as the Bangladesh Standard for Industrial Effluent (BSIE) of Department of Environment (DoE), World Health Organization (WHO) guidelines, European Union Directives (EU-DIR), and US Environmental Protection Agency (US EPA). It was observed that steel-galvanizing industries generate complex wastewater rich in highly dissolved solids and heavy metal ions. Although pH, BOD_5, and COD values were within acceptable ranges in these industries, high TDS values were observed. The Fe concentration of discharged stream areas ranged from 0.992 mg/L to 16.89 mg/L, exceeding the guideline limits. Additionally, the Cr concentration in both the inlet and outlet exhibited high concentrations, surpassing the standard limits, particularly those set by the US EPA. Thus, steel-galvanizing industries are likely contributing to water pollution through the discharge of wastewater, particularly in terms of Fe and Cr. In the case of the Paint Industries, after treatment, Fe concentration of discharged stream areas ranged from 2.333 mg/L to 5.117 mg/L exceeded the guideline limits of WHO and BSIE standards and indicated probable water pollution by Fe. Ni in those samples was under the safe limit, and Cd was found under the detectable limit. This study examined the operation of STPs in three Hotel Industries and assessed their impact on water quality in Cox's Bazar, Chattogram Division. Notably, pH levels remained relatively stable, while DO levels fluctuated. The fluctuations of COD levels reflect the presence of various pollutants and similar trends were observed for BOD_5. Additionally, TDS indicated the presence of dissolved substances and solid particles. Furthermore, elevated nitrate and phosphate levels raised concerns about nutrient pollution and eutrophication. Fe concentrations remained within regulatory limits, but Cu exceeded limits in specific areas, requiring further investigation. Cr concentrations were within acceptable ranges, while Mn levels significantly exceeded defined limits. Finally, the findings of this study underscore the importance of adopting comprehensive measures and optimizing wastewater treatment processes to address pollution in different industries.

KEYWORDS: Effluent, Chattogram, Sewerage, Treatment plants, Heavy metals, Wastewater; Environment.

বিমূর্ত

বাংলাদেশের চট্টগ্রাম বিভাগে অবস্থিত বিভিন্ন শিল্পের মধ্যে ইফ্লুয়েন্ট ট্রিটমেন্ট প্ল্যান্ট (ই.টি.পি.) এবং স্যুয়ারেজ ট্রিটমেন্ট প্ল্যান্ট (এস.টি.পি.) সহ তরলবর্জ্য পরিশোধনের গুণগত চিত্র এই গবেষণায় উপস্থাপিত হয়েছে। এজন্য চট্টগ্রামের মিরসরাই, সীতাকুণ্ড, কর্ণফুলী এবং কালুরঘাট শিল্প এলাকায় অবস্থিত স্টিল-গ্যালভানাইজিং ইন্ডাস্ট্রি ও পেইন্ট ইন্ডাস্ট্রি থেকে সংগৃহীত ই.টি.পি. নমুনা এবং কক্সবাজারের অবস্থিত বিভিন্ন হোটেল ইন্ডাস্ট্রি থেকে প্রাপ্ত এস.টি.পি. নমুনা বিশ্লেষণ করা হয়েছে। এসব শিল্প হতে বিভিন্ন ধরনের জটিল প্রকৃতির তরল মিশ্রণ উৎপন্ন হয় যাতে দ্রবীভূত কঠিন কণা, এবং ক্ষতিকারক ভারী ধাতুর উপস্থিত থাকে। চট্টগ্রামের অর্থনৈতিক ও পরিবেশগত তাৎপর্য এবং বাস্তুতন্ত্রের উপর ধাতব দূষণের ক্ষতিকর প্রভাব বিবেচনা করে, এসব শিল্প থেকে নিকটস্থ জলাধারে তরলবর্জ্য নির্গত হলে তার দূষণ চিত্র অনুধাবন গবেষণার জন্য একটি গুরুত্বপূর্ণ বিষয়। এই গবেষণার লক্ষ্য হল তরলবর্জ্য শোধনাগারগুলিতে কার্যকরী রক্ষণাবেক্ষণের অনুশীলন অনুসন্ধান করা, এবং উপরে উল্লিখিত শিল্পগুলি থেকে ই.টি.পি. ও এস.টি.পি. ইত্যাদি ট্রিটমেন্ট প্লেন্টের তরলবর্জ্যের প্রবেশ ও নিষ্কাশনের সময় ভৌত-রাসায়নিক প্যারামিটার নির্ণয় করা। ই.টি.পি. এবং এস.টি.পি. থেকে শুষ্ক মৌসুমে (জানুয়ারি-ফেব্রুয়ারি) এবং বর্ষা মৌসুমে (জুলাই-আগস্ট) রাসায়নিক বিশ্লেষণ পদ্ধতি ব্যবহার করে দ্বি-বার্ষিকভাবে তরলবর্জ্যের নমুনা সংগ্রহ করা হয়েছে। ই.টি.পি. এবং এস.টি.পি -এর ইনলেট এবং আউটলেট পয়েন্ট উভয় থেকে তরলবর্জ্যের নমুনা সংগ্রহ করা হয়েছে। পানির গুণমান পাঁচটি ভৌত-রাসায়নিক পরামিতির উপর ভিত্তি করে মূল্যায়ন করা হয়েছে যা হল pH, দ্রবীভূত অক্সিজেন (DO), বায়োলজিক্যাল অক্সিজেনের ডিমান্ড (BOD5), কেমিক্যাল অক্সিজেনের ডিমান্ড (COD), টোটাল ডিসল্ভড সলিড (TDS), এবং পাঁচটি গুরুত্বপূর্ণ ভারী ধাতুর ঘনমাত্রা (Fe, Cu, Cr, Ni, এবং Cd সহ ধাতু)। এসব পরামিতির ফলাফল জাতীয় ও আন্তর্জাতিক স্টান্ডার্ড এর সাথে তুলনা করা হয়েছে, যেমন পরিবেশ অধিদপ্তর এর বাংলাদেশ স্ট্যান্ডার্ড ফর ইন্ডাস্ট্রিয়াল ইফ্লুয়েন্ট (BSIE), বিশ্ব স্বাস্থ্য সংস্থা (WHO) নির্দেশিকা, ইউরোপীয় ইউনিয়নের নির্দেশিকা (EU-DIR), এবং ইউ.এস. এনভায়রনমেন্টাল প্রোটেকশন এজেন্সি (US EPA)। গবেষণার তথ্য পর্যালোচনায় দেখা যায় যে, ইস্পাত-গ্যালভানাইজিং শিল্পগুলি উচ্চ দ্রবীভূত কঠিন এবং ভারী ধাতু আয়ন সমৃদ্ধ জটিল তরলবর্জ্য উৎপন্ন করে। pH, BOD5, এবং COD এর মান এই শিল্পগুলির ই.টি.পি. কর্তৃক গ্রহণযোগ্য সীমার মধ্যে বিরাজ করে, যদিও উচ্চ TDS মান পরিলক্ষিত হয়। নিঃসৃত স্রোত হতে Fe ঘনত্ব 0.992 mg/L থেকে 16.89 mg/L, নির্দেশিকা সীমা অতিক্রম করে। উপরন্তু, ইনলেট এবং আউটলেট উভয় ক্ষেত্রেই Cr ঘনত্ব উচ্চ ঘনমাত্রা লক্ষিত হয়, যা US EPA এর নির্দেশিত রেফেরেন্স অতিক্রম করে। অতএব ইস্পাত-গ্যালভানাইজিং শিল্প তরলবর্জের নিষ্কাশনের মাধ্যমে পানিদূষণে সম্ভব্য ভূমিকা রাখতে পারে, বিশেষ করে Fe এবং Cr এর পরিপ্রেক্ষিতে। পেইন্ট ইন্ডাস্ট্রিজের ক্ষেত্রে, ট্রিটমেন্টের পরে নিঃসৃত স্ট্রীম এলাকায় Fe এর ঘনত্ব 2.333 mg/L থেকে 5.117 mg/L, এইভাবে WHO এবং BSIE মানের নির্দেশিকা সীমা অতিক্রম করে এবং সম্ভাব্য Fe দূষণ নির্দেশ করে। নমুনাগুলিতে Ni নিরাপদ সীমার অধীনে ছিল এবং Cd সনাক্তযোগ্য সীমার নীচে বিরাজ করেছে। এই সমীক্ষায় তিনটি হোটেল ইন্ডাস্ট্রিতে এস.টি.পি. এর নমুনা মূল্যায়ন করা হয়েছে। উল্লেখযোগ্যভাবে, pH এর মান তুলনামূলকভাবে স্থিতিশীল ছিল, যখন DO এর মানের হ্রাস-বৃদ্ধি লক্ষিত হয়। COD ও BOD5 এর মান বিভিন্ন দূষকের উপস্থিতি নির্দেশ করে। টিডিএস দ্রবীভূত পদার্থ এবং কঠিন কণার উপস্থিতি নির্দেশ করে। উচ্চতর নাইট্রেট এবং ফসফেটের মাত্রা হতে পুষ্টিকারী দূষণ এবং ইউট্রোফিকেশনের সম্ভব্য দূষণ আলোচিত হয়েছে। Fe ঘনমাত্রা রেফেরেন্স সীমার মধ্যে বিরাজ করে, কিন্তু Cu এর ঘনমাত্রা কয়েকটি বিন্দুতে সীমা অতিক্রম করেছে, যা নিশ্চিতে অধিক গবেষণা প্রয়োজন। যদিও Cr ঘনমাত্রা গ্রহণযোগ্য সীমার মধ্যে ছিল, Mn ঘনমাত্রা উল্লেখযোগ্যভাবে রেফারেন্স সীমা অতিক্রম করেছে। সার্বিকভাবে, এই গবেষণার ফলাফলগুলি বিভিন্ন শিল্পে দূষণ মোকাবেলায় যথাযথ ব্যবস্থা গ্রহণ এবং শিল্পের জলীয় বর্জ্যের ট্রিটমেন্টের পক্রিয়াকে পরিমিত করার পদক্ষেপ গ্রহণের গুরুত্বকে তুলে ধরে।

CHAPTER – 1: INTRODUCTION

1.1 Background

The increasing demand for water and the limited availability of freshwater resources have led to the development of more complex and extensive water treatment methods. Recent technological advancements and expanding human knowledge have resulted in several successful and environmentally friendly ways of treating wastewater [1]. Improper industrial water and wastewater treatment can result in a variety of issues, including corrosion, scale buildup, decreased heat transfer in heat exchangers, reduced water flow, and product contamination [2].

Therefore, efficient and cost-effective treatment of industrial water is crucial, and it necessitates the consideration of factors such as water source quantity and quality, water usage sequencing, water recycling, and discharge requirements during the design and operation of an industrial water treatment facility [3]. **Fig. 1.1** displays the wastewater treatment approaches tailored for reuse in addressing the water crisis amid rising demand and limited freshwater resources with advanced treatment technologies.

Water pollution can result from a range of sources, including natural sources and human activities such as industrial growth and urbanization [4]. Industrialization is a major contributor to water pollution; **Table 1.1** shows the types of pollutants that can be released from various industrial sectors.

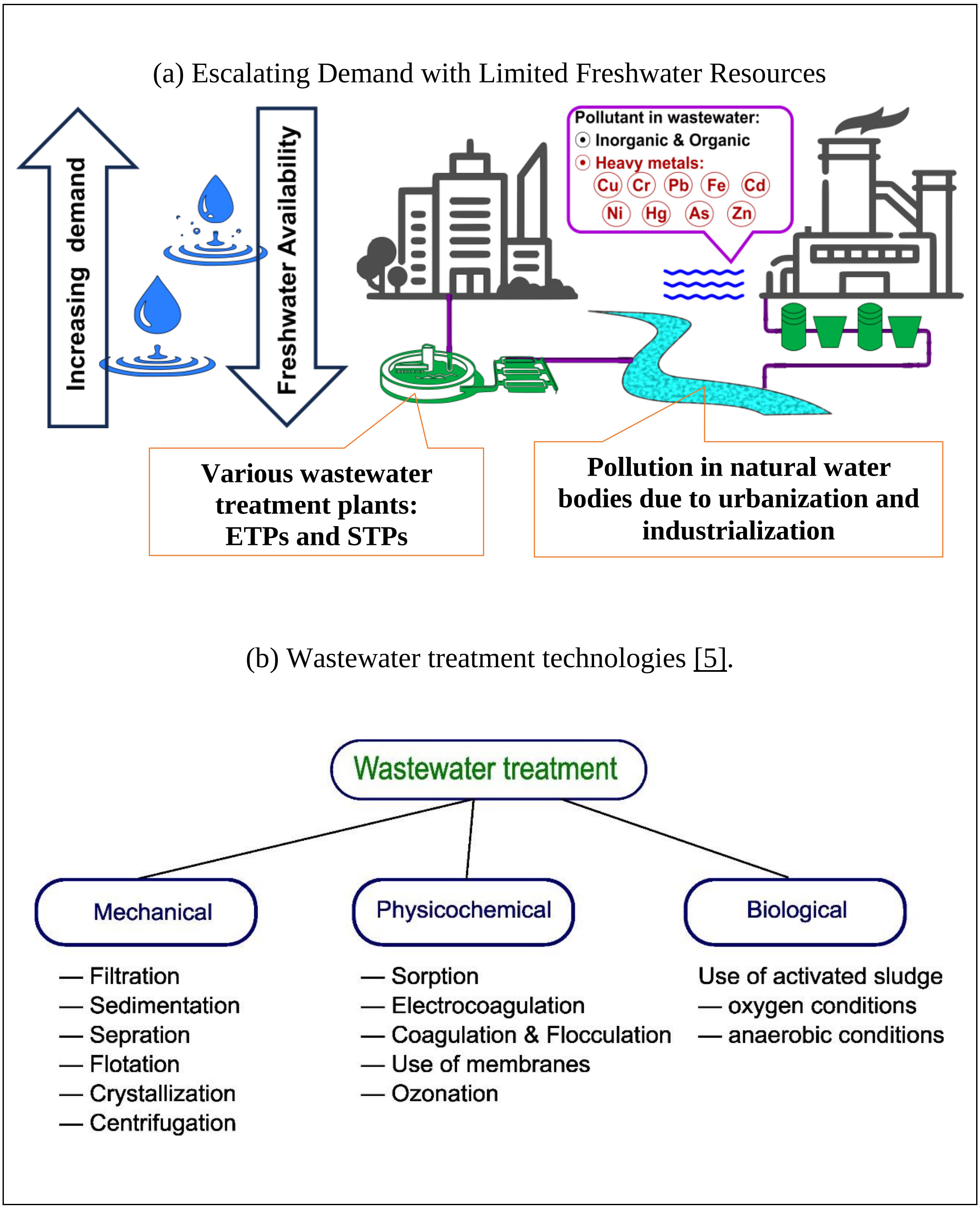

Fig. 1.1. Navigating the Water Crisis: Escalating Demand with Limited Freshwater Resources through Advanced Treatment Technologies.

Table 1.1

Water Pollutants Discharged from Various Industries [5-7]

Industry	**Types of Pollutants**
Steel and metal processing	BOD_5, COD, oil, metals, acids, cyanide, and other toxic heavy metals.
Textile and garment	BOD_5, suspended solids, dyes, and heavy metals such as Pb and Cd.
Leather and tannery	BOD_5, COD, TDS, sulfides, Cr, and other toxic heavy metals such as Pb and Cd.
Pulp and paper	BOD_5, COD, solids, organics, chlorinated compounds, and other chemicals.
Food processing	BOD_5, COD, TDS, oil, grease, and suspended solids.
Pharmaceuticals	BOD_5, COD, nitrates, sulfates, and other chemical by-products of the manufacturing process.
Petrochemicals	BOD_5, COD, mineral oil, phenols, metals, and other chemicals used in the processing.
Chemicals	COD, organics, heavy metals, suspended solids, and other toxic chemicals are used in the manufacturing process.

Industrial effluents pose a substantial challenge due to the accumulation of toxic waste containing a wide array of poisonous chemicals, including both inorganic and organic pollutants, along with commonly found heavy metals such as copper (Cu), chromium (Cr), lead (Pb), iron (Fe), cadmium (Cd), nickel (Ni), mercury (Hg), and arsenic (As), etc. [8, 9]. These harmful substances can be released into the environment through various sources, such as dental applications and industries involved in tanning, steel and galvanizing, paint, textiles, electrolysis, paper, and pulp production, among others [10]. The quality of water is primarily determined by its physical, chemical, and microbial characteristics, which play a crucial role in assessing water quality [5]. **Fig. 1.2** depicts the assessment of water quality for various purposes.

Water pollution in Bangladesh is primarily caused by sewage, industrial waste, and effluents. Industrial wastewater or effluents, when released into water bodies, result in a considerable decline in water quality [4]. During the winter, pollutants accumulate in stagnant water, causing high levels of pollution, whereas in the monsoon season, rainfall water dilutes pollution levels, resulting in lower concentrations of pollutants [11]. Industrial pollutants are the main contributors to surface water pollution in urban areas of the country.

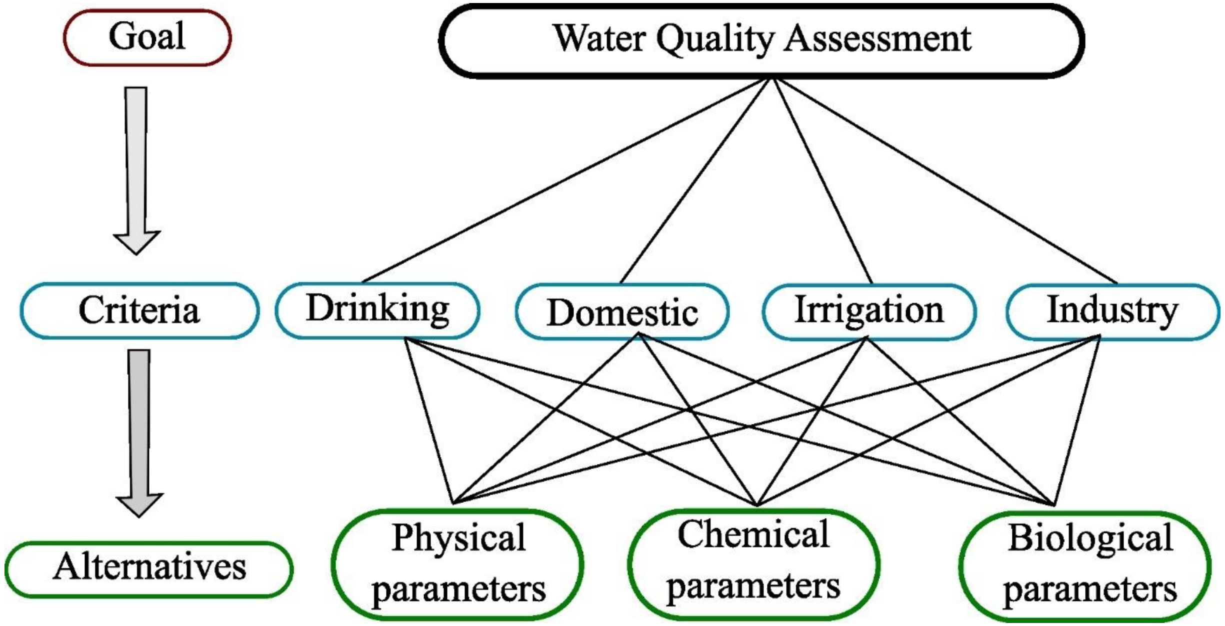

Fig. 1.2. Water quality assessment [5].

A survey conducted by the Bangladesh Center for Advanced Studies (BCAS) revealed a low implementation rate of Effluent Treatment Plants (ETPs) among industries, with a significant portion currently in the process of constructing ETPs, while a considerable number of industries have yet to establish any ETPs for managing their wastewater [12]. In 10% of industrial sectors, ETPs were under construction and about 50% of industries had no ETP establishment. In terms of overall wastewater discharge into natural waterbodies, the pulp and paper industry is the major contributor (47%), followed by pharmaceuticals (16%), metal (14%) and food industries (12%), fertilizers/pesticides (7%), industrial chemicals (1%) and other industries (3%) which includes the cumulative contribution of cement and clay, textile, wood and furniture, tanneries and leather and petroleum industries. To evaluate water pollution in natural water bodies of Bangladesh, various research was conducted by assessing various physio-chemical parameters such as pH, chemical oxygen demand (COD), biological oxygen demand (BOD, specifically BOD_5), dissolved oxygen (DO), and total dissolved solids (TDS) [4, 8, 13]. Along with the analysis of toxic/heavy metal contents; the obtained results were compared against national and international regulations, including the Bangladesh Standard for Industrial Effluent (BSIE), guidelines provided by the World Health Organization (WHO), the Directives of the European Union (EU-DIR), and the United States Environmental Protection Agency (US EPA) [11, 12, 14, 15].

1.2 Water Pollution by Heavy Metals

Several studies have investigated the extent of contamination by heavy metals from the steel industry in Bangladesh. For example, a study by Islam *et al.* [16] found that soil, water, and air pollution in the vicinity of a steel plant in Bangladesh were significantly higher than the recommended levels set by the World Health Organization (WHO). Another study by Tahir *et al*. [17] found that the concentration of Cd in rice grown near the same steel plant was also above safe levels, indicating that the contamination had spread to the local agricultural sector. **Table 1.2** presents different industrial sources of heavy metal pollution in natural water bodies, along with the maximum allowed concentrations according to BSIE, WHO, EU-DIR, and US EPA. The decline in water quality is of utmost importance as it significantly impacts soil, aquatic ecosystems, and human life. The improper discharge of untreated wastewater from these industries into nearby rivers further exacerbates water pollution issues. Therefore, it is necessary to assess the quality of wastewater considering the potential impacts associated with its discharge into water bodies.

Table 1.2

Standard Limits and Industrial Sources of Heavy Metals Pollution in Waters and Their Adverse Effects on Human Health

Heavy metal	Safe limit (mg/L)*	Industrial sources	The main organ and system affected
Fe	0.3[a,d], 0.45[b], 2.0[c]	Iron ore mining, steel galvanizing, construction materials, automotive industry, machinery, appliances, shipbuilding, and metal fabrication.	Cancer risk, aging, heart disease, Parkinson's disease, growth element for diseases, gastrointestinal stress, and oxidative damage to biological membranes.
Cu	2.0[a], 0.14[b], 0.5[c], 1.3[d]	Plumbing materials, electronic industry, mining and ore processing, agriculture, and pesticides.	Liver, brain, kidneys, cornea, gastrointestinal system, lungs, immunological system, and hematological system.
Cd	0.003[a], 0.05[c], 0.0025[d]	Batteries, paints, plastic stabilizers, metal refineries, galvanized pipes, mining, and pigments.	Bones, liver, kidneys, lungs, testes, brain, immunological, and cardiovascular systems.
Cr	0.05[a], 0.5[c], 0.011[d]	Steel mills, tanneries, leather processing, electroplating, and metalworking.	Skin, lungs, kidneys, liver, brain, pancreas, tastes, gastrointestinal system, and reproductive system
Ni	0.02[a], 0.034[c], 0.052[d]	Steel and nickel-containing alloy manufacture, electroplating, mining, smelting, and fertilizer.	Lung, kidney, gastrointestinal distress, pulmonary fibrosis, and skin.
Pb	0.01[a,c], 0.0025[d]	Batteries, paints, gasoline, pipes, roofing, ammunition, and solder.	Bones, liver, kidneys, brain, lungs, cardiovascular, and reproductive systems.
Hg	0.0020[d]	Coal-fired power plants, dental fillings,	Brain, lungs, kidneys, liver, immunological, reproductive

Heavy metal	**Safe limit (mg/L)***	**Industrial sources**	**The main organ and system affected**
		thermometers, batteries, etc.	systems.
Zn	3.0^{a}, $5.0^{c,d}$	Brass coating, rubber, cosmetics, aerosol products, galvanizing, metal plating, finishing, mining, and fertilizer.	Stomach cramps, skin irritations, vomiting, nausea, anemia, and convulsions.

*Note: [a]WHO, [b]EU-DIR, [c]BSIE, [d]US EPA. Source: [4, 18]

1.3 Statement of Problem

Chattogram (also known as Chittagong), the second-largest city in Bangladesh, is a major seaport located in the southeastern part of the country (22° 13' N–22° 27' N and 91°40'E-91°53'E) facing the Bay of Bengal [19]. With a land area of 157 km^2, Chattogram plays a significant role in national exports and imports, boasting a thriving economy closely tied to the domestic market. The city is home to some of the oldest and largest industries in the world, including steel, cement, fertilizers, and chemical production [20]. Despite its potential, Chattogram faces several challenges due to overpopulation and the growth of industrial sectors. As a result, it is crucial to investigate the environmental impact of the industries in the region. The Karnaphuli River plays a crucial role as the largest and most significant river in Chattogram, as it is used for household, irrigation, and industrial purposes [4]. Unfortunately, the river has become highly polluted in recent years due to the discharge of untreated industrial effluents from spinning mills, dyeing cotton, textiles, steel mills, fertilizer, oil refineries, cement plants, bitumen plants, and domestic sewage, as evidenced by very high levels of BOD_5, COD, and *E. coli* content [6, 7]. Moreover, the shipbreaking industry and other steel and galvanizing industries in Chattogram contribute significantly to trace metal pollution in seawater and groundwater in the coastal region of Bangladesh [21].

The steel-galvanizing industries are the major contributors to material consumption, energy consumption, CO_2 emissions, and particulate matter emissions [3, 22]. These industries are also significant water consumers, as illustrated in **Fig. 1.3**, depicting the water consumption cycle.

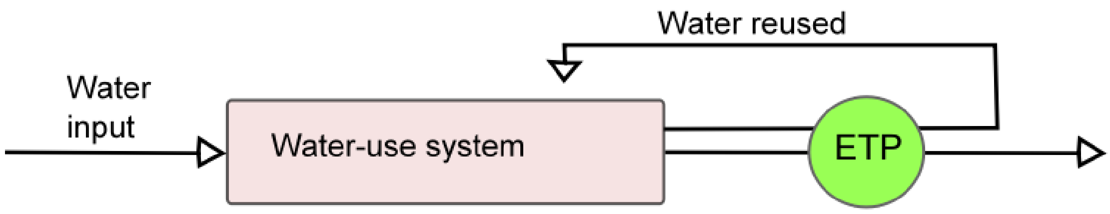

Fig. 1.3. Water Consumption, Reuse, and ETP in the Water-consuming Industry.

Steel plants generate complex process mixtures involving coking, sintering, ironmaking, steelmaking, hot rolling, and cold rolling processes [23]. The wastewater from the blast furnace unit of the steel-galvanizing industry is rich in highly dissolved solids, suspended particles, and ions. Improper wastewater treatment can cause ecological instability, harm receiving streams, and introduce hazardous chemicals that can affect living beings and the food chain. Despite various studies conducted previously, a comprehensive assessment of the situation is still required [4, 11, 24].

Paints are stable mixtures of pigments, which provide color and protect against UV rays, suspended in drying oils called vehicles [25]. Paints can serve protective or decorative purposes when applied to surfaces like metal or wood through methods such as brushing, dipping, spraying, or roller coating. Paint manufacturing industries use large quantities of water and chemicals, producing large volumes of wastewater [1, 8]. Paint industry wastewater is highly polluted wastewater that needs immediate attention for its treatment methodology before its disposal.

The coastal environment and marine ecosystem of Cox's Bazar in Chattogram Division, a renowned tourist destination, are facing contamination due to untreated sewage discharged by numerous hotels, motels, and resorts. The untreated sewage contributes to pollution during peak tourist seasons and monsoons, endangering marine life, biodiversity, and the overall city ecosystem. The frequent problems associated with Sewerage Treatment Plants (STPs) in Bangladesh include failing downstream equipment, inadequately treated effluent, odor issues, insufficient air supply, exceeding prescribed drainage limits, sludge leakage, and low dry matter content. Addressing these issues is crucial for effective wastewater treatment and environmental preservation.

1.4 Objectives and Goals

The present study aims to evaluate the wastewater quality of ETPs and STPs of different industries in the Chattogram region and also evaluate the treatment process. The collection of samples is as follows:

- ETP samples of 6 Steel-Galvanizing Industries
- ETP samples of 2 Paint Industries
- STP samples of 3 Hotel Industries

The ETP samples were taken in two distinct periods: the Dry Season (D.S.: January–February) and the Monsoon Season (M.S.: July–August).

The objectives of the present study are:

- To assess wastewater treatment processes of ETPs and STPs of different industries located in the Chattogram region.
- To assess wastewater of ETPs and STPs collected from different industries in the Chattogram region.
- To analyze physicochemical parameters (pH, DO, COD, BOD5, and TDS) and heavy metal contents (Fe, Cu, Cr, Ni, and Cd) of wastewater before and after treatment and in different seasons.
- To compare the quality of wastewater with national and international standards set by authoritative bodies like BSIE, WHO, EU-DIR, and US-EPA.
- To enhance knowledge in the field and contribute to the reduction of heavy metal pollution in effluent treatment plants.

Successful completion of this research will advance knowledge in the field. It promises to enhance the present level of understanding in this area.

CHAPTER – 2: REVIEW OF LITERATURE

2.1 Review on Industrial Transformation and Environmental Challenges

Bangladesh has recently achieved the transition from a low-income to a lower-middle-income country, as indicated by the World Bank [26]. The country aspires to further advance from its Least Developed Country (LDC) status to attain middle-income classification, a goal outlined by the United Nations [4]. The industrial landscape in Bangladesh encompasses diverse sectors including mining, manufacturing, electricity, gas, water supply, and construction. Notably, key industries like textiles, leather, food products, tobacco, pharmaceuticals, machinery, paper, cement, sugar, and chemicals have emerged [27]. Although the industrialization journey commenced gradually in the 1950s, with a primary focus on agro-based enterprises such as jute, cotton, and sugar, it rapidly gained momentum in the late 1970s, especially with the remarkable growth of the ready-made garment industry after the nation's independence in 1971 [27]. The government's proactive measures, such as establishing industrial estates and export processing zones, played a pivotal role in this trajectory. The textile and chemical sectors have demonstrated substantial progress, with 4560 registered textile industries and notable urea fertilizer production by Bangladesh Chemical Industries Corporation (BCIC) and Karnaphuli Fertilizer Company Limited (KAFCO), a joint venture between the government and foreign entities.

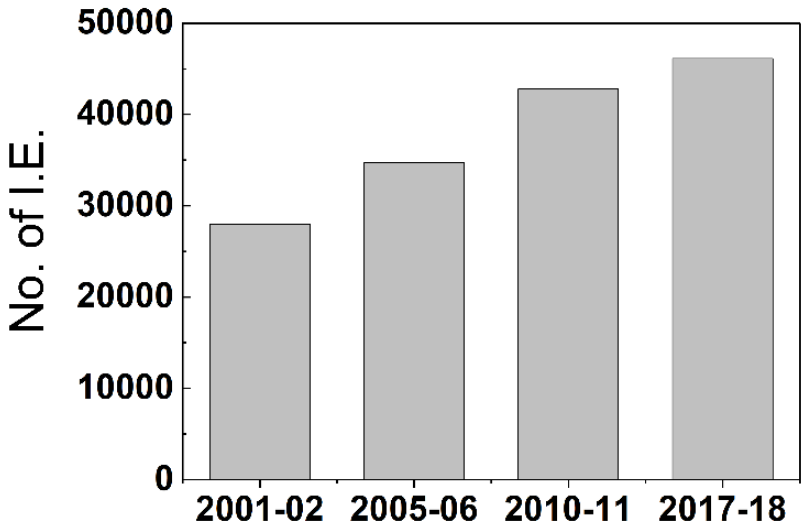

Fig. 2.1. Number of Industrial Establishments (No. of I.E.) Per Year. Based on Data From the Bangladesh Bureau of Statistics (BBS).

The number of industrial establishments in Bangladesh has been increasing steadily over the past few decades as presented in **Fig. 2.1**. In 2012, there were an estimated 31,793 industrial establishments in Bangladesh. This number increased to 46,110 in 2019. The growth of the industrial sector has been driven by several factors, including the country's growing population, rising incomes, and increasing investment in infrastructure [28].

Afolalu et al. (2022) [5] examined waste pollution, wastewater treatment, and its impact due to population growth and urbanization. Poor disposal of industrial and municipal wastewater leads to pollution with inorganic compounds and heavy metals, contributing to global warming and posing threats to human and ecological health.

These industrial advancements, while contributing significantly to the national economy and overall development, have also led to the generation of substantial wastewater, prompting the need for careful environmental management.

2.2 Review on Heavy Metal Pollution in Bangladesh

Hasan et al. (2019) [12] investigated water pollution in densely populated Bangladesh, finding widespread contamination of surface and groundwater sources with toxic trace metals, coliforms, and pollutants, leading to high health risks, especially due to elevated arsenic levels. Anthropogenic sources such as industrial effluents, waste disposal, and agricultural runoff contribute to severe water pollution and associated public health risks.

Alam et al. (2020) [29] assessed heavy metal concentrations in water, soil, and plants near a landfill in Bangladesh, revealing elevated levels of metals like Mn, Fe, Pb, Cu, Zn, and Cd, posing potential health risks. The study highlights pollution concerns exceeding permissible limits, notably in water samples, with a notable positive correlation among metal contents.

Ali et al. (2016) [7] investigated heavy metal contamination in water and sediment of the Karnaphuli River, Bangladesh, revealing unsafe levels of arsenic, chromium, cadmium, and lead in water for drinking or cooking, emphasizing the urgent need for ongoing monitoring and ecological protection. Sediment contamination indicators indicated high pollution by arsenic, cadmium, and lead, prompting the call for continued assessment and risk management in the river's ecosystem.

Parvin et al. (2022) [24] conducted an extensive review of water quality in Bangladesh, revealing critical pollution issues due to industrialization, urbanization, and agricultural practices, resulting in elevated heavy metal levels, fecal pollution, and emerging contaminants such as pesticides, antibiotics, fluorescence agents, and microplastics, highlighting the urgent requirement for stringent water quality regulations.

Briffa et al. (2020) [2] explored heavy metal pollution's global impact, discussing its origins, entry into the environment, and toxic effects on human health, highlighting the association between bioaccumulation of these pollutants, organ damage, and serious diseases, underscoring the urgent need for awareness and mitigation.

Dey et al. (2021) [30] evaluated heavy metal contamination in Bangladesh's Halda River, revealing elevated concentrations of Cd, Cr, Fe, Pb, Cu, and As beyond WHO limits, mainly attributed to industrial effluent discharge, necessitating urgent pollution management measures through multivariate analyses and source identification. The study underscores the urgency of addressing heavy metal pollution in the Halda River, a crucial breeding ground for carp, and highlights the significance of comprehensive source apportionment to mitigate environmental risks.

Hasan et al. (2013) [23] investigated trace metal pollution from shipbreaking activities in Sitakund, Bangladesh, finding significant contamination of seawater and groundwater with various metals, exceeding international and domestic quality standards. Pollution sources were attributed to both marine and ship-breaking activities, and seawater contamination was linked to groundwater pollution via seawater intrusion.

Hossain et al. (2019)[31] conducted a baseline study on heavy metal contamination in the Sangu River estuary, Bangladesh, finding minimal contamination except for Pb. The study revealed varying metal sources, with Pb and Zn likely anthropogenic, while As, Ni, Zn, Cu, and Cr originated from natural sources.

Kibria et al. (2016) [13] assessed widespread heavy metal (Cd, Cu, Fe, Ni, Pb, Zn, etc.) pollution in Bangladesh's waterways, identifying significant contamination "hot spots" in the Buriganga River near Dhaka, signaling substantial ecological and public health implications. The study highlighted the Buriganga River as the most polluted waterway due to effluents from tanneries and textiles, raising concerns about water quality, aquatic biodiversity, food security, and human health.

2.3 Review of Environmental Regulatory Framework in Bangladesh

At present, different ordinances, laws, rules, acts, and policies have been made to control environmental pollution in Bangladesh. Some of the important acts and amendments are listed in **Table 2.1** and are detailed elsewhere in the literature [4, 12].

The Department of Environment is actively addressing river pollution, yet research reveals compromised water quality in urban rivers, jeopardizing health and ecology. Despite a comprehensive environmental policy, implementation faces institutional challenges [12, 32]. Inadequate operational guidelines impede execution, especially during floods and cyclones. The Environmental Protection Act lacks disaster provisions, and barriers encompass insufficient funds, human resources, inter-agency cooperation, policy coherence, sectoral alignment, administrative capacity, outdated laws, awareness gaps, and soft enforcement.

Table 2.1

Key Environmental Acts and Policies in Bangladesh

Environmental Act	**Year**
Bangladesh Environment Conservation Act	1995 (amendment in 2010)
Bangladesh Environment Court Act	2010
Bangladesh Environment Policy	2018
Bangladesh Water Act	2013
Bangladesh Water Rules	2018
Bangladesh Climate Change Trust Act	2010
Department of Environment Organization	1989
Water Pollution Control Ordinance	1973
Environmental Conservation Rules	2023

2.4 Overview of the Steel-Galvanizing Industry

Sun et al. (2019) [22] introduced a total environmental impact score methodology to assess the combined environmental effects of wastewater discharge from the iron and steel industry, considering both quantity and water quality. Their study highlights steelmaking as the most impactful process and emphasizes the significance of total nitrogen as a dominant pollutant in the context of environmental impact assessment.

Deepti et al. (2021) [3] introduced an innovative approach utilizing closed-circuit reverse osmosis and solvent-based precipitation to effectively treat highly saline industrial wastewater, achieving remarkable desalination results and significant chloride and sulfate removal, offering potential cost-efficient solutions for water treatment in the steel industry.

Gudukeya et al. (2019) [33] explored industrial sustainability challenges in Zimbabwe's deteriorating economy, focusing on the steel industry. The study aimed to identify steel production challenges and propose solutions, ultimately aiding companies and policymakers in enhancing industrial sustainability.

Hashemi et al. (2016) [34] assessed heavy metal pollution in an Iranian steel factory's environment, particularly focusing on toxic elements like cadmium, lead, and mercury originating from urban, industrial, and agricultural sources. Their study revealed significant differences in mercury concentrations within and outside the factory, with mercury showing lower accumulation in aerial organs compared to leaves and roots of poplar trees.

2.5 Overview of Paint Industry

The paint industry is currently facing a significant challenge related to heavy metal pollution in wastewater. Recent research has delved into various techniques aimed at addressing this issue, including adsorption, coagulation-flocculation, and oxidation for pollutant removal. A comprehensive exploration of eco-friendly methods, such as biological and natural processes, is underway to treat contaminated water. Additionally, studies are focusing on developing efficient removal techniques, sustainable practices, and cost-effective solutions.

In the pursuit of addressing environmental and health impacts, researchers are optimizing coagulation methods and exploring recycling approaches. Figure 2.1 presents a process flow chart for paint production in the industry, providing an overview of the production stages.

To better understand the paints and their chemical compositions, **Table 2.2** provides a classification of different types of paints along with their respective chemical ingredients. The table encompasses a wide range of paint types, from interior wall paints to metal paints, each with its unique set of chemical components.

Table 2.3 further details the various pigments used in making paints, categorizing them by color and providing their chemical symbols or formulae [25]. This comprehensive overview facilitates a deeper understanding of the raw materials involved in the paint manufacturing process.

In tandem with the tables, **Fig. 2.2** visually illustrates the extent of water pollution caused by the paint industry.

Table 2.2

Classification of Different Types of Paints and Chemical Ingredients:

Types	Chemical Ingredients
Exterior House Paints	Pigments (ZnO, TiO_2, white lead, etc.), extenders (talc, barytes, clay, etc.), vehicles (e.g., linseed oil), thinners (e.g., mineral spirits, naphthas, etc.)
Interior Wall Paints	Pigments (e.g., white and colored pigments), vehicle (e.g., varnish or bodied linseed oil), resins (e.g., emulsified phenol-formaldehyde resins and casein)
Fire Resistant Paints	Borax, zinc borate, ammonium phosphate, synthetic resins, etc. as anti-fire chemicals
Chemical Resistant Paints	Varnishes, chlorinated rubber compositions, bituminous varnishes, and phenolic dispersions as chemical-resistant materials
Luminous Paints	Pigments (sulfides of Ca, Cd, and Zn dispersed in spirit varnish), vehicle (chlorinated rubber, styrol, etc.), sensitizer for activation in U.V. region
Marine Paints	Pigments (ZnO and Venetian red), Resin (shellac), Driers (Mn lineolate), Vehicle (coaltar), Diluent (pine oil), Toxic Components (cuprous oxide and mercuric oxide)
Emulsion Paints	Emulsion of alkyds, phenol formaldehyde, etc. (vehicle) in water, Pigments, and Extenders
Metal Paints	Coatings are applied on metal surfaces or bodies for protection and decoration. Pigment, Vehicle, Anticorrosive agents (e.g., zinc or chrome yellow), Resins (e.g., alkyds, epoxy, polyamides, chlorinated rubbers, and silicones), etc.

Table 2.3

Various Color Pigments Used for Formulating Paints

Color	**Pigments**
White	$PbCO_3$ (basic lead carbonate), TiO_2, ZnO
Red	Pb_3O_4 (red lead), CdS, CdSe, CdSeS, CdSb
Blue	Na_8-$10Al_6Si_6O_{24}S_{2\text{-}4}$ (ultramarine blue), $CoAl_2O_4$, $Fe_4[Fe(CN)_6]_3$ (Prussian blue)
Green	Cr_2O_3, $Cr_2O_3 \cdot 2H_2O$ (chrome green), $Cu(CrO_4)_2$ (copper chromate)
Yellow	PbO (litharge), $PbCrO_4$ (lead chromate), $ZnCrO_4$ (zinc chromate)
Black	C (carbon black), C (lamp black), C (furnace black)
Orange	$PbCrO_4 \cdot Pb(OH)_2$ (basic lead chromate), CdS (cadmium orange)
Brown	Natural earth pigments
Metallics	Cu (copper), Zn (zinc), Al (aluminum)
Metal Protective	Pb_3O_4 (red lead), PbO_2 (blue lead), Zn (zinc), $PbCO_3$ (basic lead carbonate)

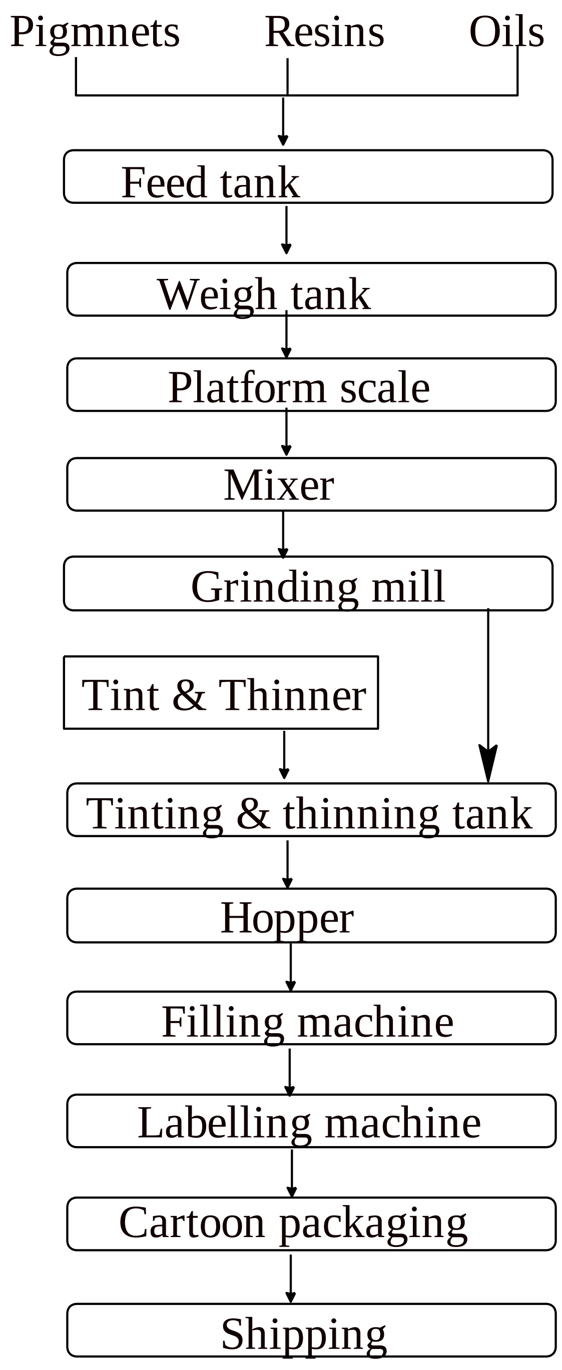

Fig. 2.2. Process flow chart for paint production in industry.

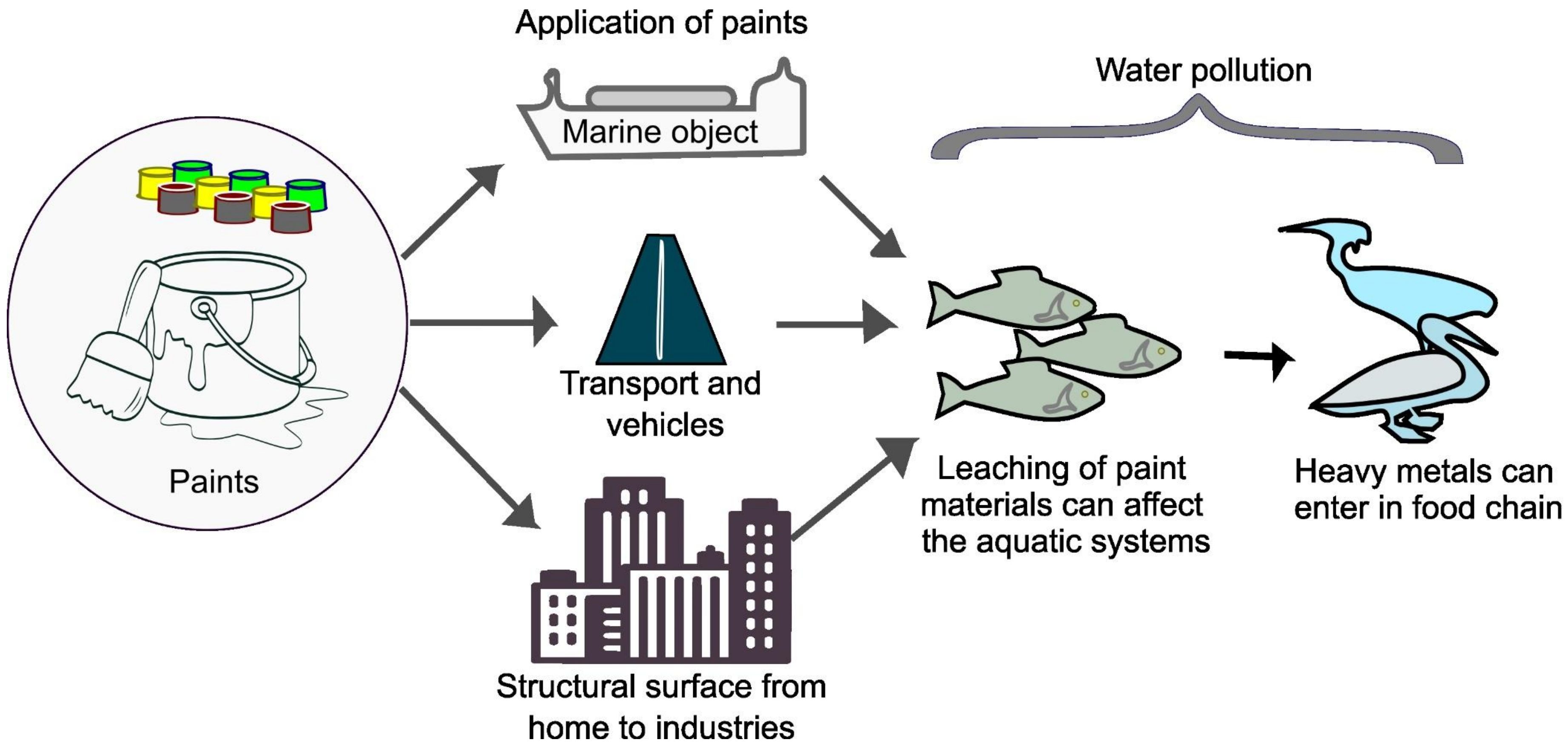

Fig. 2.3. Water pollution by the paint industry.

Kumar et al. (2021) [35] conducted a review on removing Ni and Cr pollutants from various industries like plating, tanner, mining, paint, and other metal processing industries, emphasizing the toxic impact of Cr(VI) and Ni(II) on aquatic life and human health. They discussed challenges in choosing effective, cost-efficient, and sustainable methods for treating contaminated water, highlighting the importance of integrating biological and natural processes with existing techniques for eco-friendly solutions.

Barbosa et al. (2018) [36] investigated water-based paint wastewater treatment using natural coagulant Moringa oleifera extract, enhanced with Ca^{2+}, and an electrolytic flow process with a boron-doped diamond electrode. The treated wastewater was successfully reused for new paint production, demonstrating improved quality and reduced toxicity, organic load, and microbial presence.

Nair et al. (2021) [1] conducted a comprehensive review of sustainable treatment techniques for paint industry wastewater, highlighting challenges in addressing its diverse pollutants, and emphasizing the need for combining oxidation and biological processes for effective and environmentally friendly reduction of toxicity and sludge management.

Viktoryová et al. (2022) [37] provided an overview of recent advancements and emerging trends in treating paint industry wastewater, addressing its significant environmental and health impacts, highlighting efficient reduction of chemical oxygen demand, discussing treatment factors, and emphasizing the importance of advanced analytical methods for safe disposal.

Malakootian et al. (2008) [38] investigated the use of wood ash as a natural adsorbent for removing Pb and Co from paint industry wastewater, demonstrating high removal efficiency, especially with increased wood ash dosage and lower pH conditions. The study suggests wood ash's viability as a cost-effective adsorbent for treating heavy metal-contaminated wastewater.

Dovletoglou et al. (2008) [39] investigated the coagulation of paint industry wastewater using different agents ($FeSO_4$, $Al_2(SO_4)_3$, PACl) at various pH levels. Optimal conditions were identified for each agent, achieving COD and turbidity reduction efficiencies between 30-80% and 70-99% respectively, with potential enhancements using polyelectrolytes.

Mamadiev et al. (2010) [40] examined treatment and recycling methods for heavily polluted water-based paint wastewater, achieving significant COD and color removal using coagulation-flocculation and Fenton's oxidation. Membrane filtration showed potential for sustainable recycling due to low sludge production, suggesting cost analysis is crucial for process selection.

Vishali et al. (2018) [41] explored Moringa oleifera's coagulation potential for water-based paint effluent treatment, achieving over 95% color removal via optimized conditions. The study highlights its promise as a natural substitute for chemical coagulants and proposes reusing treated wastewater for cooling and dilution in paint production.

Gaylarde et al. (2021) [42] examined paint fragments as significant contributors to ocean microplastic pollution, containing various polymers. Despite their prevalence, these particles are often overlooked in assessments, with the review discussing their characteristics, sources, effects, and colonization by marine organisms, particularly from antifouling paints, emphasizing their understudied impact.

By examining advanced treatment methods for pollutants found in the industrial waste of paint industry effluents, these research offer valuable insights for identifying sustainable approaches.

2.6 Review of Physicochemical Properties of Wastewater

The physicochemical properties of water, including temperature, turbidity, electrical conductivity, and chemical parameters like DO, BOD_5, and COD, play a crucial role in aquatic ecosystem health. Elevated BOD levels indicate organic pollution, while DO, pH, and TDS impact water quality and aquatic life. Trace element contamination is a global concern due to adverse effects even at low concentrations, originating from various sources including human activities and natural leaching. Trace elements in Bangladesh's water often exceed guideline values, posing risks to both human health and ecosystems [12].

Chromium (Cr) exists in nature as Cr (III) and Cr (VI) oxidation states, with contrasting physiological effects [43]. While WHO and Bangladesh standards set a maximum chromium concentration of 0.05 mg/Lin drinking water, some studies indicate surface water samples exceeding this range at various locations. Higher chromium levels are observed in rivers. Cr(VI) oxidation state, prevalent in chromium, can lead to health issues such as lung cancer and nasal irritation through dermal and inhalation exposure [44].

Copper (Cu) is an essential trace element with a vital role in the biochemistry of all organisms [45]. The WHO sets a maximum acceptable concentration of 2 mg/L for Cu. Excessive copper accumulation leads to toxicosis, causing hepatic cirrhosis, hemolytic anemia, and basal ganglia degeneration [46].

Iron (Fe), abundant in the earth's crust, raises global concerns about deficiency [47]. In Bangladesh, 60% of water samples exceeded the standard (1.0–0.3 mg/L), with averages of 2.65 mg/L in shallow and 1.37 mg/L in deep tubewell water [12]. Excessive iron, linked to diabetes, anemia, and heart issues, poses risks [48].

Nickel (Ni) is an essential trace element for living materials. However, it can pose risks to human when present in contaminated drinking water and food [49]. The WHO recommends a Ni concentration of no more than 0.02 mg/L in drinking water, while Bangladesh permits levels of up to 0.1 mg/L for drinking water and 1 mg/L for industrial discharge. Nickel hypersensitivity can lead to health issues such as asthma, conjunctivitis, and inflammatory reactions to nickel-containing prostheses and implants [50]. Furthermore, nickel compounds have been linked to cancer [51].

Cadmium (Cd) is an extremely toxic trace metal due to its exceptionally long half-life [52]. The WHO recommends a Cd concentration of no more than 0.003 mg/L in drinking water. However, various investigations in Bangladesh have revealed significant Cd contamination in different surface water sources. Although limited data are available regarding Cd contamination in groundwater, a recent study found mean Cd concentrations almost five times higher (0.014 mg/L) than the WHO limit in groundwater [53].

2.7 Human Health Impacts of Toxic Exposure

Toxic metals and harmful microorganisms in polluted water have been found to cause severe aquatic toxicity, including DNA and tissue damage, restlessness, neurotoxicity, and genotoxicity. Cr contamination in fish has led to genotoxic and toxic effects, while some fish species suffer from significant toxicity due to polluted rivers. The iconic hilsa fish has seen reduced production and genotypic changes due to pollution and climate change. Similarly, the Halda River's natural breeding grounds for carp fish are threatened by heavy metal accumulation.

Waterborne diseases resulting from water pollution are a global concern, claiming millions of lives annually. In Bangladesh, water-related diseases such as cholera, typhoid, and polio are particularly concerning, especially among children. Arsenic contamination in water sources has severe health consequences, causing skin lesions, diabetes, high blood pressure, and chronic diseases. Microbial and pesticide contamination also poses health threats, leading to diseases like typhoid, dysentery, diarrhea, and respiratory difficulties.

Exposure to heavy metals like Cu, Cd, Pb, As, etc. is highly connected with wide range of health issues as presented in **Table 2.4**. The information underscores the urgent need for comprehensive and effective water pollution control measures in Bangladesh to safeguard both aquatic ecosystems and public health.

Table 2.4

Various Reports on Heavy Metal Contamination in Aquatic Ecosystems

No.	Report	Reference
1.	Cr in fish from the Buriganga River causes genotoxic and serious toxic effects.	Ahmed et al. 2013 [54]
2.	Severe Cr toxicity is observed in some fish species in polluted rivers.	Islam et al. 2020 [55]
3.	Decline in Hilsa fish production and genotypic changes due to river pollution and climate change.	Khatua et al. 2020 [56]
4.	Hilsa fish, a global delicacy, sees reduced production.	Khatua et al. 2020 [56]
5.	Halda River serves as the world's largest natural breeding ground for carp species.	Khatua et al. 2020 [56]
6.	Analysis of shellfish and fish shows elevated Zn, Ni, and Pb concentrations exceeding dietary limits.	Ahmed et al. 2020 [57]

Toxic metals exhibit severe aquatic toxicity, causing tissue and DNA damage, neurotoxicity, hyperactivity, and cellular harm. Escalating water pollution poses threats to billions worldwide, affecting both physical and environmental health [58]. Non-biodegradable heavy metals can induce far-reaching toxic effects, leading to diseases like kidney damage, cancer, and behavioral impacts [59]. Elevated trace elements in vegetables and fruits, including Cu, Cd, and Pb, heighten the risk of upper gastrointestinal cancer [60]. Diverse ions and compounds exhibit varying effects; Cr and Ni increase lung cancer risk, excessive Zn consumption leads to imbalance, and long-term cadmium exposure heightens the likelihood of kidney failure, bone issues, and prostate cancer [23].

CHAPTER – 3: METHODOLOGY

3.1 Experimental Framework

In this chapter, we delve into the intricacies of our experimental design and methods, which formed the backbone of our investigation into water quality parameters within industrial effluents. Our study focused on effluent samples sourced from ETPs in the steel and paint industries situated across Mirsharai, Sitakunda, Karnaphuli, and Kalurghat in Chattogram, as well as STP samples from hotel industries in Cox's Bazar, Chattogram Division. To comprehensively assess the operational efficiency and maintenance practices of Wastewater Treatment Plants (ETPs and STPs) within the Chattogram region, the investigation involved a thorough examination of the wastewater treatment process, encompassing the documentation of operational procedures, including ETP and STP process flows.

Focusing on diverse industries such as steel, paint, and hotels, we investigate the wastewater quality of ETP samples from specific industrial sectors. The samples were meticulously collected bi-annually during the Dry Season (D.S.) and Monsoon Season (M.S.), encompassing both inlet and outlet points of the industrial aquatic environment. The evaluation of key physicochemical parameters, including pH, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), and Total Dissolved Solids (TDS), alongside heavy metal concentrations (Fe, Cu, Cr, Ni, Cd, etc.), was executed through rigorous triplicate analyses, following established methodologies. This chapter provides a comprehensive overview of our study area, sampling procedures, and the analytical protocols employed to unravel the complexities of water quality in the selected regions. The meticulous examination of these industrial sectors forms the foundation for the forthcoming chapter – Results and Discussion.

Table 3.1

Geographical Distribution of Sampling Sites of Industries

Sl No.	Sample Code	Latitude	Longitude
		Steel Industry/ Galvanizing Industry	
1.	S-1	22°30' 58.813" N	91°42' 37.393" E
2.	S-2	22°30' 0.137" N	91°42' 53.535" E
3.	S-3	22°26' 38.1984" N	91°44' 14.6688" E
4.	S-4	22°30' 26.424" N	91°42' 44.604" E
5.	S-5	22°52' 18.9156" N	91°33' 7.164" E
6.	S-6	22°18' 36.45" N	91°52' 11.118" E
		Paint Industry	
7.	P-1	22°23 '16.3536"N	91°52 '9.5052"E
8.	P-2	22°22 '49.0008"N	91°51 '58.9392"E
		STP Plants of Hotel Industry	
9.	H-1	21° 24' 51.6594"N	E 91° 59' 2.7234"E
10.	H-2	21° 25' 15.2394"N	E 91° 58' 51.204"E
11.	H-3	21° 25' 34.752"N	E 91° 58' 34.4994"E

3.2 Study Area

Table 3.1 provides a detail of the study area, while **Fig. 3.1 (a,b)** depicts the geographical location of the sampling of effluents from six steel-galvanizing industries' ETP inlets and outlets. Most of the study sites are near the important water bodies such as rivers, lakes, and seashores. Specifically, S-1, S-2, S-3, S-4, and S-5 are situated near the Dhaka-Chattogram highway, the Bay of Bengal, and the Karnaphuli River seashore, while S-6, P-1, and P-2 are located beside Karnaphuli River. The industrial effluents from S-1 to S-5 are carried by the canal to the Bay of Bengal, while S-6 discharges into the Karnaphuli River directly.

H-1, H-2 and H-3 are located near the Cox's Bazar Sea beach, the Bay of Bengal. The effluents from H-1, H-2, and H-3 discharged to the Bay of Bengal through the drain.

A large amount of sewage effluent is discharged here daily from different hotels. By keeping this view, it was thought that this hotel activity might cause an adverse effect not only on the environment but also on the humans and sea species; the impact on humans is in the form of health hazards as well as over the socioeconomic strata of them. Moreover, to comprehend the wastewater treatment process, we meticulously documented the operational procedures, including the ETP and STP process flows for each sampling site.

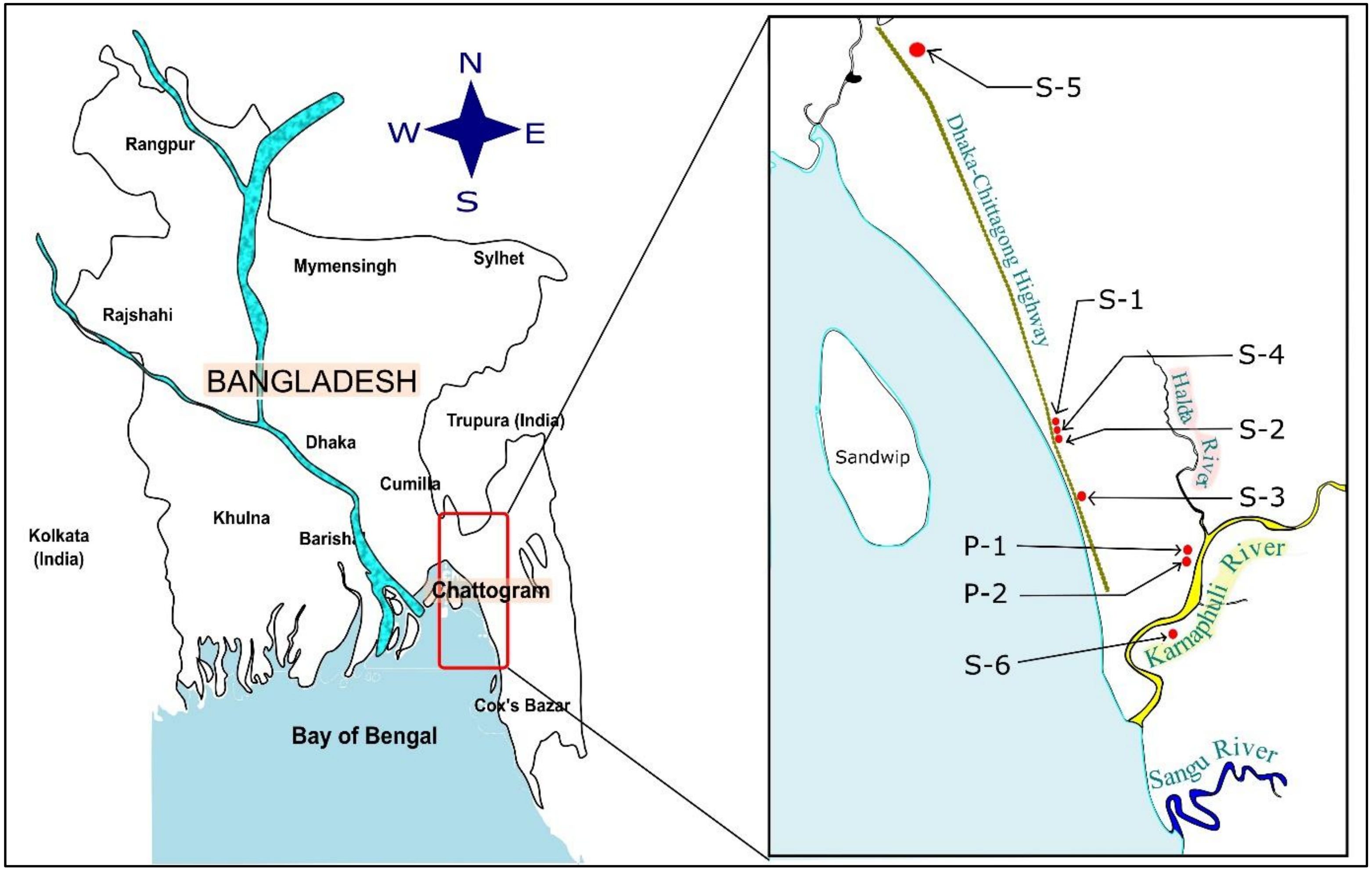

Fig. 3.1. Map of Chattogram showing the places of sampling points: **(a)** Steel and paint industries.

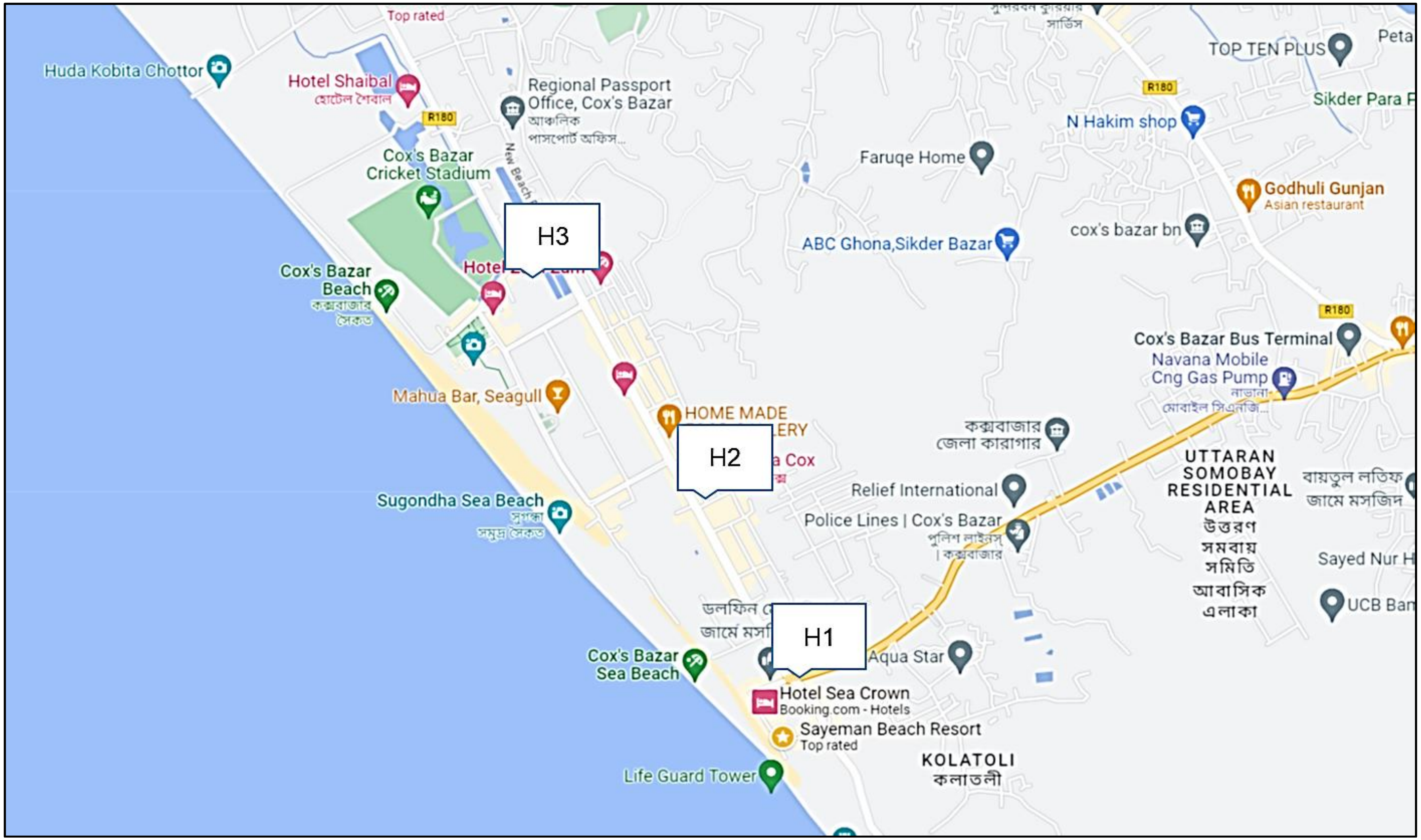

Fig. 3.1. Map of Chattogram showing the places of sampling points: (b) Hotel industries in Cox's Bazar.

3.3 Sampling

Effluent samples were obtained from the ETP-Inlet and ETP-Outlet points of the industrial aquatic environment surrounding the ETP for physiochemical and heavy metal analysis. The samples were collected bi-annually, with the first batch in the D.S. (January- February) and the second batch in the M.S. (July- August). Sufficient samples were collected for physio-chemical and heavy metal content analysis and stored in 500 mL HDPE narrow-mouth laboratory bottles. Before laboratory analysis, all effluent samples were pre-washed with 10% nitric acid and rinsed with distilled water. To analyze heavy metals in ETP effluents, 10 mL of 2M HNO_3 solution was added to the samples to prevent fungal and pathogenic attacks. The samples were collected from midstream and a few centimeters below the surface and were protected from direct sunlight by placing them in a lightproof box for transportation. Afterward, the samples were transported to the laboratory for further analysis. The effluent sample collection date, location, and other details were recorded carefully. Some photos taken in sampling sites are given in Fig. A1 (Please see **Appendix-A**)

Each sample was collected in a plastic bottle, labeled with a unique identification number, and then analyzed for five physio-chemical characteristics (DO, BOD_5, COD, pH, and TDS) and five heavy metals, namely, Fe, Cu, Cr, Ni, and Cd. To remove unwanted solid and suspended materials, the samples were filtered using Whatman No. 42 filter paper. The bottles were kept in a clean, cool, dark, and dry place in the laboratory, and chemical analyses were performed as quickly as possible upon arrival.

3.4 Analytical Procedures

Wastewater samples collected from ETP plants were analyzed for various parameters, including pH, COD, BOD_5, DO, and TDS, as well as heavy metals including Fe, Cu, Cr, Ni, and Cd (**Table 3.2**). All sample analyses were performed in triplicate, and mean values were reported.

The methods for sample analysis were approved in the "Standard Methods for Examination of Water and Wastewater (APHA, 1998)" as reported by Rice *et al*. in 2012 [61].

3.5 Physicochemical Parameters

3.5.1 pH

Water samples were tested for pH using a Hanna pH meter (Model HI 2211 pH/ORP meter).

3.5.2 Total Dissolved Solids (TDS)

Values of TDS in water samples were determined following the US EPA Direct Measurement Method (Method 8160) [62].

Table 3.2

The Analyzed Parameters with Their Respective Instruments

SL.	Parameters	Methods and Instruments
1	DO	Titrimetric method, glass stopper bottle, burette, pipet, measuring cylinder, conical flask, wash bottle, etc.
2	BOD_5	Same as DO instrument, BOD Bottles, BOD_5 Incubator
3	COD	COD vials, UV spectrophotometer, COD digestor, etc.
4	pH	Digital pH meter-Rex, Model pHs-25
5	TDS	Hach multimeter (Model HQ 40d)
6	Metal ion concentration	Atomic Absorption Spectrophotometer, AAS (CONTRAA-700, Analytik Jena, Germany).

3.5.3 Dissolved Oxygen (DO)

Values of DO in water samples were measured using the Standard Methods: Azide Modification Method (method # 4500-0C) [62, 63]. The chemicals required are manganous sulfate solution, alkali iodide azide reagent, sulfuric acid, starch, standard thiosulfate titrant, and standard potassium bi-iodate solution prepared as per the method. First, 250 ml of sample was taken, and 1mLof $KMnO_4$, and 1 ml of alkali iodide azide reagent were added. After the precipitate was settled, 1ml of H_2SO_4 and Titrate by Na_2SO_3 standard solution was added and DO was tested.

3.5.4 Chemical Oxygen Demand (COD)

Values of COD were measured using the standard method: Chemical Oxygen Demand of Water by the Standard Methods: 5220 D [62, 63]. The first Digestion Solution is prepared as per the method. After digestion, using a portable DR-1900 spectrophotometer (HACH, USA). COD is measured against blank and sample results are observed by UV Spectrophotometer at a definite wavelength.

3.5.5 Biological Oxygen Demand (BOD_5)

Values of BOD_5 were measured using the Five-Day Biochemical Oxygen Demand method (APHA 5210 B) [62, 63]. BOD bottle was prepared and incubated at 20°C for five days in the dark. After five days, the incubated BOD bottle was tested.

3.6 Heavy Metals

The total concentration of heavy metals (Fe, Cu, Cr, Ni, and Cd) in wastewater samples was precisely determined using an Atomic Absorption Spectrophotometer, AAS (CONTRAA-700, Analytik Jena, Germany), employing flame techniques. The front view is shown in **Fig. 3.2**. The flame techniques involved the use of coded titanium burner heads, featuring different slot widths optimized for various purposes. Throughout the analysis, all flame parameters were continuously monitored using sensors to maintain accuracy. In this analysis, a mono-element hollow Xenon lamp was employed to determine the presence of each heavy metal. To perform the measurements, filtered water samples were directly introduced into the AAS for analysis. Before this, a standard line was prepared by measuring the absorbance of standard solutions containing metal ions. To quantify the concentration of metals in the wastewater samples of interest, the AAS readings obtained were plotted against the standard line generated from the absorbance of the metal ion standard solutions. The calibration was validated by checking the R^2 value (**Fig. 3.3**) which estimates the correlation coefficient for calibration.

The wavelengths used for monitoring each metal ion during the analysis were as follows: Fe at 248 nm (R^2 = 0.9904), Cd at 228 nm (R^2 = 0.9980), Ni at 232 nm (R^2 = 0.9985), Cr at 357 nm (R^2 = 0.9989), and Cu at 324 nm (R^2 = 0.9980).

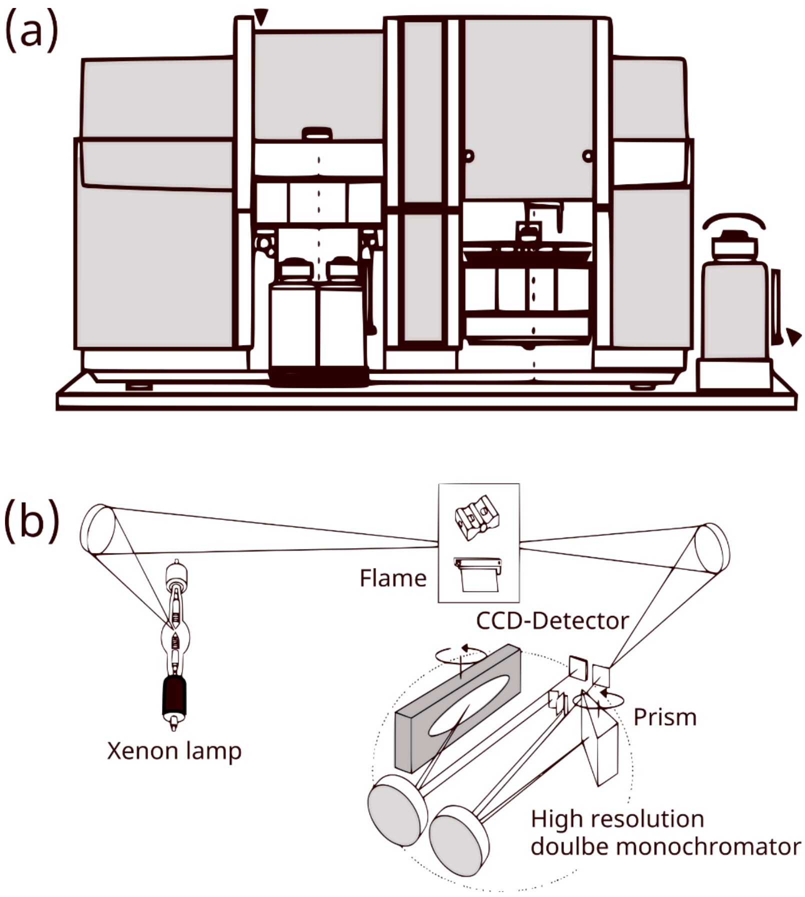

Fig. 3.2. Atomic absorption spectrophotometer (a) layout and (b) optical path.

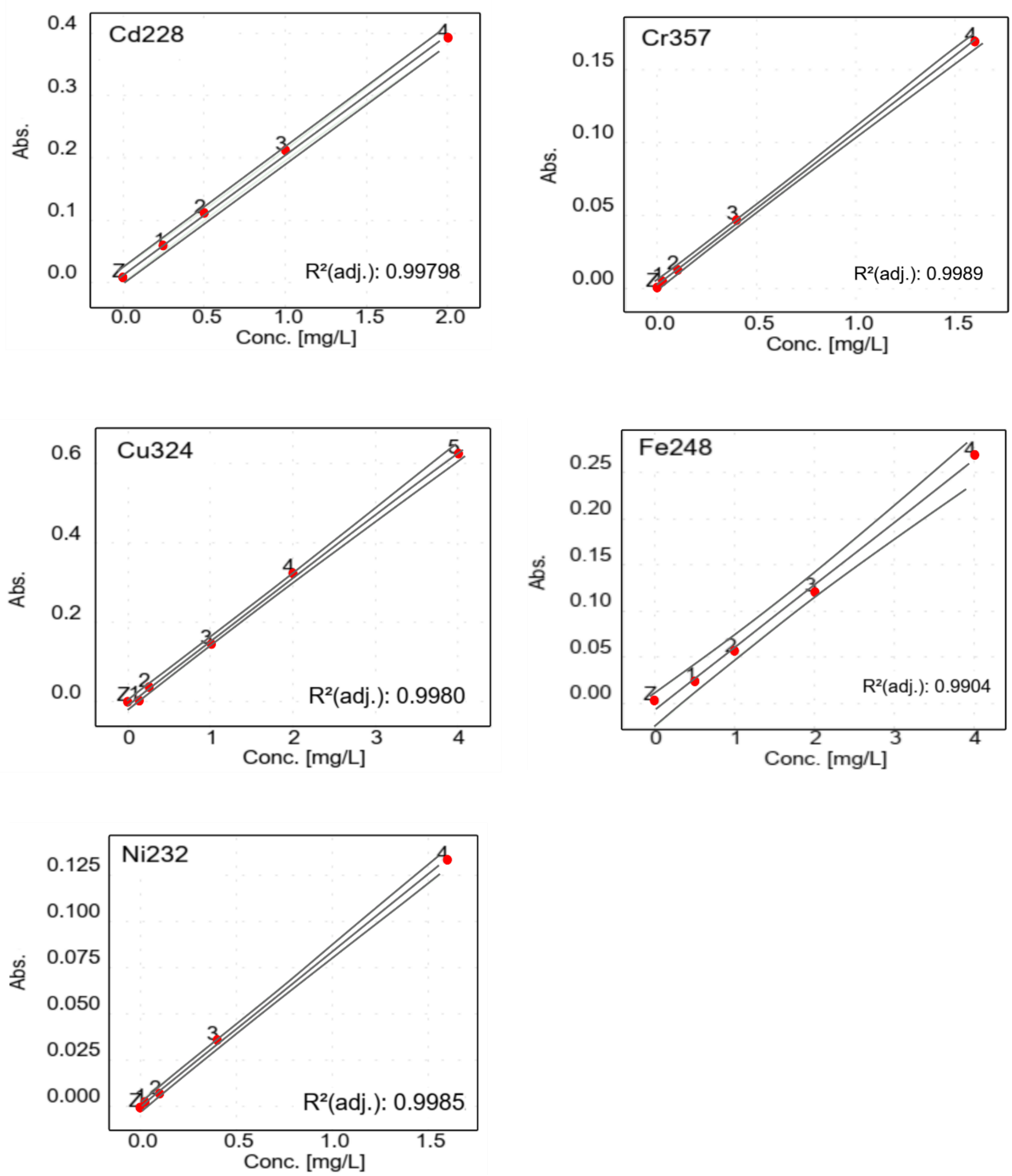

Fig. 3.3. Calibration curve for different metal elements.

3.7 Data Analysis

Data collected from the analysis of water samples were compiled, tabulated, and analyzed using Microsoft Office Excel and OriginLab Software.

CHAPTER – 4: RESULTS AND DISCUSSION

4. GENERAL DISCUSSION

This study comprehensively assesses the operational efficiency and maintenance practices of Wastewater Treatment Plants (ETPs and STPs) in various industries in Chattogram region of Bangladesh. It specifically examines wastewater quality of ETP samples from steel and paint industries in different industrial areas of Chattogram, as well as STP samples from hotels in Cox's Bazar due to their discharge of complex liquid waste with high levels of dissolved solids, suspended particles, and heavy metals. Five important physio-chemical parameters (pH, DO, BOD_5, COD, and TDS) and the presence of five heavy metals (Fe, Cu, Cr, Ni, and Cd) are studied from the collected wastewater samples of six steel industries, two paint industries, and three hotel industries.

Samples were collected during the Dry Season (D.S.) and Monsoon Season (M.S.), and the results were compared with the standards set by the WHO, BSIE, EU-DIR, and US EPA [11, 12, 14, 15, 64]. The effluent water quality of steel and paint industries has been discussed under appropriate headings compared with the standard values of industrial effluents. The results and elaborate discussion are arranged in the following parts.

Part A: Study on Steel-galvanizing Industry ETPs and ETP Samples

Part B: Study on Paint Industry ETPs and ETP Samples

Part C: Study on Hotel Industry STPs and STP Samples

Part A: Study on Steel-galvanizing Industry ETP samples

4.1 Industrial Effluents Analysis of the Steel-galvanizing Industry

This study assessed the environmental impact of pollutants from the steel-galvanizing industry by analyzing water quality samples [3]. The assessment focused on five key physiochemical parameters (pH, DO, BOD_5, COD, and TDS) and five heavy metals (Fe, Cu, Cr, Ni, and Cd) present in the wastewater. Physicochemical parameters and concentration of some heavy metals of the discharged wastewater of six steel industries close to Karnaphuli River and the sea-shore side of the Bay of Bengal were measured analytically.

4.2 Operation and Maintenance of ETP Plants of Steel Industries

ETPs are vital for wastewater treatment in steel industries. In steel industry's ETPs, several key stages ensure effective wastewater treatment, as depicted in **Fig. 4.1(a-f).**

Sampling site: S-1

Geographical Location: 22°30' 58.813'' N 91°42' 37.393'' E

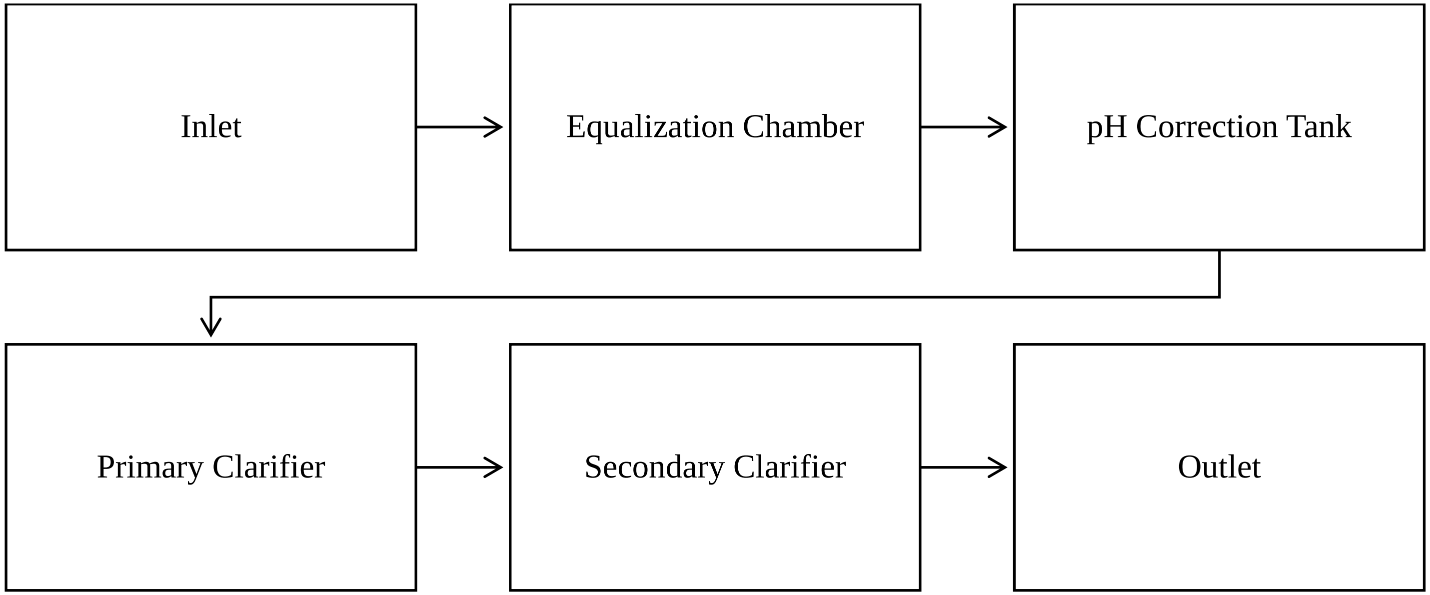

Fig. 4.1 (a). ETP Process flow of six steel industries.

Sampling site: S-2

Geographical Location: 22°30' 58.813'' N 91°42' 37.393'' E

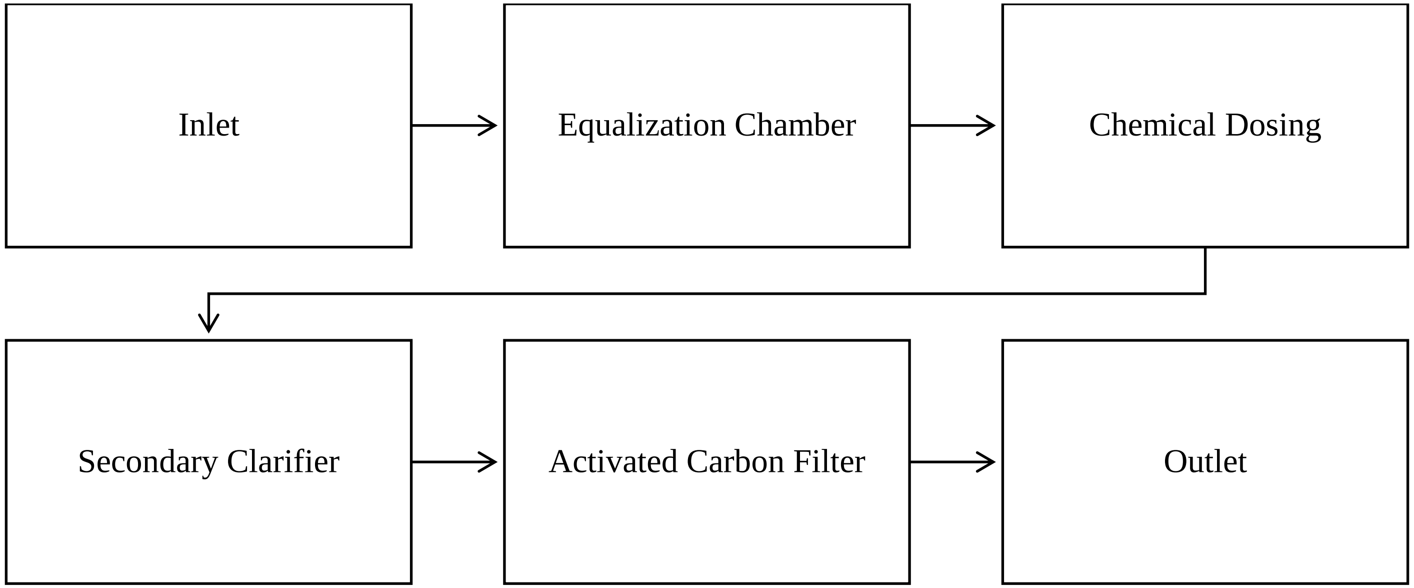

Fig. 4.1 (b). ETP Process flow of six steel industries.

Sampling site: S-3

Geographical Location: 22°26' 38.1984'' N 91°44' 14.6688'' E

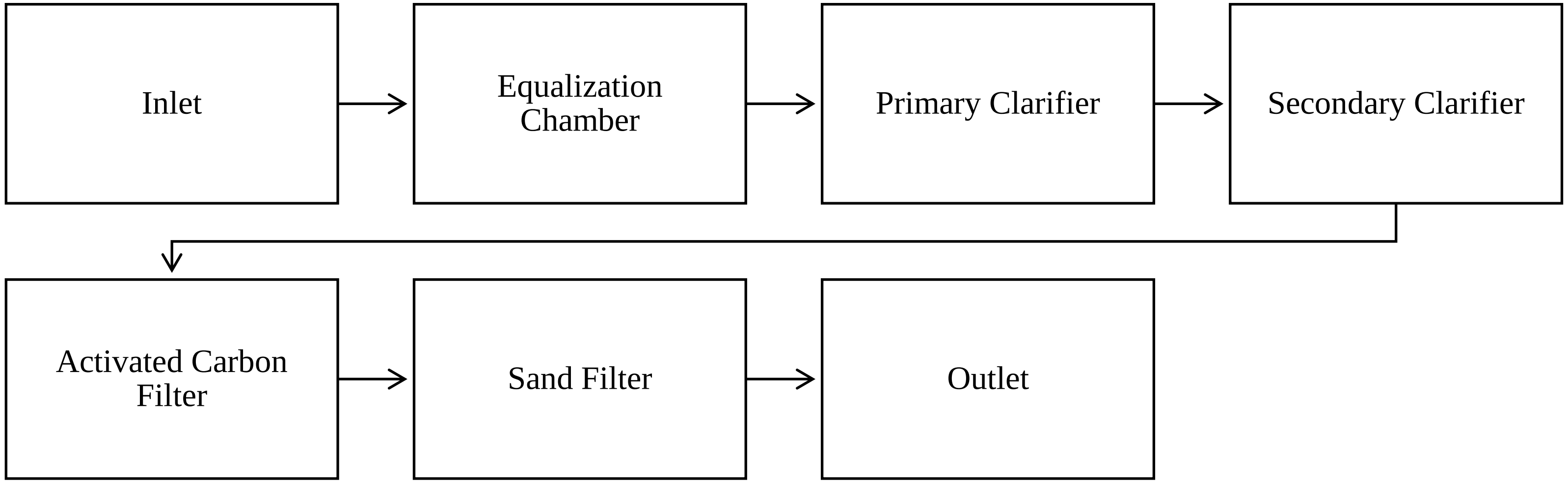

Fig. 4.1 (c). ETP Process flow of six steel industries.

Sampling site: S-4

Geographical Location: 22°30' 26.424'' N 91°42' 44.604'' E

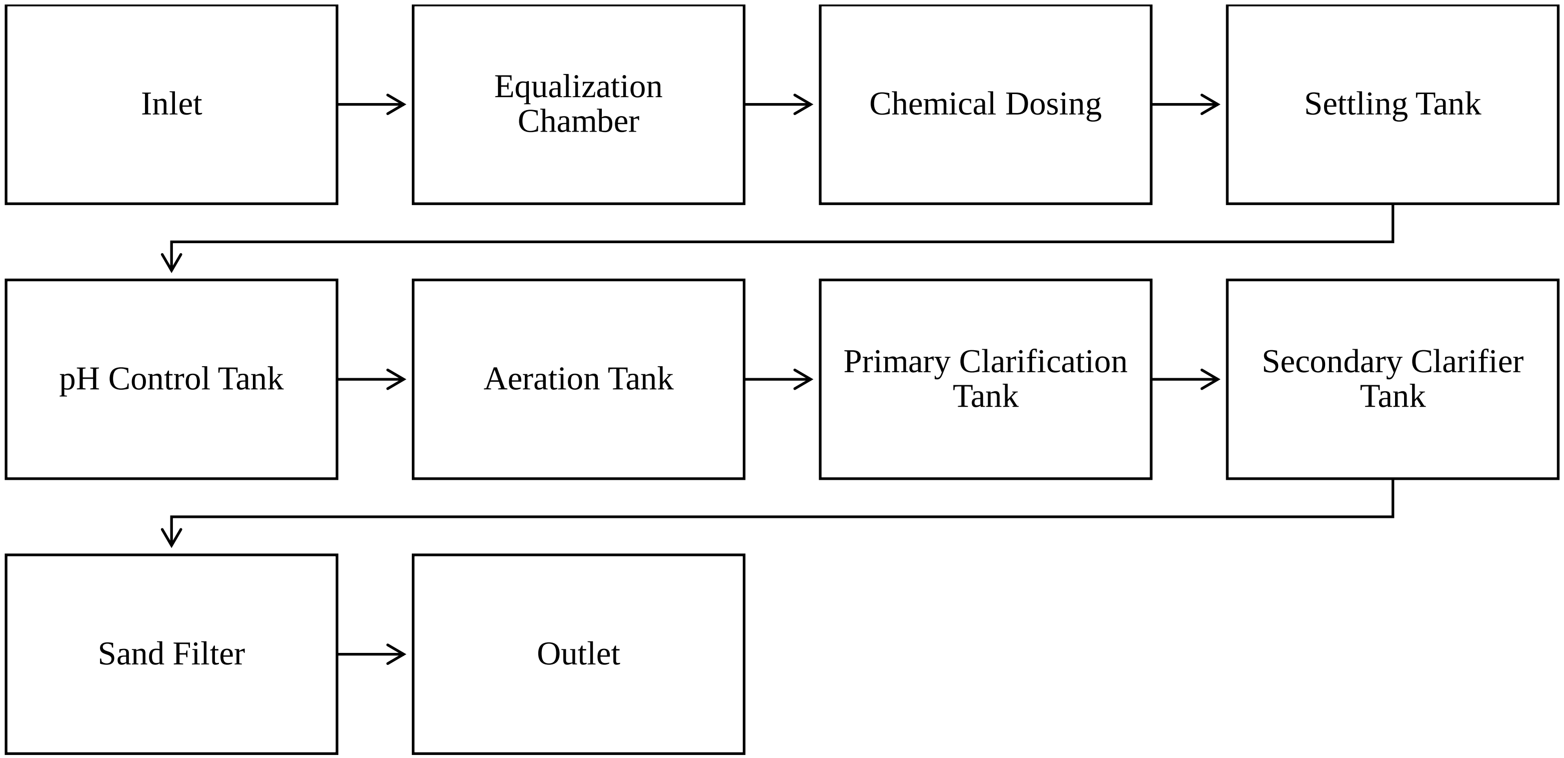

Fig. 4.1 (d). ETP Process flow of six steel industries.

Sampling site: S-5

Geographical Location: 22°52' 18.9156'' N 91°33' 7.164'' E

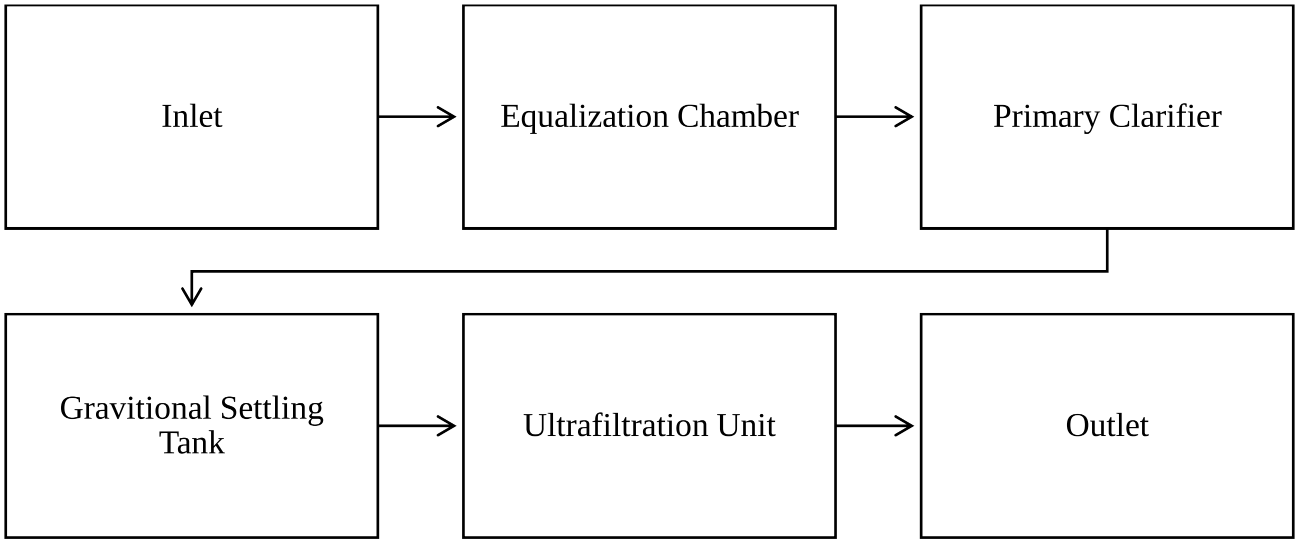

Fig. 4.1 (e). ETP Process flow of six steel industries.

Sampling site: S-6

Geographical Location: 22°18' 36.45'' N 91°52' 11.118'' E

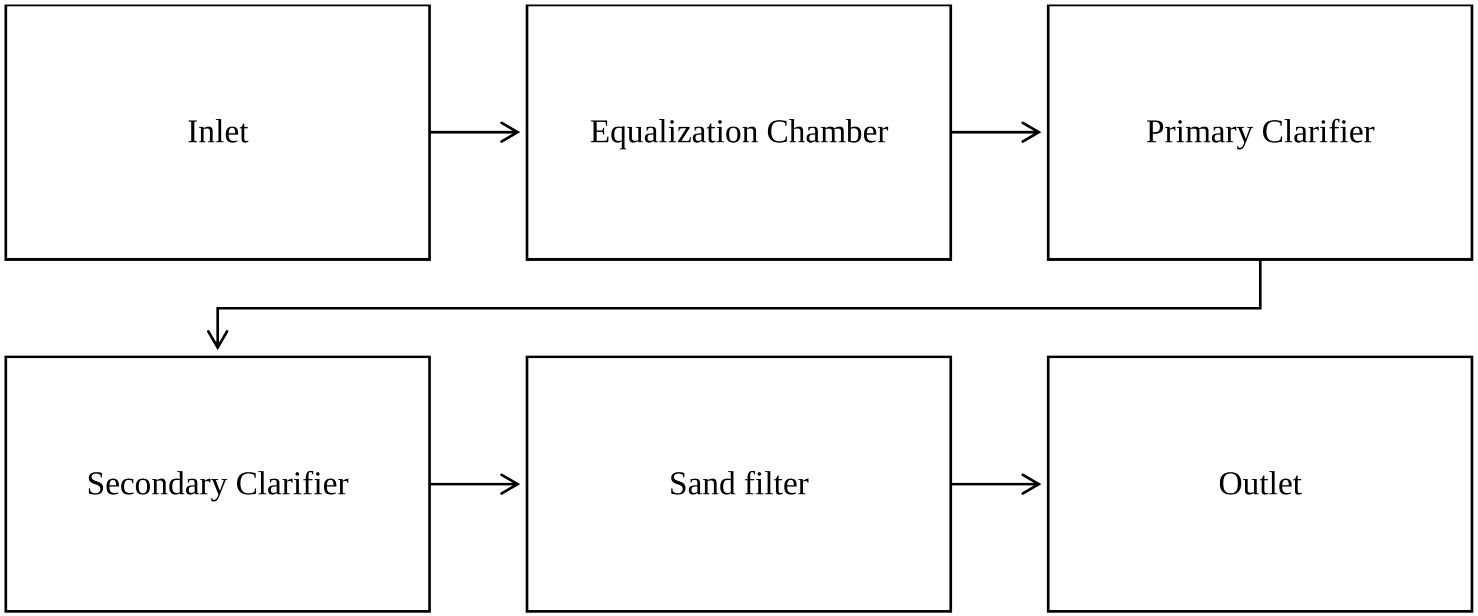

Fig. 4.1. (f) ETP Process flow of six steel industries.

4.2.1 Inlet of ETP: This marks the initial point of wastewater entry for treatment, equipped with bar screens to filter large items and debris. Government guidelines necessitate flow measurement devices for control and compliance monitoring. The inlet chambers often include provisions for sampling, aiding in effluent composition analysis. This stage is a common feature in the ETPs of galvanizing and steel industry. S1 to S6 maintain proper inlet of ETP according to government guidelines.

4.2.2 Equalization Chamber: The Equalization Chamber plays a pivotal role in stabilizing incoming wastewater flow, crucial for ensuring consistent flow rates despite variations due to production processes, shifts, or weather conditions. It also helps in averting temperature fluctuations and can facilitate pH adjustments when necessary. All six industries (S1-S6) installed the equalization chamber.

4.2.3 Chemical Dosing Tank or Primary Clarifier: Controlled chemical dosing is critical for contaminant removal, involving coagulants for destabilizing suspended solids and flocculants for particle agglomeration. Precise dosing, often automated with feedback control, is essential to avoid inefficiencies or environmental issues. Chemical dosing strategies align with wastewater characteristics and local regulations. S-1 includes a separate pH correction tank, while S-2, S-3, S-4, S-5, and S-6 stabilize pH in the Equalization Chamber or Primary Clarifier Tank.

4.2.4 Secondary Clarifier: Secondary clarifiers are integral in separating solid particles from treated wastewater, following biological treatment. Suspended solids settle to the bottom, while clear, treated wastewater rises to the top. Some settled sludge is typically returned to aeration tanks to maintain microorganism populations. Periodic removal of settled sludge is necessary to maintain efficiency. All ETPs (S1-S6) feature a Secondary Clarifier Tank.

4.2.5 Activated Carbon Filter: These filters are effective at adsorbing organic compounds, and eliminating odors, residual chlorine, chlorinated compounds, and some heavy metals. They improve effluent quality, making it suitable for potable use or sensitive environments. S-1 and S-2 employ activated carbon filters, while S-5 utilizes an Ultrafiltration unit instead of activated carbon filters.

4.2.6 Sand Filter: Sand filters play a crucial role in removing contaminants and improving effluent quality. They effectively reduce suspended solids, support biological treatment, and contribute to nutrient removal. These filters are particularly valuable when effluent is intended for surface water discharge or industrial reuse. S-3, S-4 and S-6 ETPs incorporate sand filters.

4.2.7 Outlet of ETP: The treated effluent exits at the discharge point, determined by treatment goals, environmental regulations, water quality standards, and intended use. Compliance with these standards is vital for protecting the environment and ensuring safe water disposal. Options may include surface water discharge, wetland release, or other natural systems, depending on effluent quality, environmental regulations, water availability, and intended use. The outlet of ETP is maintained in the studied area.

In conclusion, the operation and maintenance of ETPs in steel industries involve a well-defined sequence of stages, for serving a critical role in ensuring efficient wastewater treatment and environmental compliance. We focused on whether they collectively contribute to safeguarding water resources and ecosystems while meeting stringent quality standards. Hence, we studied the physicochemical properties and presence of heavy metals in water before and after treatment.

4.3 Physicochemical Parameters of Steel & Galvanizing Industries

Variations of five physicochemical parameters (pH, DO, BOD_5, COD, and TDS) for D.S. and M.S. are presented in **Table 4.1** and their mean variations are plotted in **Figs. 4.2-4.6**.

4.3.1 pH

The pH values of effluent samples were estimated from the samples of six steel-galvanizing industries' ETP inlet and outlet points. In such industries, acids are used to remove rust from the raw coil, and thus the pH range might be affected in wastewater. Variations of pH are presented in **Fig. 4.2**. The pH of the inlet points varied from 0.36 (S-4, D.S.) to 12.1 (S-6, M.S.).

The pH at the inlet point was dominantly observed acidic in 9 samples and in some cases, pH values were observed basic in 3 samples among the 12 samples collected in D.S. and M.S. After treatment, the pH of discharged stream areas ranged from 6.87 to 8.76.

The recommended pH values for safe water are as follows: WHO and US EPA (6.5–8.5), and BSIE (6.0–9.0). The values of pH in the discharged stream from ETP at the outlet point were within the suitable range defined by WHO, US EPA, and BSIE. The pH of the Karnaphuli River was reported 8.17 in winter and 7.89 in summer [7]. Most fishes can tolerate a pH ranging from 5.0 to 9.0, and aquatic life is not directly impacted by a smaller change in pH. The pH of waterbodies is also influenced by air temperature and various chemical and biochemical reactions. Hence, discharge of the effluent may not hamper aquatic life considering the pH values.

Table 4.1.

Physio-Chemical Parameters Present in Effluent at Various Sampling Sites

Sampling Point	Dry Season (D.S.)		Monsoon Season (M.S.)	
	Before Treat.	After Treat.	Before Treat.	After Treat.
	pH			
S-1	2.11	7.97	3.56	7.32
S-2	1.41	8.76	2.20	7.52
S-3	1.98	7.52	1.55	7.93
S-4	**0.36**	7.61	7.69	8.01
S-5	2.19	7.21	8.79	6.88
S-6	8.28	6.87	**12.1**	7.25
	DO (mg/L)			
S-1	1.10	7.50	1.20	3.80
S-2	4.68	7.75	4.25	7.14
S-3	**7.88**	7.17	7.13	7.80
S-4	2.50	6.55	1.11	7.92
S-5	4.16	4.82	3.21	3.61
S-6	4.42	8.00	**1.02**	7.90
	COD (mg/L)			
S-1	573	178	692.0	172
S-2	496	42.0	406.0	216
S-3	710	72.0	576.0	44.0
S-4	596	246	1564	156
S-5	549	162	**762.0**	152
S-6	**472**	58.0	486.0	138
	BOD_5 (mg/L)			
S-1	115	46	139	48
S-2	135	18	**81.0**	82
S-3	92.0	25	138	19
S-4	152	98	**402**	47
S-5	117	42	113	41
S-6	102	19	145	42
	TDS (mg/L)			
S-1	6390.0	2078	5830.0	1978
S-2	14730	2464	**1884.0**	1685
S-3	13700	2139	**13800**	2658
S-4	2020.0	1592	3812.0	1257
S-5	13470	2056	6821.0	1857
S-6	2200.0	976.0	4180.0	1162

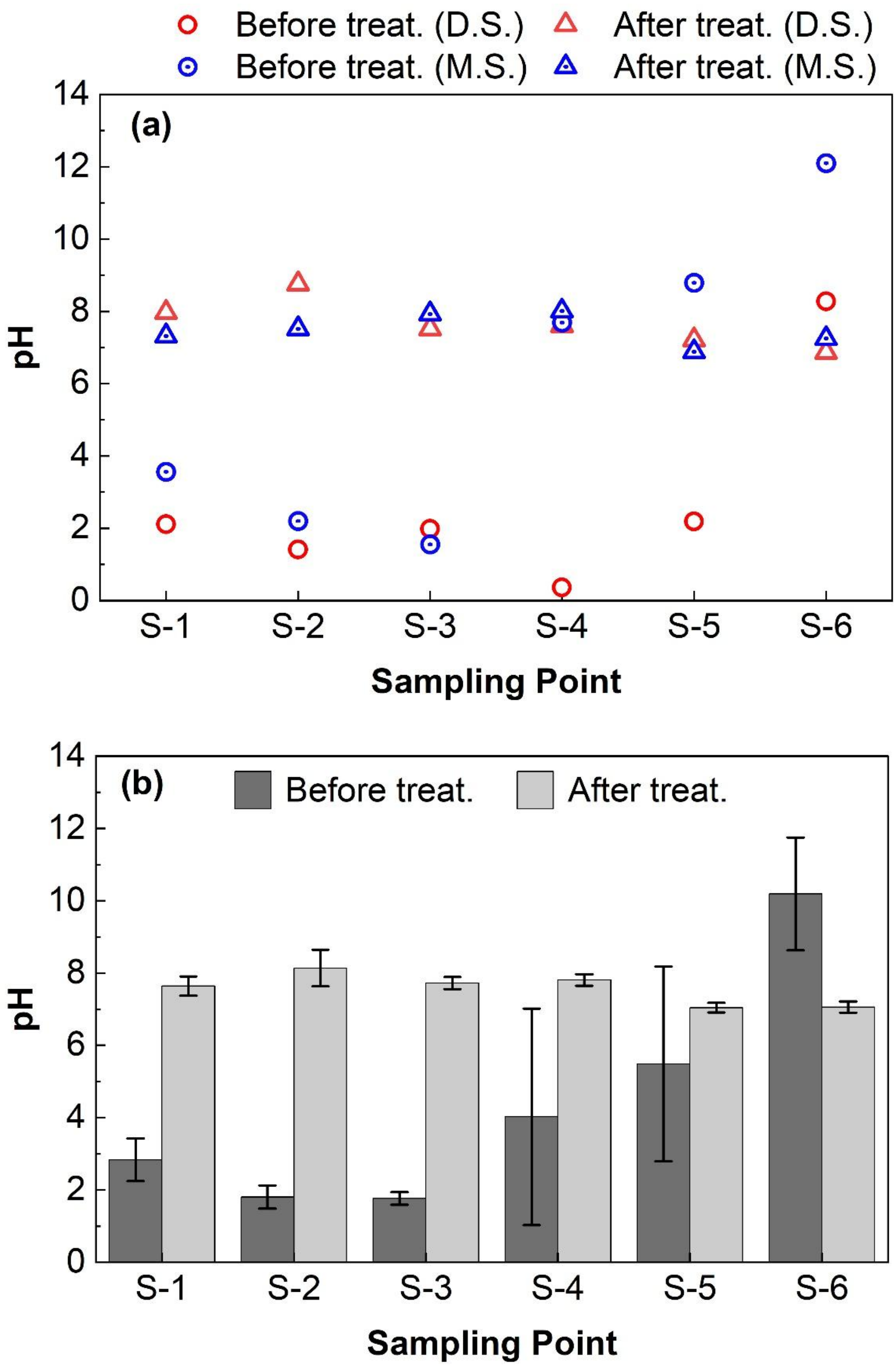

Fig. 4.2. Variation of pH in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.3.2 DO

Variations of DO are presented in **Fig. 4.3**. The DO of the inlet varied from 1.10 mg/L (S-1, D.S.) to 7.88 mg/L (S-3, M.S.). After treatment, the DO of the discharged stream at outlet points ranged from 3.61 mg/L to 8 mg/L. Overall, the mean values of DO in the effluent samples before treatment ranged from 1.15 to 7.505 mg/L, and after treatment, the range was 4.215 to 7.95 mg/L.

These values were within the standard range recommended by BSIE for DO, which is 4.5–8.0 mg/L. The values of DO of the discharged wastewater from ETP at the outlet points were found within an acceptable range, except in two cases with slightly higher values than the recommendation of BSIE. The DO of the Karnaphuli River was reported to be found a s 9.92 mg/L in the winter and 8.07 mg/L in the summer [7]. In industry, the increased temperature of the chemical process led to a decrease in DO due to the high rate of decomposition of organic matter. The maximum tolerance limit for fish is 5 mg/L, and below 2 mg/L, is fatal for fish [65].

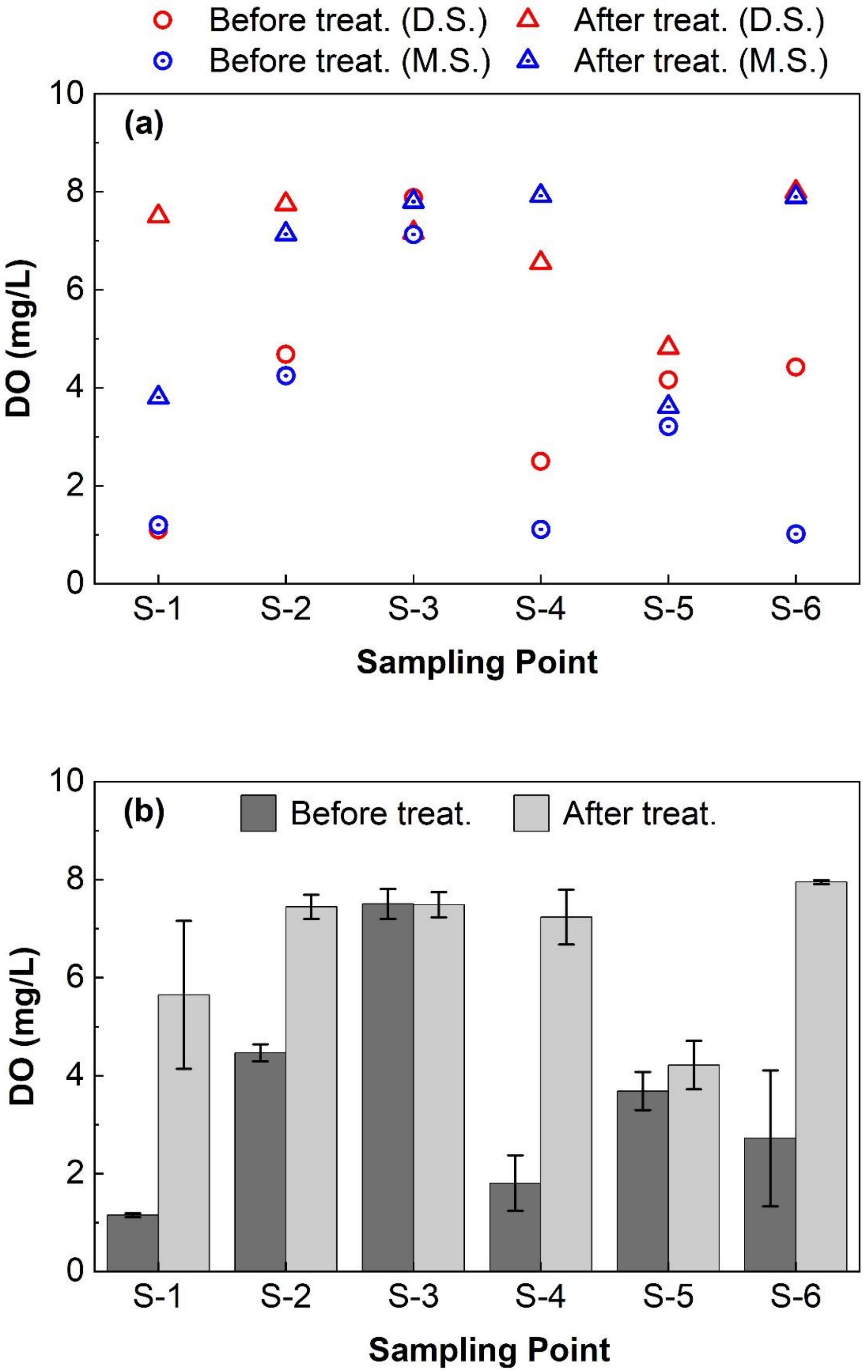

Fig. 4.3. Variation of DO (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.3.3 BOD_5

BOD_5 can be used to indicate the extent of organic pollution in aquatic systems, that adversely affects water quality. Variations of BOD_5 are presented in **Fig. 4.4**.

The range extended from 81 mg/L (at S-2, M.S. inlet) to 402 mg/L (at S-4, M.S. inlet), indicating considerable organic contamination at the inlet points of steel industries. The mean BOD_5 value recorded at the ETP inlet points of steel industries was 43.9 mg/L. This suggests that the water entering the treatment plant is significantly polluted with organic matter.

Across the outlet points of the ETPs, there were a notable decrease in BOD_5 levels compared to the inlet points. The range of BOD_5 at outlet points varied from 18 mg/L (at S-2, D.S.) to 92 mg/L (at S-4, D.S.), indicating the efficacy of the treatment process in reducing organic pollution.

Though there is no guideline value for BOD_5 set by WHO, the BSIE limit is 50 mg/L for BOD_5 in effluent water [12]. While the WHO does not specify a guideline value for BOD_5, the BSTI sets a limit of 50 mg/L for BOD_5 in effluent water. With the exception of two cases (S-4, D.S., and S-2, M.S.), the BOD_5 values observed were within the range set by BSTI, suggesting compliance with local regulatory standards.

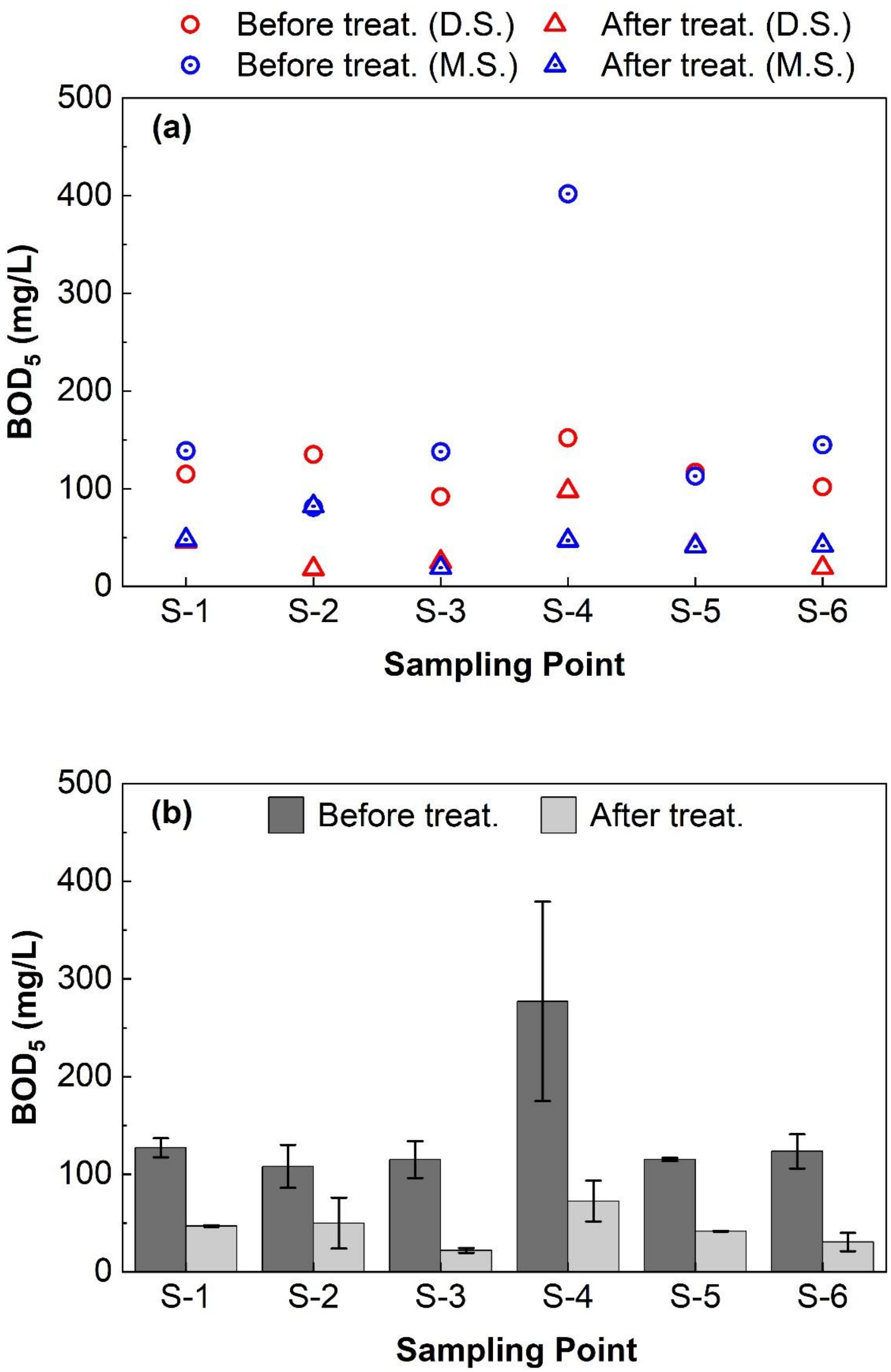

Fig. 4.4. Variation of BOD_5 (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.3.4 COD

COD is a practical parameter for determining polluted water [62]. Variations of COD are presented in **Fig. 4.5**. COD demonstrated significant variation at the ETP inlet points of steel industries. Ranging from 406 mg/L (S-2, M.S.) to 1564 mg/L (S-4, M.S.), these values indicate substantial contamination of the incoming water with organic and inorganic pollutants. The study revealed a notable reduction in COD levels at the outlet points of the ETPs. COD values at outlet points ranged from 42 mg/L (S-2, D.S.) to 246 mg/L (S-4, D.S.), reflecting the efficacy of the treatment processes in mitigating the pollution load in the industrial effluents. The Bangladesh Standards and Testing Institution (BSIE) sets a maximum COD limit of 200 mg/L for effluent water. With the exception of two cases (S-4, D.S., and S-2, M.S.), the COD values observed were within the prescribed range. This suggests a general adherence to local regulatory standards for COD levels in discharged effluent. The study supports the assertion that COD is a practical parameter for assessing water pollution. The wide range of COD values at inlet points highlights the diversity and magnitude of pollutants in the industrial effluents, making COD a useful and sensitive indicator for monitoring water quality. While the majority of COD values meet the BSIE standards, the two exceptions (S-4, D.S., and S-2, M.S.) may warrant closer examination. Identifying and addressing specific sources of elevated COD in these cases could lead to further improvements in the treatment processes and overall environmental performance.

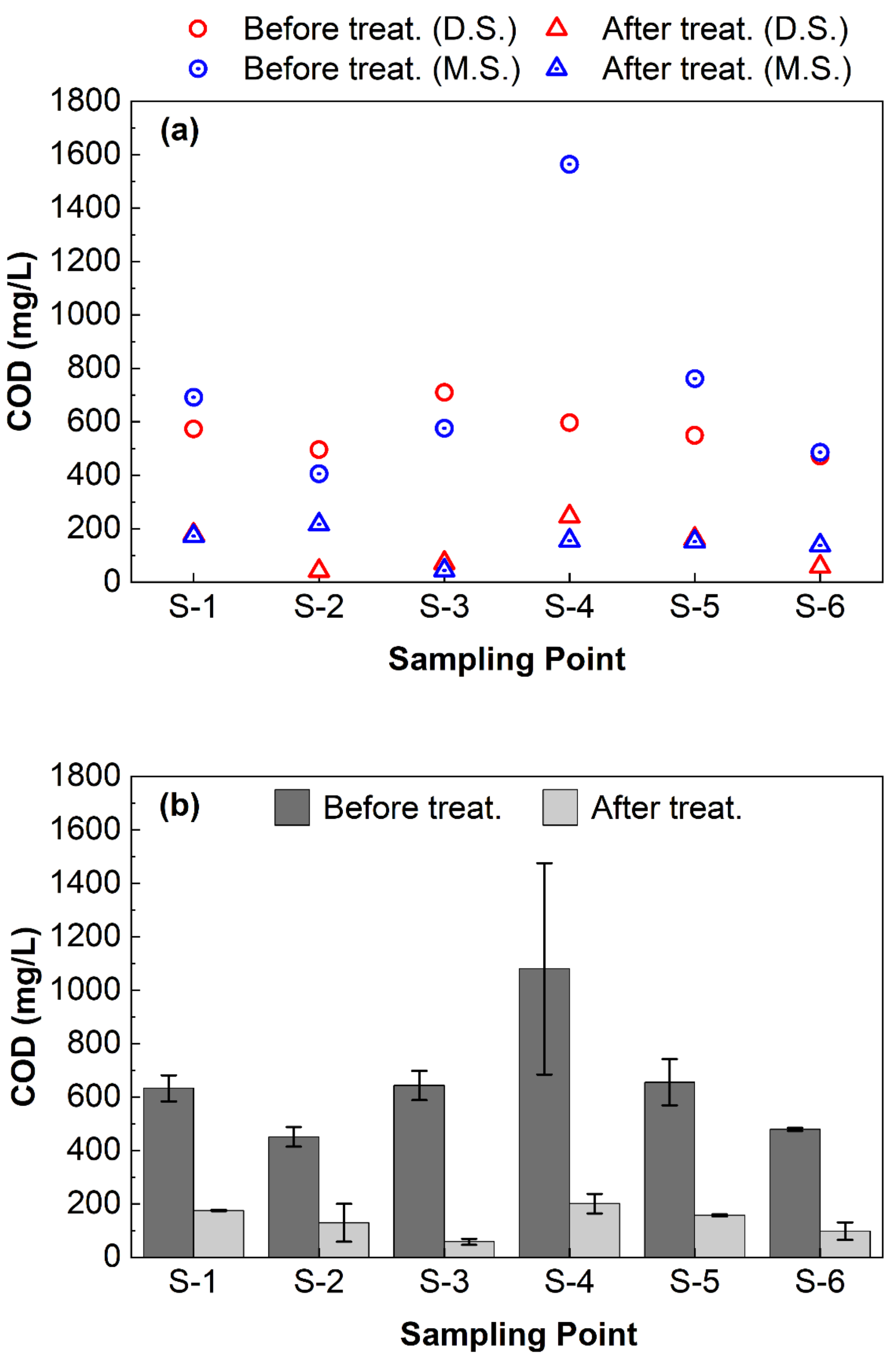

Fig. 4.5. Variation of COD (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.3.5 TDS

The TDS values of effluent samples were measured from six steel industries' ETP inlet and outlet points. Variations of TDS are presented in **Fig. 4.6**. The TDS of the inlet varied from 1884 mg/L (S-2, M.S.) to 14730 mg/L (S-2, D.S.). After treatment, the TDS of discharged stream areas ranged from 976 mg/L to 2658 mg/L.

WHO recommended that the TDS of the water should be 1000 mg/L [15]; Whereas, the BSIE recommendation is 2100 mg/L. Values of TDS of the discharged wastewater from ETP at the outlet point were close to BSIE standard but higher than the WHO standard. Excessive TDS increases water temperature, hinders photosynthesis, and reduces water clarity [66]. Hence, the TDS values have to be maintained below the BSIE limit to protect fisheries, aquatic life, and environmental aspects.

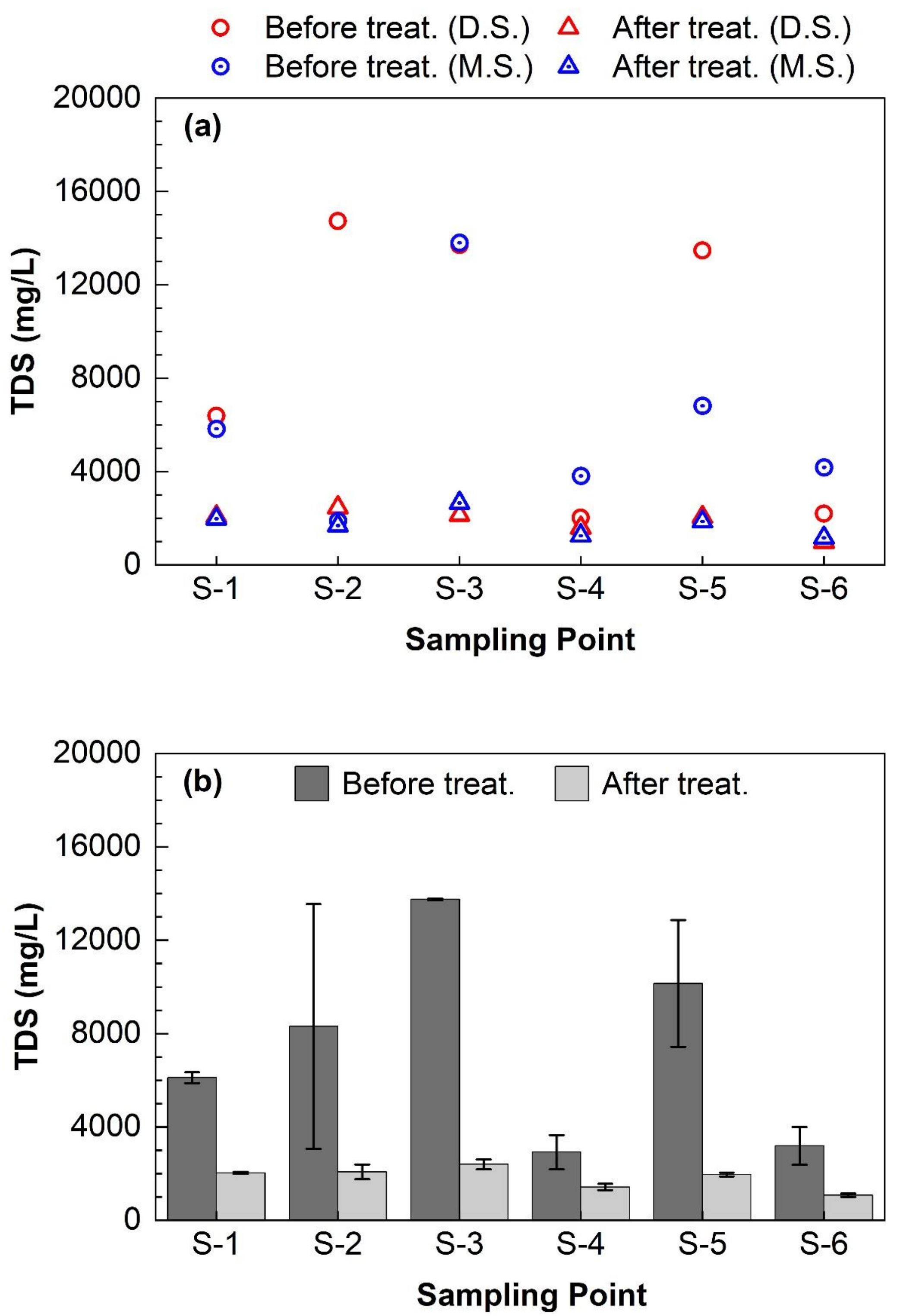

Fig. 4.6. Variation of TDS (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.4 Heavy Metals in Steel Industries Wastewater

The concentrations of five heavy metals including Fe, Cu, Cr, Ni, and Cd were analyzed spectrophotometrically and the results of heavy metal contents for D.S. and M.S. are listed in **Table 4.2**, and their mean variations are plotted in **Figs. 4.7-4.11.**

4.4.1 Iron (Fe)

Fe is abundant in the earth's crust, yet iron deficiency remains a global concern [66]. Variations of Fe in samples are presented in **Fig. 4.7**. The total Fe concentration ranged from 4.512 mg/L (S-6, D.S.) to 44.51 mg/L (S-3, D.S.) in the inlet, while after treatment, discharged stream areas show the fluctuation of Fe concentrations from 0.992 mg/L to 16.89 mg/L. Several organizations have defined maximum contaminant levels for Fe content in water, such as WHO (0.3 mg/L), US EPA (0.3 mg/L), EU (0.45 mg/L), and BSIE (2.0 mg/L) [15], where concentrations above 0.3 mg/L could lead to aquatic environment pollution. Although Fe is essential for human nutrition, its elevated presence in aquatic ecosystems poses serious pollution and health problems.

Table 4.2.

Heavy Metals (mg/L) Present in Effluent at Different Steel-Galvanizing Industry Locations

Sampling Point	Dry Season (D.S.)		Monsoon Season (M.S.)	
	Before Treat.	After Treat.	Before Treat.	After Treat.
		Fe (mg/L)		
S-1	39.95	4.968	40.40	4.146
S-2	16.88	6.067	13.57	0.992
S-3	44.51	16.89	44.06	6.009
S-4	36.38	3.806	37.49	1.481
S-5	39.52	4.591	38.19	6.089
S-6	4.512	4.449	25.48	10.38
		Cu (mg/L)		
S-1	0.3184	0.0922	0.3205	0.0629
S-2	0.1643	0.0584	0.1907	0.0590
S-3	0.2896	0.0907	0.2504	0.0803
S-4	0.1055	0.0833	0.1519	0.0665
S-5	0.1598	0.1317	0.1020	0.0774
S-6	0.2239	0.0791	0.0974	0.0870
		Cr (mg/L)		
S-1	0.9280	0.0359	0.9276	0.1321
S-2	1.1330	0.2229	0.0799	0.0156
S-3	0.6728	0.0895	0.5739	0.0016
S-4	0.4206	0.0912	0.3486	0.0019
S-5	0.8214	0.0753	0.9988	0.0038
S-6	1.3260	1.2620	1.0510	0.4430
		Ni (mg/L)		
S-1	0.1384	—	0.1404	0.0093
S-2	0.1147	—	0.0762	—
S-3	0.1814	0.0181	0.175	0.0238
S-4	0.0908	—	0.104	—
S-5	0.0719	0.0359	0.0268	0.0042
S-6	0.0195	0.0103	0.0134	0.0129
		Cd (mg/L)		
S-1	—	—	—	—
S-2	—	—	—	—
S-3	0.012	0.0105	0.0058	—
S-4	0.0126	0.0022	0.0112	—
S-5	0.0105	—	0.0013	—
S-6	0.0016	—	0.0095	0.005

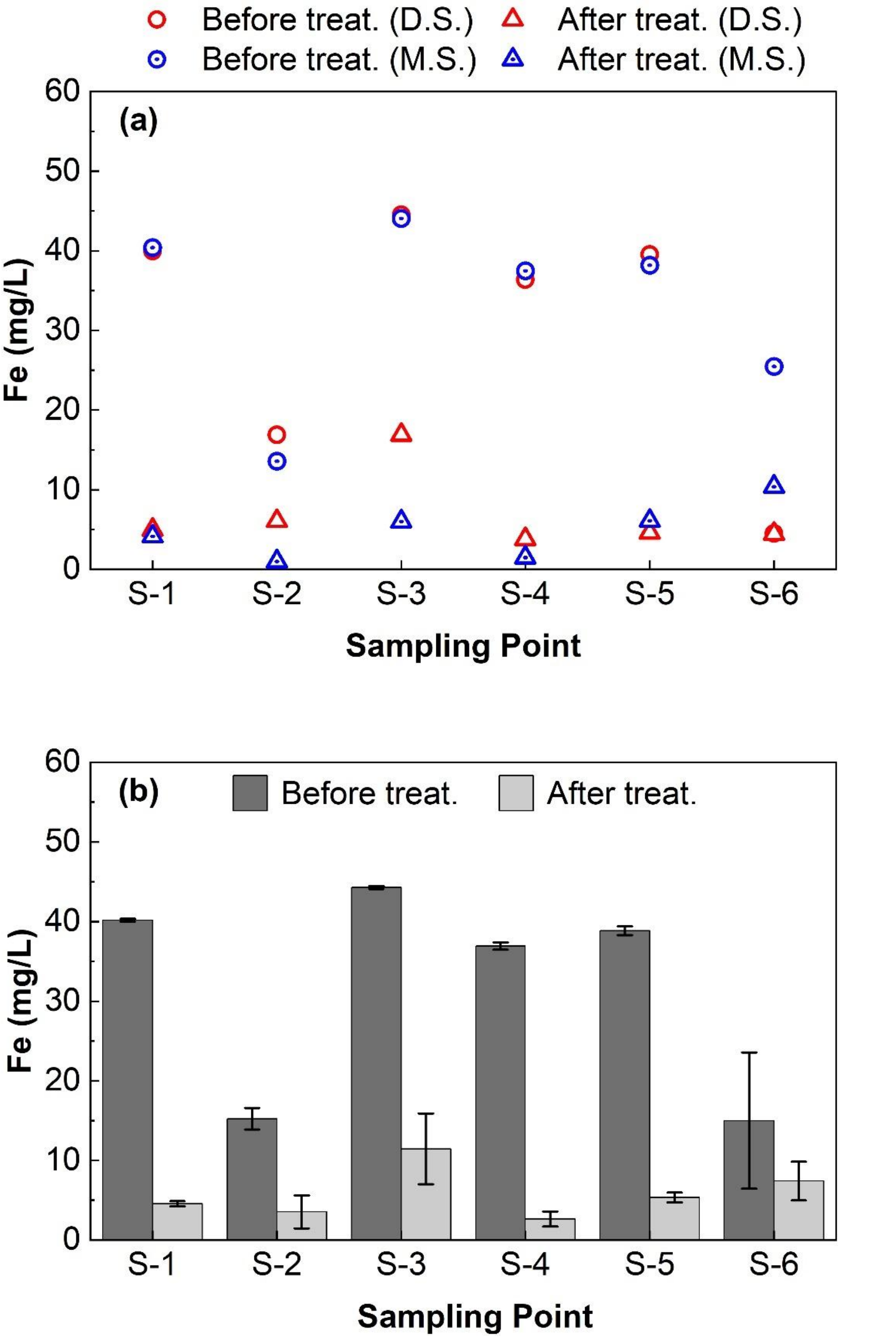

Fig. 4.7. Variation of Fe (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

This study's results indicate that the Fe concentration in water exceeded the permissible limits set by international regulatory bodies, even though national standards are maintained, suggesting probable Fe pollution. In the Halda River, Fe concentrations were reported to be varied from 0.311 mg/L to 0.494 mg/L [30], surpassing the standard limit of both WHO and US EPA (0.3 mg/L). Thus, high Fe concentration of natural water bodies is possibly linked to effluent discharge from nearby industries.

4.4.2 Copper (Cu)

Cu is an indispensable trace element that shows a significant role in bio- or micro-organisms. Variations of Cu collected samples are presented in **Fig. 4.8**. The Cu concentration of the inlet varied from 0.102 mg/L to 0.3205 mg/L. After treatment, the Cu concentration of discharged stream areas ranged from 0.0584 mg/L to 0.1317 mg/L. **Table 1.2** presents allowable limits for Cu contents in water set by various organizations, such as WHO (2.0 mg/L), EU (0.14 mg/L), BSIE (0.5 mg/L), and US EPA (1.3 mg/L). The Cu concentration treated by ETP plants falls within the range of these established standard limits.

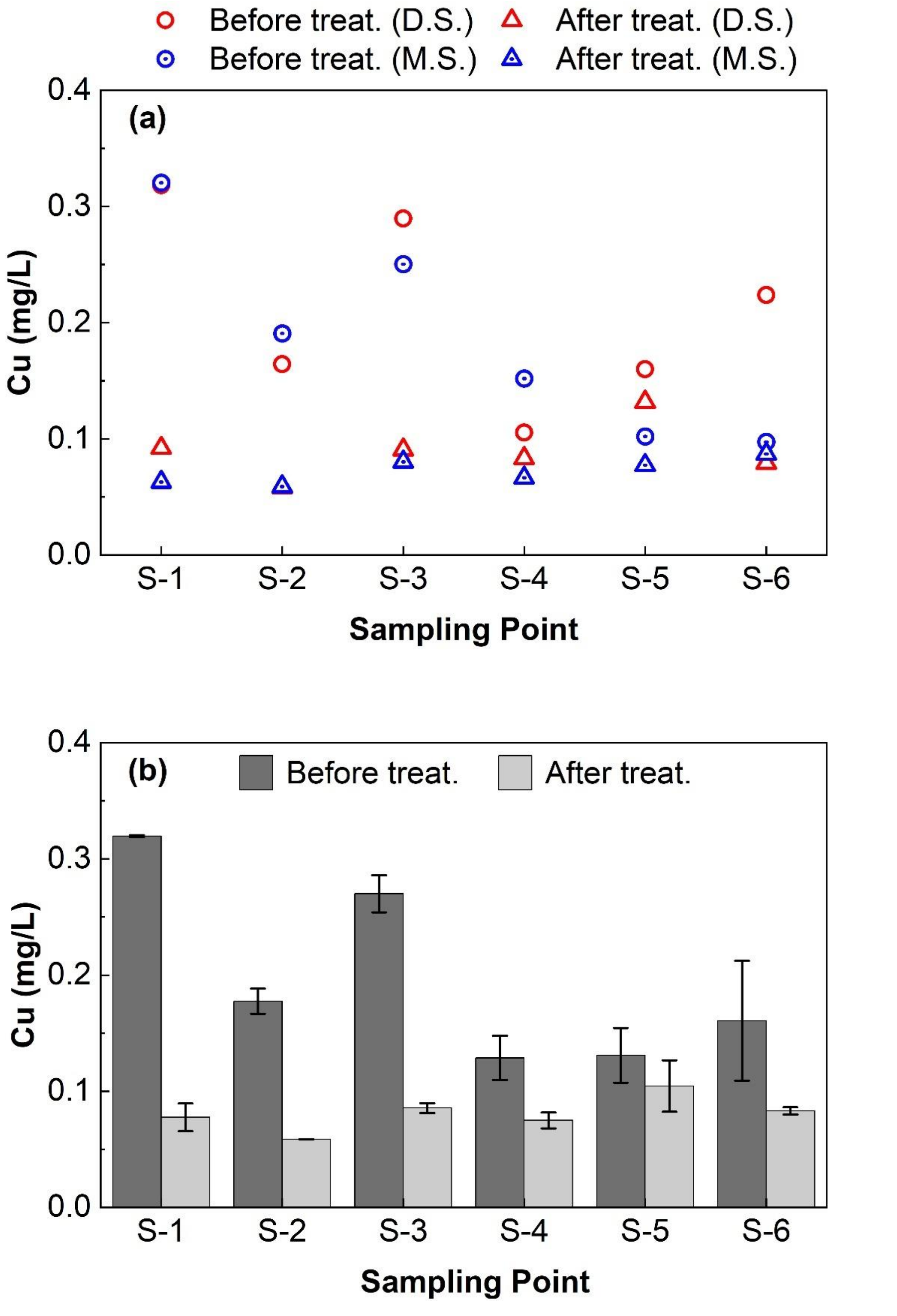

Fig. 4.8. Variation of Cu (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.4.3 Chromium (Cr)

In nature, Cr exists in two oxidation states, Cr (III) and Cr (VI), with different physiological effects [12]. Cr(VI) is the prevalent and toxic form found in shallow aquifers, and its inhalation exposure is classified as "carcinogenic to humans" (Group 1) by IARC [2, 67]. Variations of Cr in collected samples are presented in **Fig. 4.9**.

In the studied area, the total Cr content at the inlet points ranged from 0.0799 mg/L to 1.326 mg/L, while after treatment, the Cr concentration in the discharged stream areas varied from 1.262 mg/L to 0.0016 mg/L. Different organizations have defined safe limits for Cr content in water, including WHO (0.05 mg/L), BSIE (0.5 mg/L), and US EPA (0.011 mg/L). Notably, during the dry season, elevated Cr levels were observed at the inlet points, suggesting the possible utilization of surface water sources. The Cr concentrations found in this study often exceed the range of WHO and BSIE standards, indicating that the industries in the area might be a probable source of Cr contamination. Some rivers, such as the Karnaphuli River with Cr concentrations of 0.0869 mg/L in winter and 0.0696 mg/L in the summer season [7], and the Buriganga River with levels of 0.003-0.013 mg/L during the monsoon and 0.001-0.008 mg/L in winter, have been reported to be affected by Cr pollution respectively [11]. Thus, Cr contamination of natural water bodies is probably connected to effluent discharge from nearby industries.

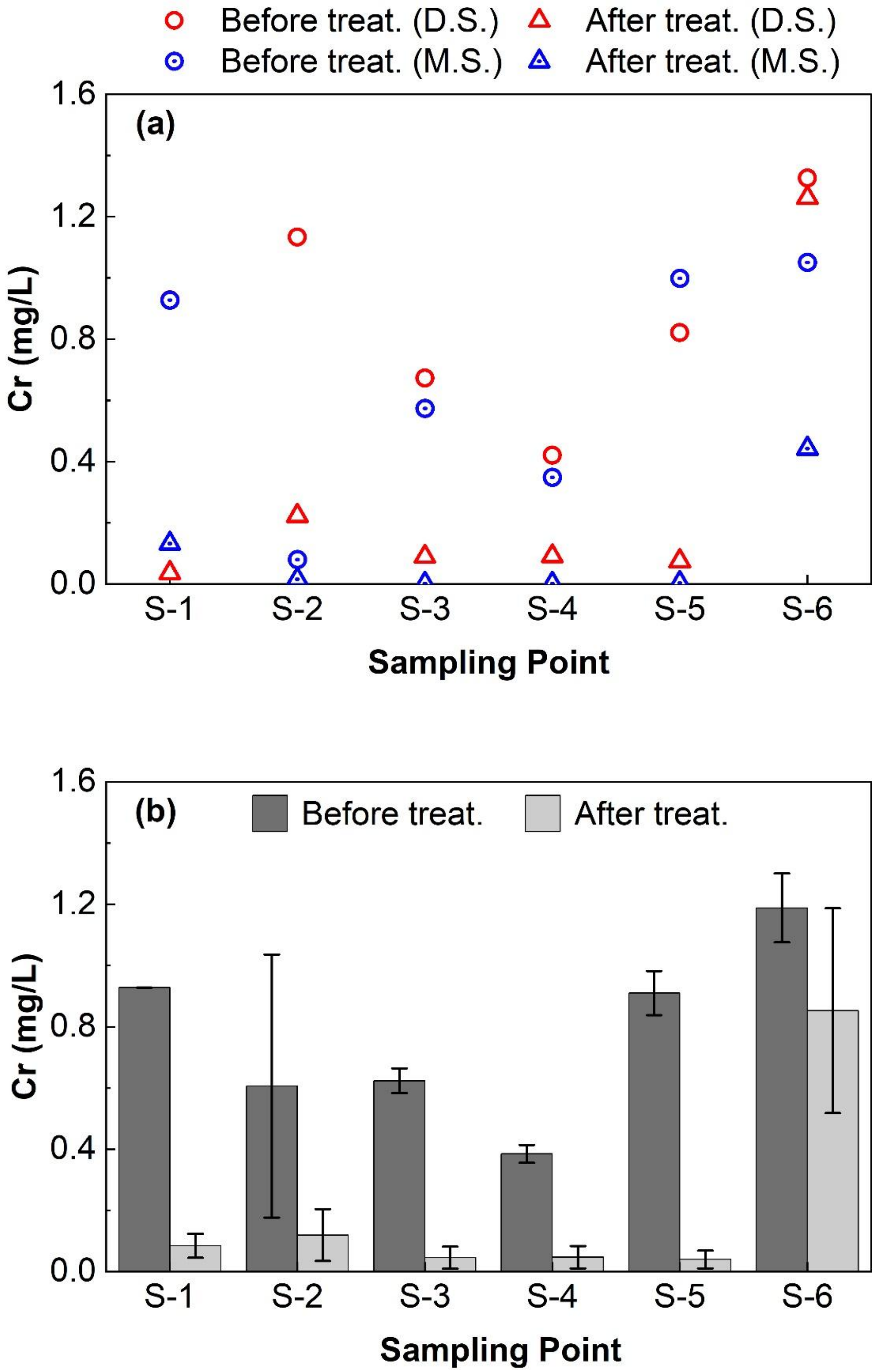

Fig. 4.9. Variation of Cr (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.4.4 Nickel (Ni)

Ni is a nutritionally essential trace element for humans, animal species, and plants. However Ni can affect the mass population through contaminated drinking water and food intake. Nickel compounds can cause cancer [68]. Variations of Ni are presented in **Fig. 4.10**.

Different organizations have defined safe limits for Ni content in water, including WHO (0.02 mg/L), BSIE (1.0 mg/L), EU-DIR (0.034 mg/L), and US EPA (0.052 mg/L). The Ni of the inlet varied from 0.0134 to 1.1814 mg/L. After treatment, the Ni concentration of discharged stream areas ranged from 0.0359 mg/L to the lower values of the detection limit. Hence, Ni concentrations were close to the safe limit maintained by the steel industries.

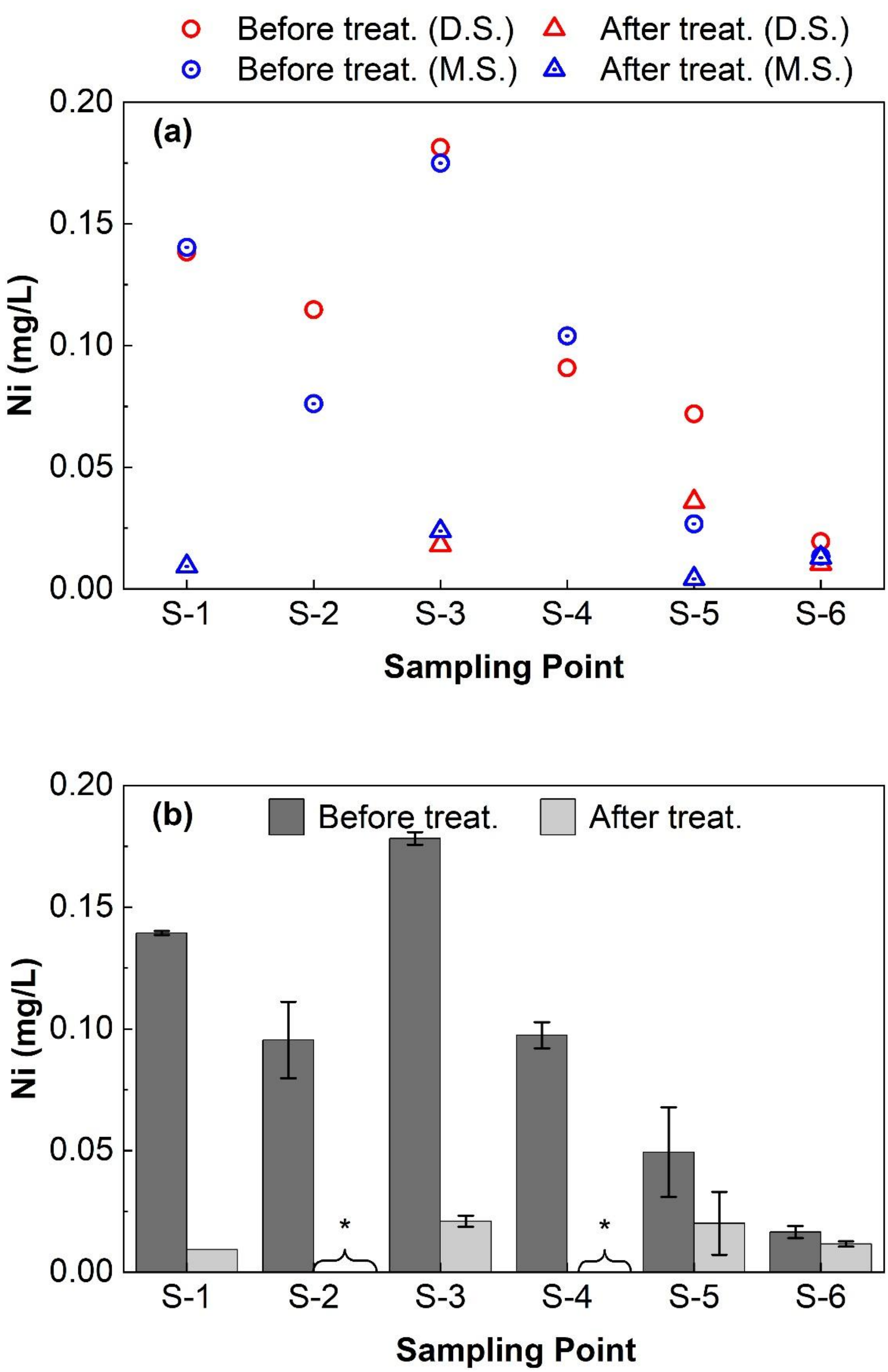

Fig. 4.10. Variation of Ni (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season. * Under detection limit.

4.4.5 Cadmium (Cd)

Cd is a very toxic trace metal because of its long half-life [52]. Variations of Cd are in different samples presented in **Fig. 4.11**. The Cd of the inlet varies from 0.0126 mg/L to trace (under detection limit). After treatment Cd concentration of discharged stream varied from 0.0105 mg/L to trace (under detection limit). Different organizations have defined safe limits for Cd content in water, including WHO (0.003 mg/L), BSIE (0.05 mg/L), and US EPA (0.0025 mg/L). The Cd concentration of Karnaphuli River is 0.0106 mg/L in winter and 0.0065 mg/L in summer season [7]. Cd concentrations of the discharged wastewater from ETP at the outlet points are found within a suitable range of BSIE.

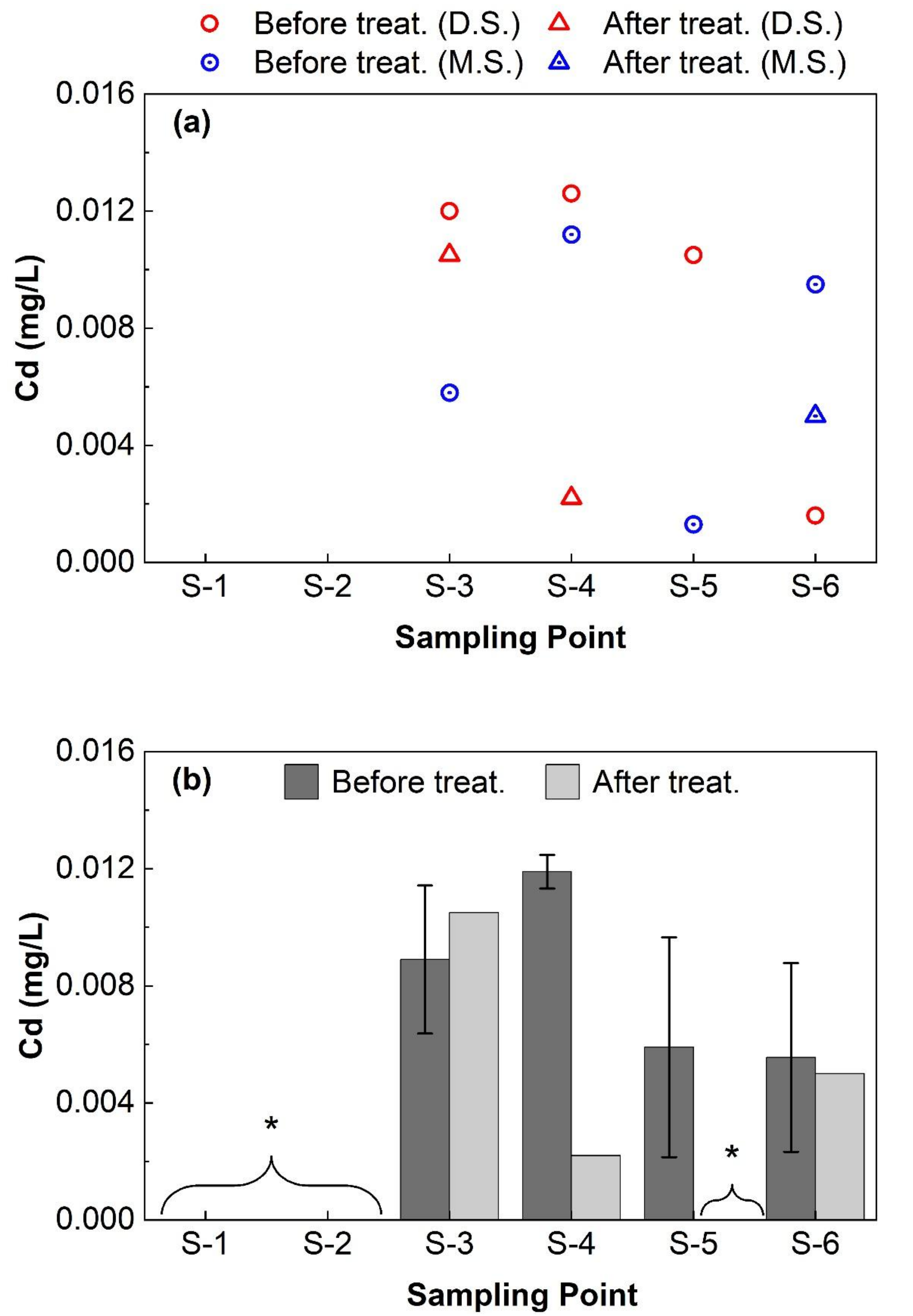

Fig. 4.11. Variation of Cd (mg/L) in wastewater samples collected at ETP inlet and outlet of steel-galvanizing industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season. * Under detection limit.

4.5 Removal Efficiency

The removal efficiency of Fe, Cu, and Cr has been depicted in **Fig. 4.12**. Overall, ETP plants S-1 and S-5 demonstrated relatively effective metal removal efficiencies for these metals. However, S-2, S-3, S-4, and S-6 require improvements, particularly in the removal of Fe and Cr. The industries analyzed exhibited safe levels of Cd, Ni, and Cu, but elevated concentrations of Fe and Cr, suggesting that wastewater from these industries has the potential to contribute to water pollution.

When determining the most suitable combination of treatment solutions, several factors should be considered, including the intended usage of the water, specific contaminants of concern, costs, energy consumption, and waste disposal alternatives [2]. Various approaches for wastewater treatment, designed for reuse, can be combined to achieve optimal results. Implementing appropriate measures and designing ETPs accordingly can effectively reduce the potential pollution caused by Fe and Cr. The findings of this study underscore the significance of optimizing ETP processes to minimize environmental pollution resulting from steel industry wastewater. Sharing these findings can assist industries in adopting best practices and addressing environmental concerns.

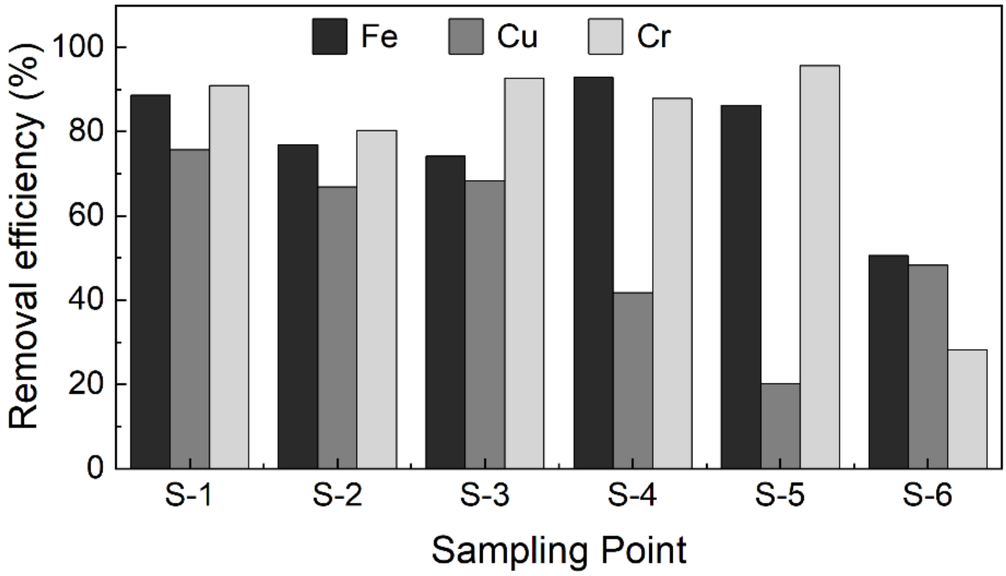

Fig. 4.12. Removal efficiencies of Fe, Cu, and Cr expressed in percentage.

Part B: Study on ETP and ETP samples of Paint Industry

4.6 Industrial Effluents Analysis of the Paint Industry

The paint industry's wastewater is highly polluted wastewater that needs immediate attention for its treatment methodology before its disposal. Physicochemical parameters and concentration of some heavy metals in the discharged wastewater of two paint industries situated near the Karnafuli River were measured analytically. In the ETP of paint industries, various processes are conducted such as coagulation, flocculation, sedimentation, filtration, electrocoagulation, radiation, and adsorption [1]. Depending on the manufacturing processes of individual industrial units, the composition of paint industry wastewater varies widely [39].

4.7 Operation and Maintenance of ETP Plants of Steel Industries

In the operation and maintenance of Effluent Treatment Plants (ETPs) in paint industries, various crucial components and processes are involved to ensure effective wastewater treatment. **Fig. 4.13 (a,b)** illustrates the ETP process flow of the paint industry, providing an overview of the treatment stages.

Sampling site: P-1

Geographical Location: 2°23 '16.3536''N 91°52 '9.5052''E

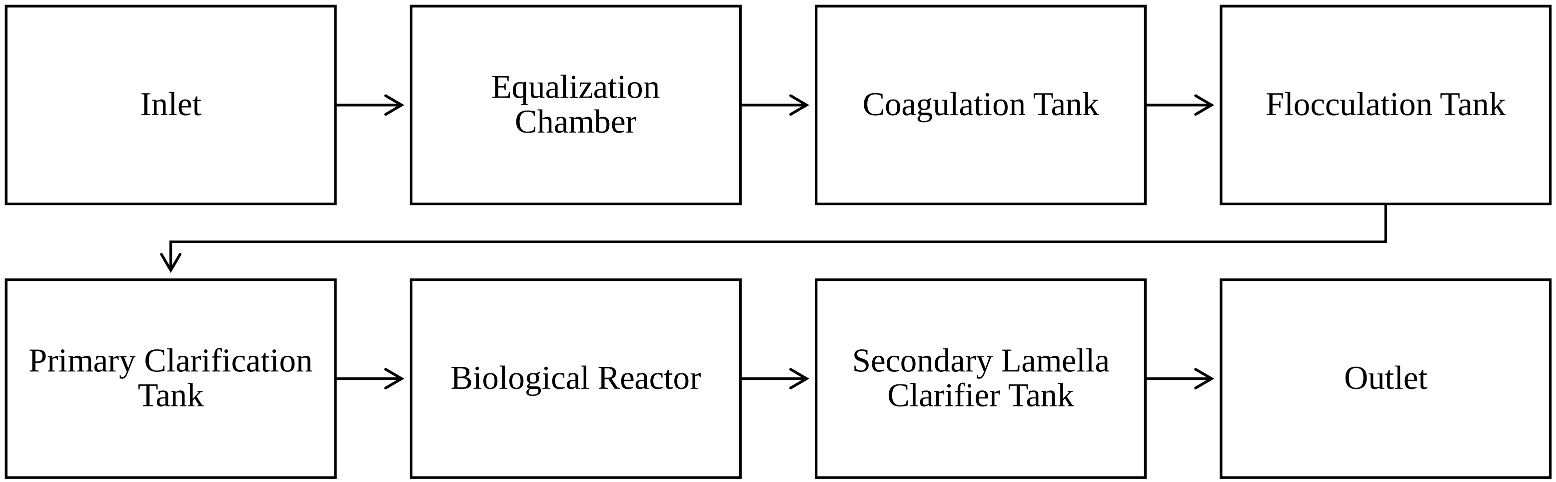

Fig. 4.13 (a). ETP Process Flow of the Paint Industry

Sampling site: P-2

Geographical Location: 22°22 '49.0008''N 91°51 '58.9392''E

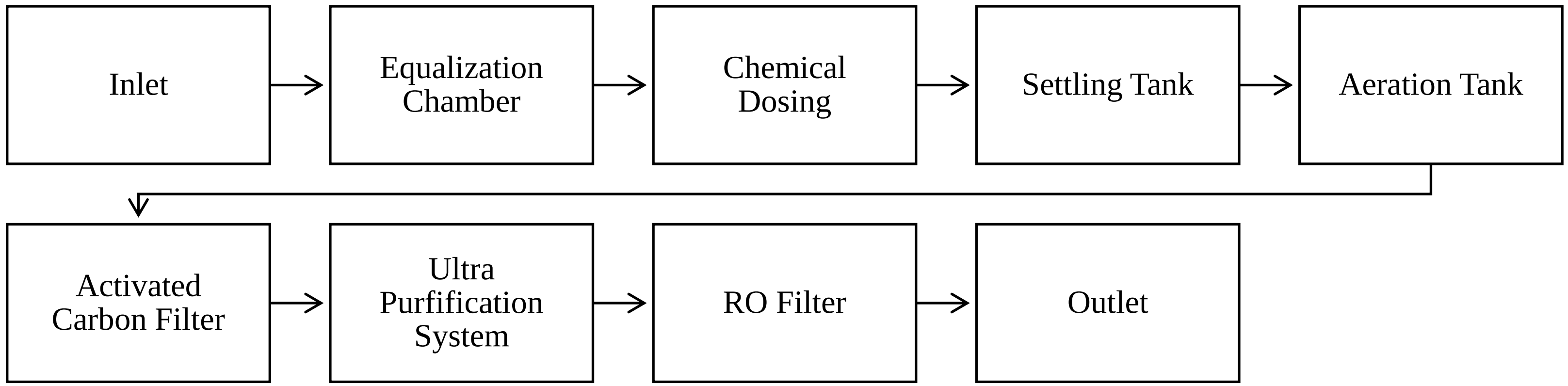

Fig. 4.13. (b). ETP Process Flow of the Paint Industry

Continuing from the preceding **Section 4.2** (Operation and Maintenance of ETP Plants in Steel Industries), the current discussion focuses on presenting the ETP operation within the paints industry.

4.7.1 Inlet of ETP: In the paints industry, the inlet chamber serves as the initial point for wastewater treatment, employing bar screens to eliminate large items and debris. The emphasis on sampling for effluent composition analysis aligns with the rigorous standards observed in the steel galvanizing industry. Variations possibly exist in specific requirements based on the nature of paint industry effluents.

4.7.2 Equalization Chamber: Commonality with the steel industry is found in the role of the equalization chamber in stabilizing wastewater flow amid fluctuating conditions. Its contributions to pollutant load regulation, temperature management, and pH adjustment echo the universal importance of this stage. Both the industries (P1 and P2) installed the equalization chamber.

4.7.3 Chemical Dosing Tank: The controlled chemical dosing is made, with a particular focus on coagulants and flocculants for suspended solids destabilization and agglomeration. Variances may arise in the choice of chemicals, aligning with the unique characteristics of paint industry effluents.

4.7.4 Biological Reactor Tank: The biological reactor tank, a stage dedicated to the breakdown of organic and inorganic pollutants by microorganisms, signifies a shared commitment to biological treatment. Such tank is in application in the first industry (P1).

4.7.5 Secondary Clarifier: The secondary clarifier's function in separating solid particles following biological treatment mirrors the standardized approach seen in both industries. The necessity for sludge removal for clarifier efficiency maintenance remains a constant, demonstrating the ongoing need for operational vigilance. In P1, both primary and secondary clarifier tank have been noted.

4.7.6 Activated Carbon Filter: Activated carbon filters, employed for the removal of organic compounds and improvement of water quality, find relevance in both industries. However, the specifics of challenges posed by paints industry effluents may influence the design and utilization of these filters differently. In P2, such filter has been found in application.

4.7.7 Reverse Osmosis (RO) Unit: The incorporation of a reverse osmosis unit for desalting brackish water and producing purified water is notably absent in the steel industry's ETP. This divergence highlights the industry-specific challenges in the paints sector, emphasizing the need for advanced treatment methods. In P2, RO unit has been recorded.

In summary, despite shared aspects in ETP operation, the paints and steel galvanizing industries employ distinct treatment methods and components tailored to their specific needs. Both prioritize efficiency, regulatory compliance, and environmental protection, albeit through unique operational strategies.

4.8 Physicochemical Parameters of Paint Industries

Variations of five physicochemical parameters (pH, DO, BOD_5, COD, and TDS) for D.S. and M.S. are presented in **Table 4.3** and their mean variations are plotted in **Figs. 4.14-4.18**.

Table 4.3

Physicochemical Characterization of Effluent Samples of Paint Industries

Sampling Point	Dry Season (D.S.)		Monsoon Season (M.S.)	
	Before Treat.	After Treat.	Before Treat.	After Treat.
		pH		
P-1	5.08	6.77	5.9	6.29
P-2	8.81	8.26	7.73	7.8
		DO (mg/L)		
P-1	1.05	4.03	2.13	4.61
P-2	2.36	7.75	2.23	7.79
		COD (mg/L)		
P-1	582	122	622	224
P-2	378	26	411	48
		BOD_5 (mg/L)		
P-1	132	38	148	58
P-2	79	12	91	17
		TDS (mg/L)		
P-1	2318	736	2016	535
P-2	2111.8	203	2415.4	270

4.8.1 pH

pH (potential hydrogen) of a solution refers to its hydrogen ion activity and is expressed as the logarithm of the reciprocal of the hydrogen ion activity at a given temperature. Variations of pH are presented in **Fig. 4.14**.

The pH of the inlet varies from 5.08 (P-1, D.S.) to 8.81 (P-2, D.S.). After treatment, pH of discharged stream areas ranged from 6.29 to 8.26. pH of the discharged wastewater from ETP at the outlet point is found within a suitable range of WHO (6.5 — 8.5) and BSIE (6.0 — 9.0). As the paint industry is very close to the Karnaphuli River (pH is 8.17 in winter and 7.89 in summer season reported by Ali et al [7] the values are found comparable to river water. Most fishes can tolerate pH ranging from 5.0 to 9.0 and aquatic life is not directly impacted by a smaller change in pH. Thus, discharge of the effluent may not hamper marine life considering the pH.

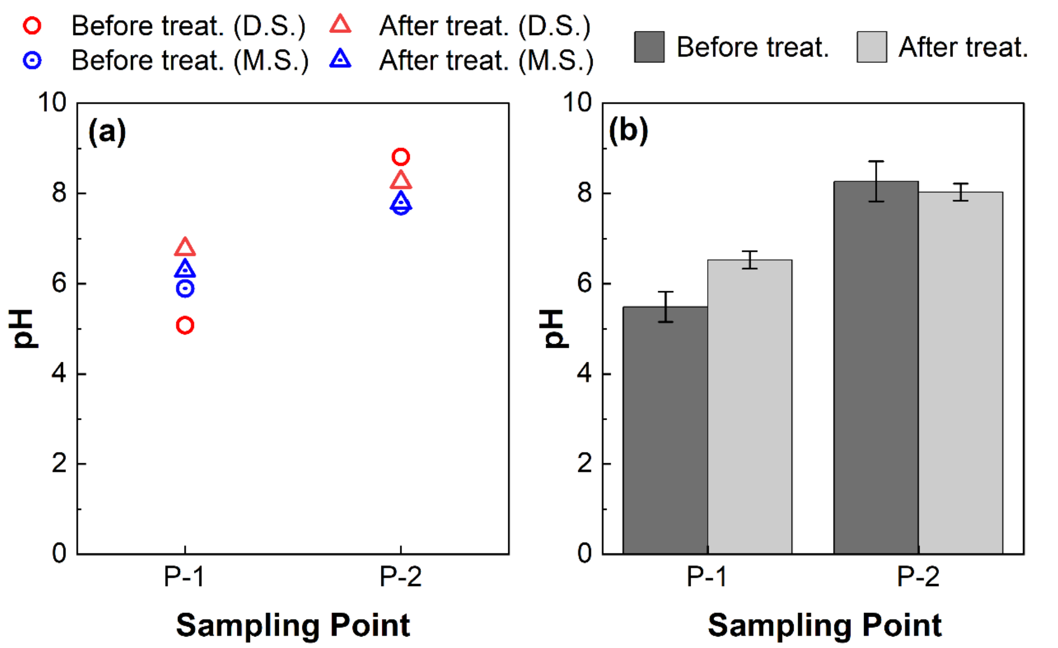

Fig. 4.14. Variation of pH in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.8.2 DO

DO is a measure of the degree of pollution by organic matter and the destruction of organic substances, as well as the self-purification capacity of the water body. The DO values of effluent samples were collected from the ETP inlet and outlet points of two paint industries. Variations for DO are presented in **Fig. 4.15**.

Inlet DO varied from 1.05 mg/L (P-1, D.S.) to 2.36 mg/L (P-2, D.S.). After treatment, the DO of the discharged stream at outlet points ranged from 4.03 mg/L to 7.79 mg/L. BSIE recommendation for DO is 4.5-8.0 mg/L. DO of the discharged wastewater from ETP at the outlet point is found within a suitable range provided by BSIE and lower than the DO of Karnaphuli River (9.92 mg/L in winter and 8.07 mg/L in summer season as reported by Ali et al [7]. Lower DO at the inlet point is due to chemical processing and increased chemical temperature led to a decrease in DO resulting by decomposition of organic matter.

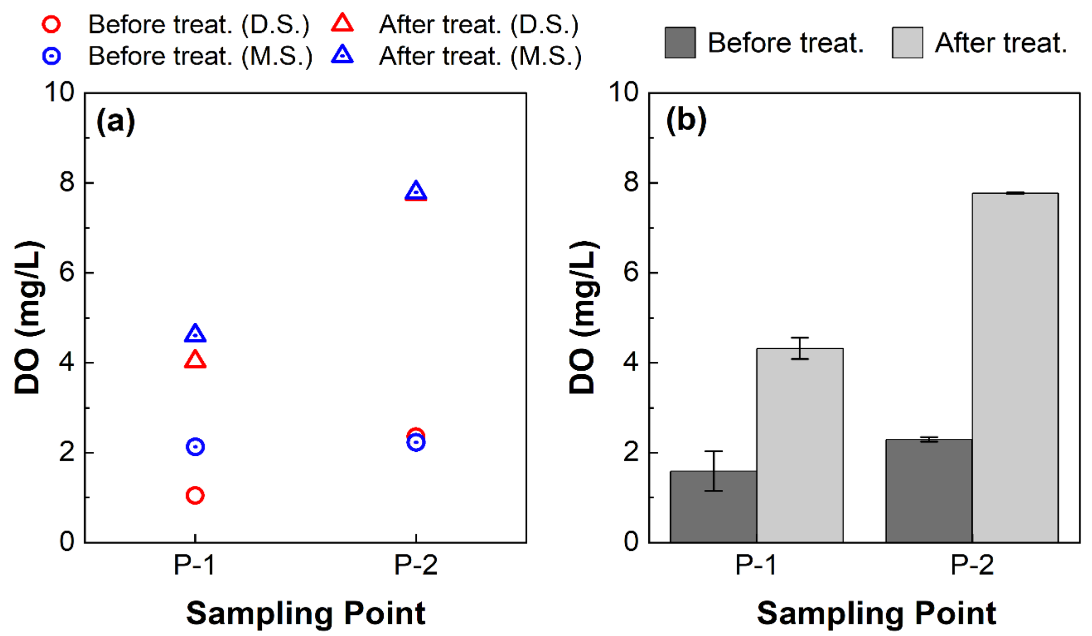

Fig. 4.15. Variation of DO (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.8.3 BOD_5

BOD_5 measures the quantity of oxygen consumed by microorganisms during the decomposition of organic matter. Variations of BOD_5 are presented in **Fig. 4.16**. BOD_5, which measures the quantity of oxygen consumed during the decomposition of organic matter, exhibited variation at the ETP inlet points of the two paint industries. BOD_5 levels ranged from 79 mg/L (P-2, D.S.) to 148 mg/L (P-1, M.S.). This indicates differences in the organic content of effluent streams from different paint manufacturing processes, reflecting diverse sources of organic pollutants.

The study revealed a significant reduction in BOD_5 levels at the outlet points of the ETPs. BOD_5 values at outlet points ranged from 12 mg/L to 58 mg/L, suggesting the effectiveness of the treatment processes in decreasing the organic pollution load before discharging the effluent into the environment. While the WHO does not specify a guideline value for BOD_5, the Bangladesh BSIE recommends a maximum BOD_5 limit of 50 mg/L for effluent water. The BOD_5 values recorded at the outlet points of the paint industry ETPs fall within the range set by BSIE, indicating compliance with local regulatory standards for organic pollution.

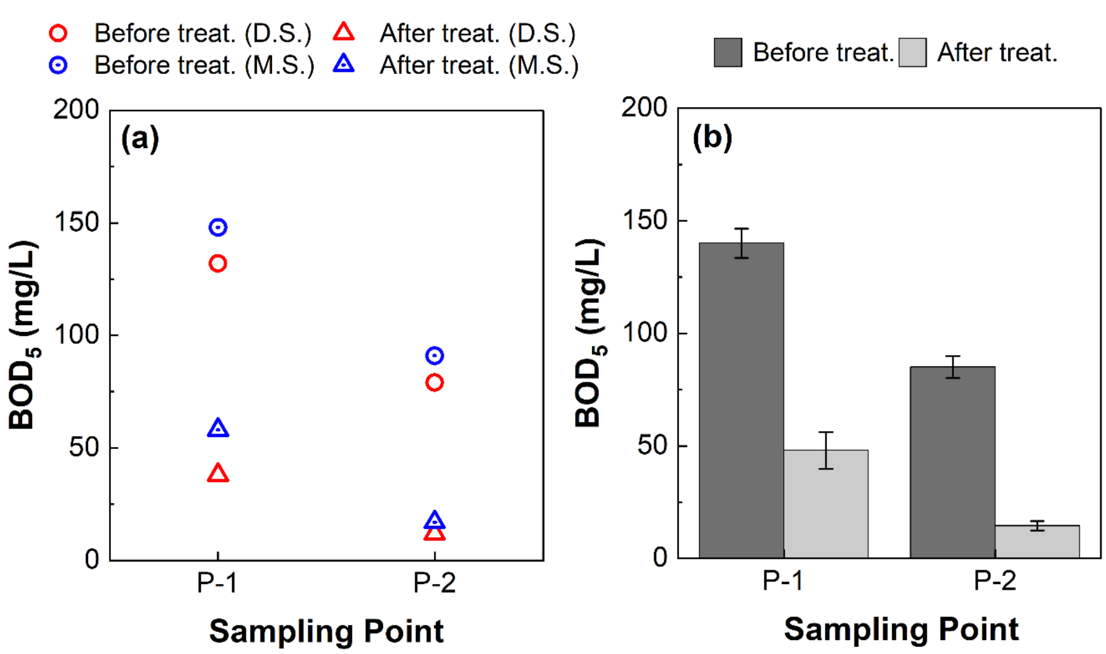

Fig. 4.16. Variation of BOD_5 (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.8.4 COD

Variations of COD in ETPs of paint industries are presented in **Fig. 4.17**. The COD levels at the ETP inlet points of paint industries exhibited notable variation, ranging from 378 mg/L (P-2, D.S.) to 622 mg/L (P-1, M.S.). This variability suggests differences in the composition of effluent streams from various paint manufacturing processes, indicating diverse sources of organic pollutants and other contaminants.

The study revealed a substantial decrease in COD levels at the outlet points of the ETPs. COD values ranged from 26 mg/L to 224 mg/L, indicating the efficacy of the treatment processes in reducing the organic pollution load before discharging the effluent into the environment.

While the WHO does not specify a guideline value for COD, the BSIE recommends a maximum COD limit of 200 mg/L for effluent water. The COD values recorded at the outlet points of the paint industry ETPs fall within the range set by BSIE, indicating compliance with local regulatory standards. The results suggest that the treatment processes implemented by the paint industry ETPs are effective in reducing COD levels to within acceptable limits. This is crucial for mitigating the impact of organic pollutants on water quality and environmental health.

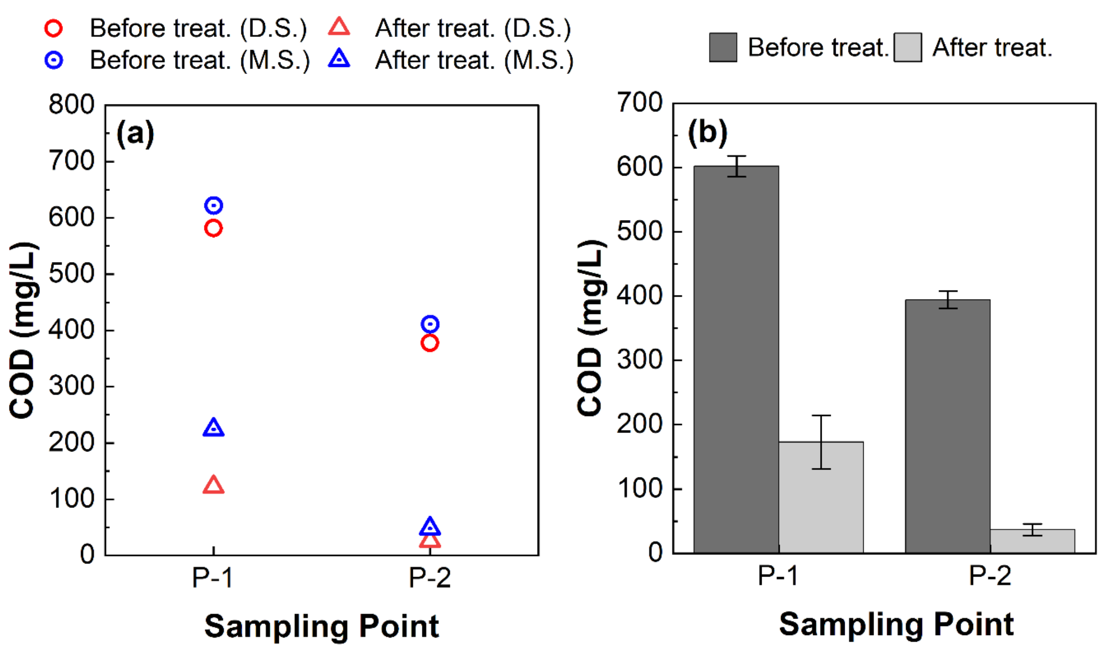

Fig. 4.17. Variation of COD (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.8.5 TDS

The TDS values of effluent samples were collected from two paint industries' ETP inlet and outlet points. Variations of TDS are presented in **Fig. 4.18**. The TDS levels at the inlet points of the ETPs for the paints industry varied notably. The range extended from 2016 mg/L (P-1, M.S.) to 2415 mg/L (P-2, M.S.). This variation suggests differences in the composition of effluent streams from different paint manufacturing processes, indicating diverse sources of dissolved solids. Following treatment processes, there was a significant reduction in TDS levels observed in the discharged effluent streams. TDS values ranged from 203 mg/L to 736 mg/L at outlet points, indicating the efficacy of the treatment processes in removing dissolved solids from the industrial wastewater.

The WHO standard for TDS in water is set at 1000 mg/L, while the BSIE guidelines allow for TDS levels up to 2100 mg/L. The TDS values recorded at the outlet points of the industrial ETPs fell within both the WHO and BSIE limits, indicating compliance with national and international standards for water quality. The results suggest that the treatment processes implemented by the paints industry ETPs are effective in reducing TDS levels to within acceptable limits. This indicates a commitment to environmental stewardship and compliance with regulatory requirements governing industrial effluent discharge.

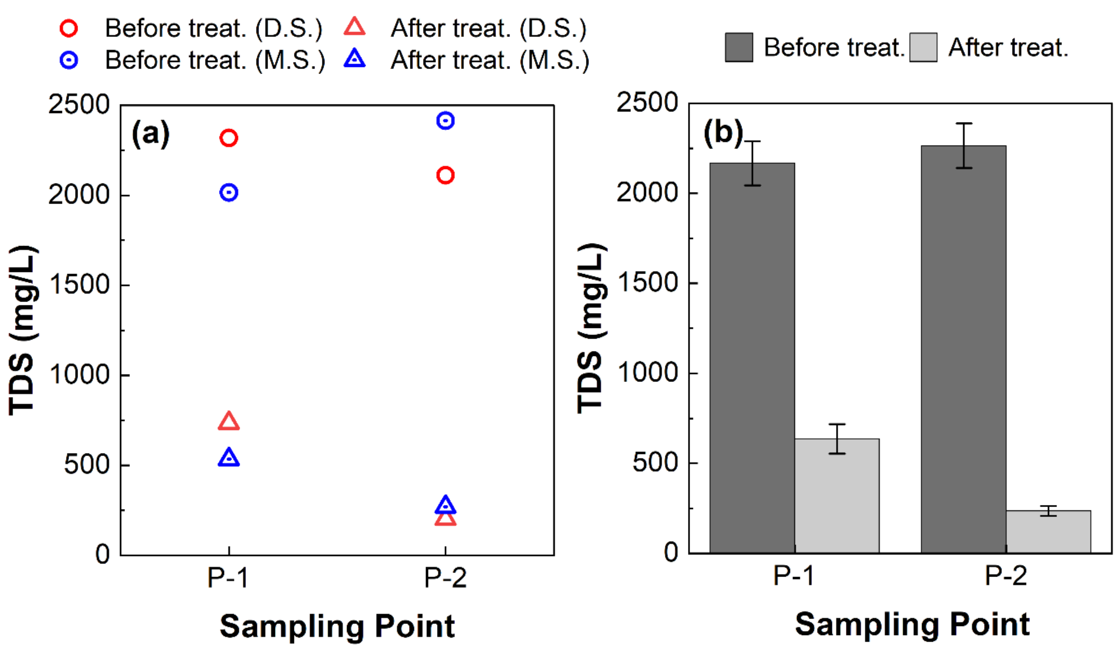

Fig. 4.18. Variation of TDS (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

4.9 Heavy Metal Concentration in Paint Industry Wastewater

Table 4.4 shows the concentration and range of heavy metals (Cd, Cu, Cr, Ni, and Cd) found in effluent samples collected from two paint industrial areas in Chattogram. The higher concentration of heavy metals in water may cause health hazards to the ecology's population and living people.

Variations for Fe are presented in **Fig. 4.19**. The Fe concentration of the inlet varies from 8.39 mg/L (P-1, M.S.) to 20.48 mg/L (P-2, D.S.). After treatment, Fe concentration of discharged stream areas ranged from 2.333 mg/L to 5.117 mg/L.

According to the WHO guideline for Drinking Water Quality value, maximum contaminant levels of 0.3 mg/L (water) for Fe are acceptable. Above 0.3 mg/L might lead to pollution of the aquatic environment. BSIE recommendation is 2.0 mg/L. From this study, the iron concentration in water has exceeded the guideline limits of WHO and BSIE standards indicating a probable Fe pollution.

Table 4.4

Heavy Metals (mg/L) Present in Effluent of Paint Industries

Sampling Point	Dry Season (D.S.)		Monsoon Season (M.S.)	
	Before Treat.	After Treat.	Before Treat.	After Treat.
		Fe (mg/L)		
P-1	11.53	3.288	8.39	2.595
P-2	20.48	2.333	18.78	5.117
		Cu (mg/L)		
P-1	0.1284	0.0626	0.0941	0.0592
P-2	0.0807	0.0759	0.0713	0.0644
		Cr (mg/L)		
P-1	0.1417	—	0.1417	0.0935
P-2	0.1205	0.0527	0.1128	0.0093
		Ni (mg/L)		
P-1	—	—	—	—
P-2	0.0248	0.0139	0.0131	0.0103
		Cd (mg/L)		
P-1	0.0407	—	—	—
P-2	—	—	—	—

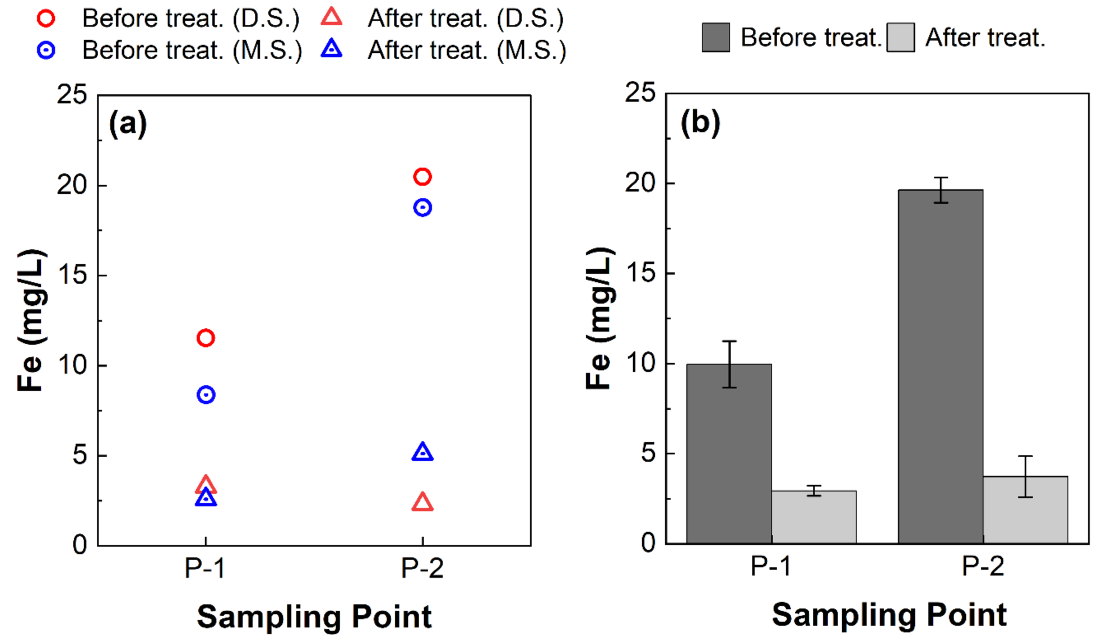

Fig. 4.19. Variation of Fe (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

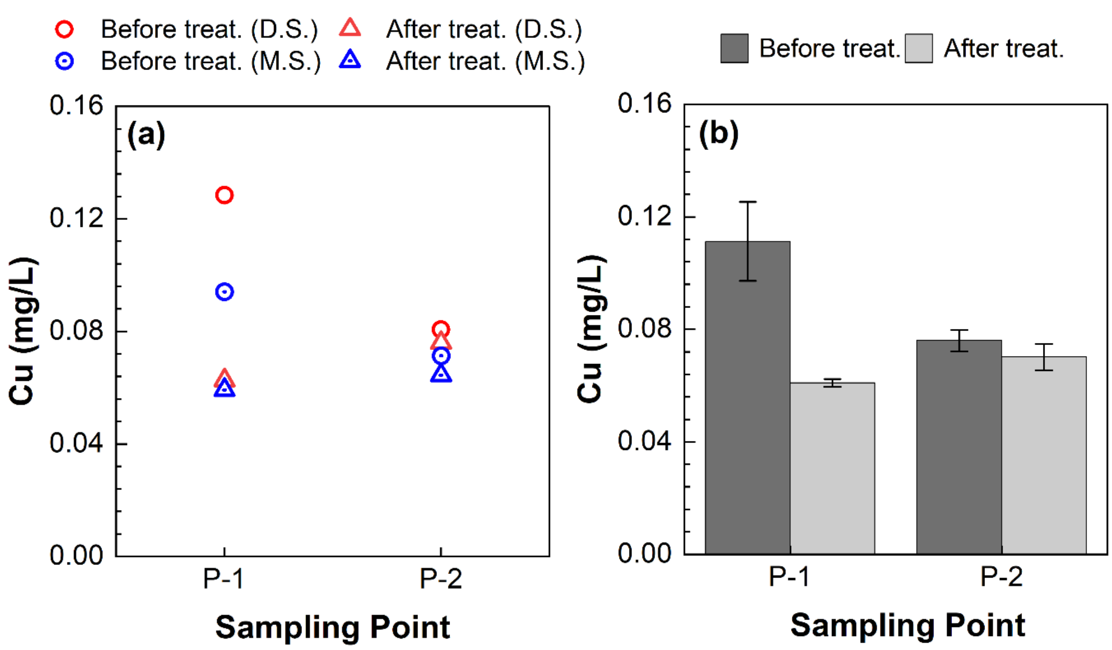

Fig. 4.20. Variation of Cu (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

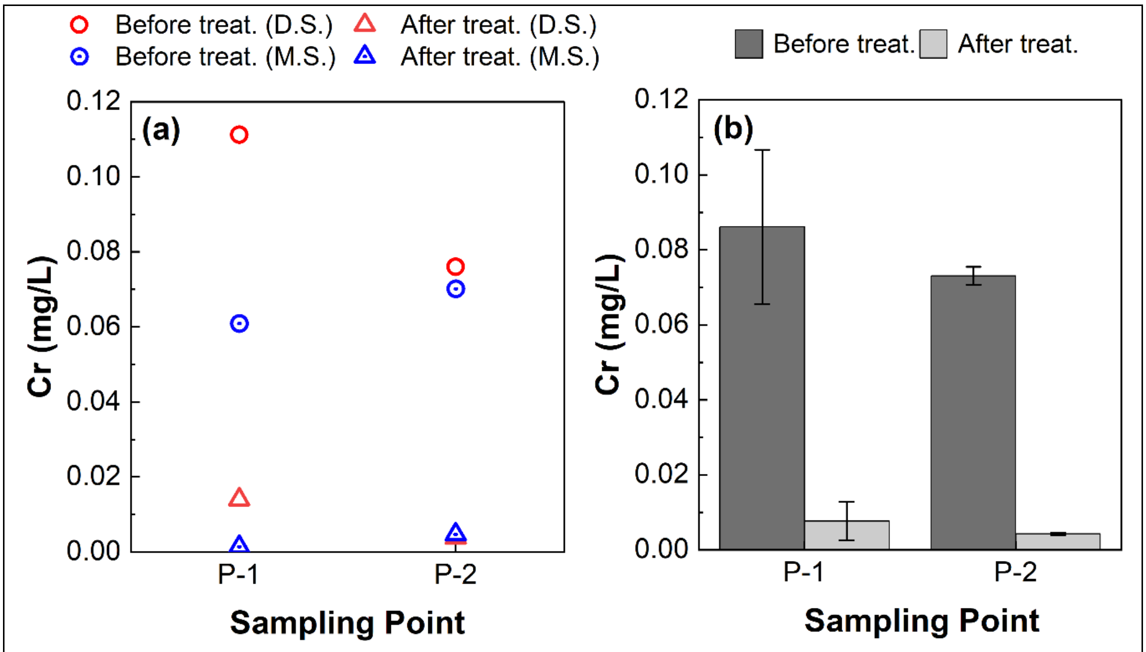

Fig. 4.21. Variation of Cr (mg/L) in wastewater samples collected at ETP inlet and outlet of paint industries: (a) Seasonal variation for D.S. and M.S. and (b) Mean variation of dry and monsoon season.

Copper (Cu) is an indispensable trace element that shows a significant role in the biochemistry of all living organisms [45]. Variations for Cu concentration are presented in **Fig. 4.20**. The Cu concentration of the inlet varies from 0.1284 mg/L (P-1, D.S.) to 0.0713 mg/L (P-2, M.S.). After treatment, Cu concentration of discharged stream areas ranged from 0.0592 mg/L to 0.0759 mg/L. WHO prescribed the maximum acceptable concentration of 2 mg/L for Cu (WHO, 2011). BSIE recommendation is 0.50 mg/L. Cu concentration is in the range of WHO and close to BSIE standard.

Variations for Cr concentration are presented in **Fig. 4.21**. The Cr concentration of the inlet varies from 0.1417 mg/L to 0.1128 mg/L. After treatment Cr concentration of discharged stream areas ranged from 0.0527 mg/L to trace (under detection limit). According to WHO and BSIE, the maximum Cr of chromium in drinking water is 0.05 mg/L. The Cr concentration of Karnaphuli River is 0.0869 mg/L in winter and 0.0696 mg/L in summer season, as reported by Ali et al. [7]. Cr concentration is around the range of WHO and BSIE standards and also been effectively treated several times in the ETP of paint industries.

According to WHO standards, Ni concentration should not exceed 0.02 mg/L in drinking water, whereas Bangladesh standard allows the presence of Ni up to 0.1 mg/L in drinking water and 1 mg/L for industrial discharge. Ni is below the detection limit in industry P-1. After treatment, Ni concentration of discharged steam of P-2 was below 0.0139. Hence Ni is under the safe limit maintained by the steel industries studied in this study.

Cadmium **(Cd)** is a very toxic trace metal because of its long half-life [52]. In paint industries, the Cd concentrations were below trace (under detection limit) except in sample P-1 (D.S.) where the Cd concentration was 0.0407 mg/L. WHO recommended that the Cd of the water be 0.003 mg/L; Whereas the BSIE recommendation is 0.05. Cd of the discharged wastewater from ETP at the outlet point is found below the detection limit.

Among all the studied heavy metals (Cd, Cu, Pb, Zn, and Ni), the concentration of Fe was in the highest in all the sampling points of steel industries. Though concentrations of Cu, Cd, Ni, and Cr are under the safe limit, the concentrations of Fe were higher and may cause water pollution from paint industries. Suitable measures and ETP design may be taken to reduce the probable pollution.

Part C: Study on Hotel industry STP samples

4.10 Operation and Maintenance of STPs of Hotel Industries

Efficient operation and maintenance of Sewerage Treatment Plants (STPs) are crucial for managing wastewater in hotel industries. **Fig. 4.22** illustrates the STP process flow in these settings, comprising various essential components.

4.10.1 Inlet of STP: The STP begins with the entry of untreated sewerage water from septic tanks into the STP inlet.

4.10.2 Oil & Grease Tap or Coarse Screener: In STPs, a grease tap is used to collect and remove grease, oil, and fats present in wastewater. This prevents clogs, and equipment interference, and ensures the effective functioning of the STP. Our study revealed that three STP systems employed Oil and grease tappers or bar screeners to remove solid particles.

4.10.3 Primary Clarifier: Different STP systems in hotel industries employ various configurations for primary clarification. H-1 utilizes a Solid Separator tank, an aeration tank, and a Sedimentation Tank. H-2 combines a pre-aeration tank with a Chemical Mixing Tank, while the third system integrates all functions in a single tank. Coagulants like alum are commonly used in these STPs to facilitate the removal of suspended solids and colloidal particles. Subsequently, flocculants, often polyelectrolytes, are employed to further aggregate particles for efficient sedimentation.

Sampling site: H-1

Geographical Location: 21° 24' 51.6594''N E 91° 59' 2.7234''E

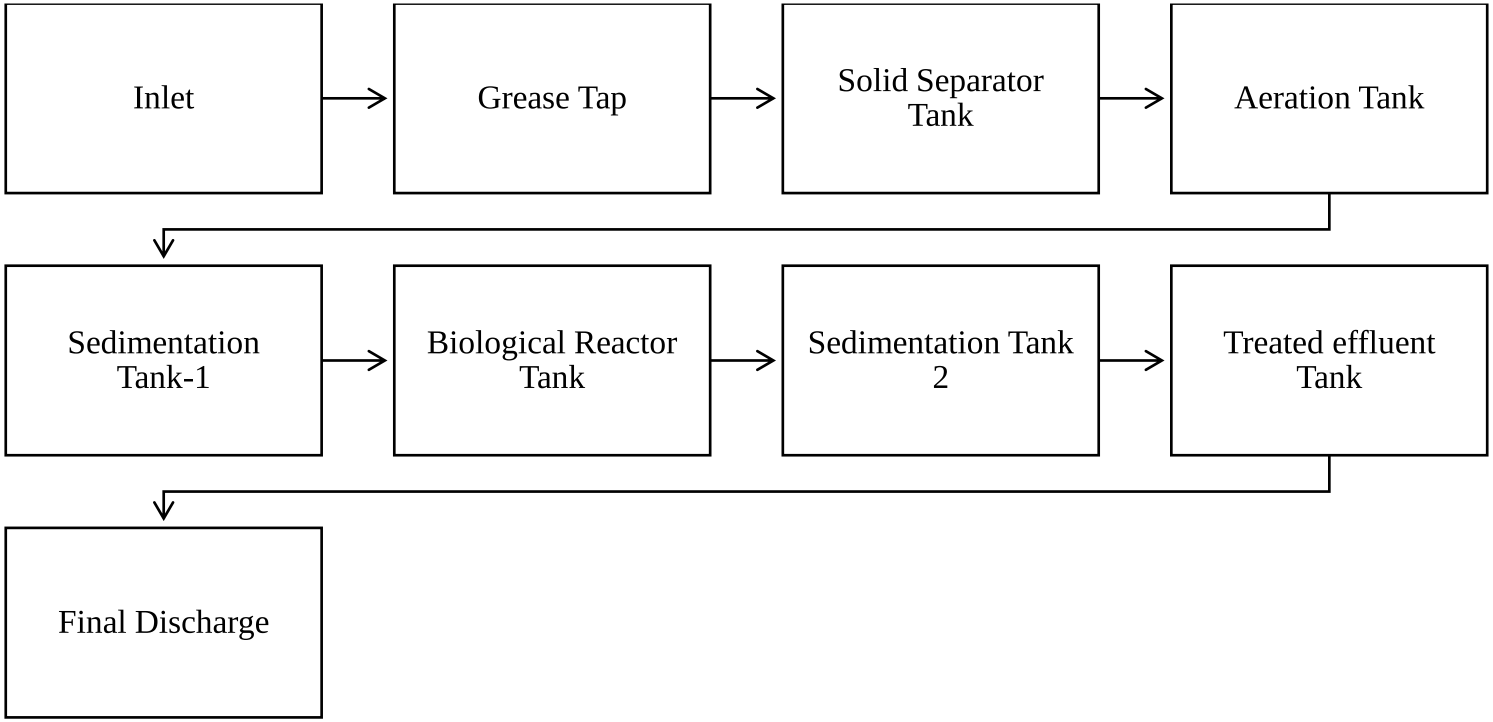

Fig. 4.22. (a). STP Process Flow of Hotel Industries.

Sampling site: H-2

Geographical Location: 21° 25' 15.2394''N E 91° 58' 51.204''E

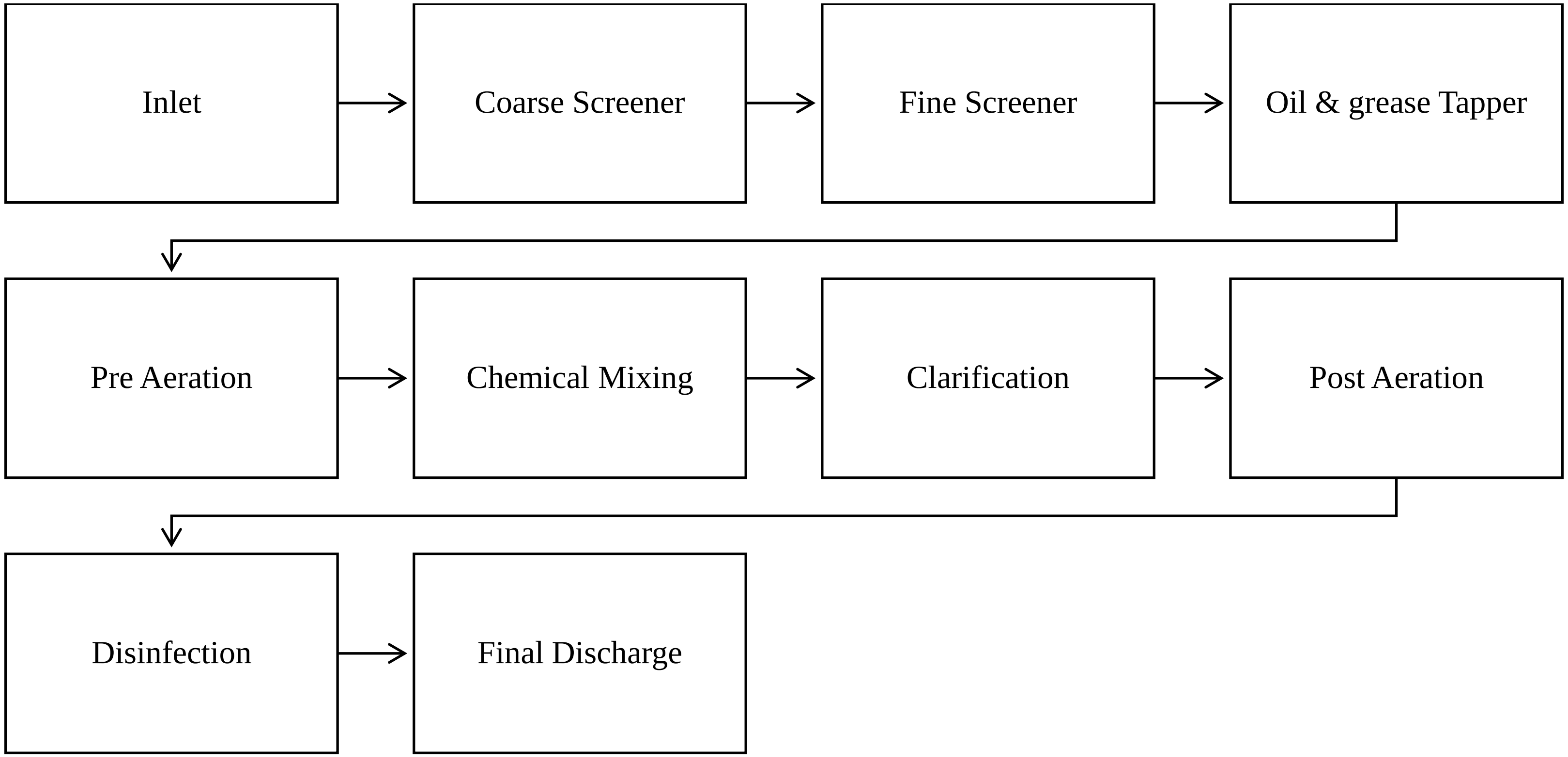

Fig. 4.22. (b). STP Process Flow of Hotel Industries.

Sampling site: H-3

Geographical Location: 21° 25' 34.752''N E 91° 58' 34.4994''E

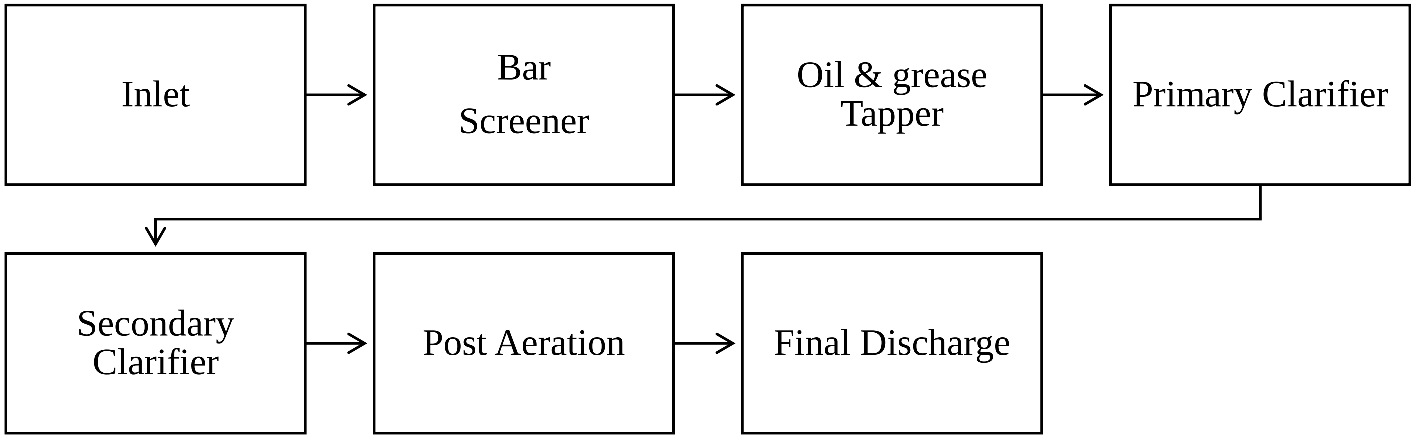

Fig. 4.22. (c). STP Process Flow of Hotel Industries.

4.10.4 Secondary Clarifier: The secondary clarification stage varies among STP systems. In H-1, a Biological Reactor Tank and Sedimentation tank follow primary treatment. In H-2, a combination of clarification and a post-aeration tank is used. H-3 employs a Secondary Clarifier and a Post-aeration tank. Additionally, a disinfection system is installed in H-2 to eliminate any remaining pathogens. The treated water is discharged after the secondary clarification stage in two of the hotel industries.

4.10.5 Outlet of STP: The treated effluent exits the STP at the outlet, adhering to specific water quality standards and environmental regulations. Depending on environmental goals, the treated effluent may be discharged into nearby surface water bodies or specially designed wetlands to further enhance water quality and support local ecosystems. Proper operation and maintenance of these STP components are essential to ensure the integrity of the sewage infrastructure and environmental compliance in hotel industries.

4.11 Physicochemical Parameters of Hotel Industries

To evaluate the physicochemical properties and potential water pollution of sewage treatment plant discharges from hotel industries in COX'S BAZAR during the D.S. and M.S. were examined and listed in **Table 4.5**. These parameters include pH, dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total dissolved solids (TDS), total suspended solids (TSS), nitrate, and phosphate for three different treatment plants labeled as H-1, H-2, and H-3.

4.11.1 pH: The pH values during both seasons seem relatively stable across the treatment plants (ranging from 7.1 to 7.8), with slight fluctuations. The standard deviation indicates moderate variability in pH measurements, suggesting a relatively consistent level of acidity/alkalinity in the discharges.

4.11.2 Dissolved Oxygen (DO): In the dry season, DO concentrations vary significantly, with values ranging from 0.93 to 7.25 mg/L. H-1 exhibits a significant decrease in DO levels during the monsoon season, indicating potential oxygen depletion due to increased organic matter from rainfall runoff. H-2 and H-3 also experience drops in DO during the monsoon, albeit not as drastic. This variation indicates potential fluctuations in oxygen levels that can affect aquatic life. In the monsoon season, DO levels appear to be more consistent, ranging from 4.6 to 5.12 mg/L.

Table 4.5

Physicochemical Characterization of STP Samples of Hotel Industries

Sampling Point	Dry Season (D.S.)	Monsoon Season (M.S.)	S.DEV
pH			
H-1	7.76	7.8	0.03
H-2	7.21	7.49	0.20
H-3	7.1	7.22	0.08
DO (mg/L)			
H-1	7.25	4.91	1.65
H-2	0.93	4.6	2.60
H-3	2.1	5.12	2.14
COD (mg/L)			
H-1	57	40	12.0
H-2	182	58	87.7
H-3	68	62	4.24
BOD5 (mg/L)			
H-1	17	23	4.24
H-2	121	29	65.1
H-3	29	26	2.12
TDS (mg/L)			
H-1	237.5	227	7.42
H-2	554	520	24.0
H-3	460	489	20.5
TSS (mg/L)			
H-1	29	10	13.4
H-2	70	43	19.1
H-3	23	19	2.83
Nitrate (mg/L)			
H-1	2.2	3.4	0.85
H-2	3.8	3.9	0.07
H-3	12.1	22	7.00
Phosphate (mg/L)			
H-1	2.1	7.6	3.89
H-2	29.7	4.11	18.1
H-3	9.2	7.7	1.06

4.11.3 Chemical Oxygen Demand (COD): COD values also exhibit variability. High COD levels, especially in H-2, during both seasons suggest elevated organic and inorganic pollutants in the discharges. In the dry season, COD ranges from 40 to 182 mg/L, indicating the presence of organic pollutants. During the monsoon season, COD levels generally decrease across the treatment plants.

4.11.4 Biochemical Oxygen Demand (BOD_5): BOD_5 values show a similar trend to COD, with higher values indicating organic pollution, particularly in H-2. In the dry season, BOD_5 ranges from 17 to 121 mg/L, and in the monsoon season, it decreases in most cases.

4.11.5 Total Dissolved Solids (TDS) and Total Suspended Solids (TSS): TDS concentrations are within the range of 227 to 554 mg/L during the dry season and 227 to 520 mg/L during the monsoon season. These values suggest the presence of dissolved substances in the discharges, possibly including salts and other compounds. TSS concentrations indicate solid particles suspended in the water. There is a decrease in TSS values from the dry season to the monsoon season, suggesting potential sedimentation during heavy rainfall. Both TDS and TSS levels are generally higher in H-2 during both seasons. These higher levels suggest a higher load of pollutants in H2's discharges.

4.11.6 Nitrate and Phosphate: Nitrate and phosphate levels demonstrate variations between the two seasons and across treatment plants. Elevated nitrate and phosphate levels in H-3, particularly during the monsoon season, suggest the potential for nutrient pollution. Elevated levels of nitrate and phosphate can cause eutrophication.

In summary, the data suggests potential water pollution concerns in the sewage treatment plant discharges. Fluctuations in DO, COD, BOD_5, TDS, and TSS indicate the presence of pollutants, possibly due to the discharge of organic matter and nutrients. The variation in nitrate and phosphate levels also raises concerns about nutrient pollution. Monitoring and addressing these fluctuations are crucial to ensure the protection of aquatic ecosystems and public health. It's essential to compare these values against local and national water quality standards to make informed assessments about the extent of pollution and necessary mitigation measures.

4.12 Heavy Metals

The evaluation of heavy metal concentration and pollution levels in sewage treatment plant discharges involves meticulous analysis of the provided data for four key metals: Fe, Cu, Cr, and Mn originating from three distinct treatment facilities labeled as H-1, H-2, and H-3 as provided in **Table 4.6**. Through a process of calculating the average concentration of each metal, we can determine whether these concentrations surpass the regulatory limits established for the safe discharge of these substances into the environment. It is important to acknowledge that regulatory limits can differ across various countries and regions, thereby necessitating a general overview of the findings.

For Fe, the specified regulatory limit is set at 1.0 mg/L. The average concentration computed at 0.0712 mg/L falls substantially below this regulatory threshold, signifying adherence to the prescribed standards. Conversely, the case of Cu unveils a more intricate picture. The general regulatory limit for Cu concentration varies from 0.03 to 0.05 mg/L based on the specific region. With an average concentration of 0.0587 mg/L, the data indicates that, in certain areas, the Cu concentration slightly exceeds the acceptable limit, raising concerns about potential copper-related pollution.

Table 4.6.

Heavy Metal (mg/L) Contents of STP Samples of Hotel Industries

Heavy metal	**The concentration of heavy metals (mg/L) in the sampling site**			**Std. Dev.**
	H-1	**H-2**	**H-3**	
Fe	0.026	0.117	0.0715	0.046
Cu	0.08	0.034	0.062	0.023
Cr	0.027	0.013	0.006	0.011
Mn	0.456	0.595	0.605	0.083

Moving on to Cr, its regulatory limit fluctuates between 0.05 and 0.1 mg/L contingent upon geographical differences. The calculated average concentration of 0.0153 mg/L remains well beneath this permissible range, affirming compliance with regulatory standards. Meanwhile, the assessment of Mn concentration against the regulatory limit of 0.1 mg/L reveals a significant disparity. The average concentration of 0.552 mg/L for manganese content considerably surpasses the defined limit, signifying a conceivable issue linked to Mn pollution.

In summary, the analysis of heavy metal concentrations in sewage treatment plant discharges outlines potential concerns concerning copper and manganese pollution, underlining the criticality of regulatory variations across different regions. Recognizing that regulatory thresholds are geographically variable; it is crucial to consult local environmental regulations and collaborate with relevant authorities for precise assessments and strategic interventions aimed at mitigating the potential repercussions of pollution.

CHAPTER – 5: CONCLUSION

This study examined the wastewater treatment process and evaluated the water quality of industrial wastewater before and after treatment in ETP and STP setups in steel-galvanizing, paint industries, and hotel industries situated in Chattogram, Bangladesh. Various physiochemical parameters (pH, DO, BOD_5, COD, and TDS) and heavy metal concentrations (Fe, Cu, Cr, Ni, Cd) were analyzed and compared against different national and international standards, including BSIE, WHO, EU-DIR, and US EPA. Wastewater was analyzed over two different periods (D.S. and M.S.)

Steel-Galvanizing Industries. The findings revealed that the steel industries produced complex liquid waste containing high levels of dissolved solids and heavy metal ions. Following treatment, the pH and DO levels in the wastewater samples generally lie within the recommended range. The BOD_5 and COD values met the standards in most cases, although a few exceptions were observed. While the TDS levels were higher and below international standards but they complied with the BSIE limit. On the other hand, the Fe concentration in the discharged stream areas ranged from 0.992 to 16.89 mg/L exceeded the guideline limits. Similarly, the Cr concentration, both in the inlet and outlet, frequently surpassed the standard limits, especially those defined by the US EPA. In conclusion, this study suggests a probable connection between steel-galvanizing industries and water pollution, primarily through the discharge of Fe and Cr in wastewater. It highlights the importance of optimizing effluent treatment plant processes to enhance the removal efficiency of certain heavy metals. Furthermore, the implementation of effective measures and the design of efficient effluent treatment plants are crucial for mitigating potential pollution and promoting sustainability in the steel-galvanizing industry.

ETPs of Paint Industries. A comprehensive analysis of physicochemical parameters and heavy metal concentrations in wastewater samples collected from two paint industries was presented. Inlet pH ranged from 5.08 to 8.81, with treated wastewater lie between 6.29 and 8.26. Discharged wastewater pH met WHO and BSIE standards. Inlet DO levels (1.05–2.36 mg/L) were low due to chemical processing. Inlet BOD_5 values (79–148 mg/L) exceeded WHO but stayed within BSIE limits. Outlet BOD_5 (12–58 mg/L) indicated effective treatment. Inlet COD (378–622 mg/L) decreased at outlets (26–224 mg/L), conforming to BSIE standards. Inlet TDS (2016–2415 mg/L) decreased at outlets (203–736 mg/L), meeting WHO and BSIE standards. Fe concentrations in inlet wastewater exceeded WHO (0.3 mg/L) and BSIE (2.0 mg/L) guidelines indicated potential water pollution by Fe. Cu concentrations were within the acceptable range defined by WHO (2.0 mg/L) and were closed to BSIE standards (0.50 mg/L). Cr concentrations met both WHO (0.05 mg/L) and BSIE standards and were effectively treated in ETPs. Ni and Cd concentrations were below WHO limits and within BSIE limits for industrial discharge. Thus, while most parameters conform to environmental standards, the elevated levels of Fe highlight the need for pollution control measures in the paint industries.

STPs of Hotel Industries. Efficient operation and maintenance of STPs in hotel industries are vital for managing wastewater and preserving environmental quality. The study revealed fluctuations in physicochemical parameters, indicating potential water pollution in Cox's Bazar, Chattogram division. In the context of STP analysis, pH levels exhibited a relatively stable pattern, consistently ranging from 7.1 to 7.8, with moderate variability throughout our study period. However, DO levels displayed significant fluctuations, particularly during the monsoon season. The assessment of COD revealed fluctuating levels that suggest the presence of various organic and inorganic pollutants in the wastewater. The trends in BOD_5 closely corresponded to those of COD, further emphasizing the prevalence of organic pollution. Additionally, an investigation into nitrate and phosphate levels raised concerns regarding nutrient pollution and the potential for eutrophication. The concentrations of Fe consistently remained well below the regulatory limit of 1.0 mg/L, indicating compliance with established standards. However, Cu concentrations exceeded acceptable limits in specific areas, demanded further investigation. Conversely, concentrations of Cr consistently fell within permissible ranges. Mn concentrations significantly surpassed the defined limit, suggesting a potential issue associated with Mn pollution.

CHAPTER – 6: RECOMMENDATIONS & FUTURE ASPECTS

I. Recommendations

- Suitable measures and ETP design: Implementing appropriate measures and designing efficient Effluent Treatment Plants (ETPs) are pivotal in tackling pollution emanating from both steel and paint industries. By adopting well-designed ETPs, these industries can significantly curtail their environmental footprint.
- Evaluation of water quality before discharge: Conducting comprehensive evaluations of water quality before discharge is of paramount importance. This practice not only ensures compliance with regulatory standards but also prevents potential harm to the environment.
- Importance of monitoring and managing wastewater: The continuous monitoring and proficient management of wastewater play a vital role in mitigating detrimental effects. This approach aids in minimizing adverse impacts on soil health, aquatic ecosystems, and human well-being.
- Optimization of ETP processes for steel industries: In the realm of steel industries, there exists a crucial need to optimize ETP processes. Special focus should be directed towards reducing pollution caused by heavy metals such as iron and chromium. By enhancing these processes, the industries can effectively curb their heavy metal discharge.
- Compliance with national and international guidelines: Adherence to both national and international guidelines is a cornerstone in the protection of water quality and the preservation of aquatic ecosystems. Upholding these guidelines is instrumental in maintaining a sustainable environment.

- Addressing the Fe pollution in the paint industry: The issue of iron (Fe) pollution in the paint industry necessitates the implementation of proper treatment and management practices. By employing appropriate strategies, the industry can effectively manage and mitigate iron-related pollution.
- Research for sustainable solutions: Promoting research aimed at identifying sustainable solutions holds the key to reducing pollution and safeguarding the environment. This research-driven approach seeks to devise innovative methods that minimize pollution and ensure the well-being of the ecosystem.

II. Future Aspects

Considering the observed issues in steel-galvanizing and paint industries contributing to water pollution through the discharge of wastewater rich in heavy metal ions, the adoption of adsorption-based methods emerges as a viable solution. Various physicochemical or biological techniques, such as chemical precipitation, membrane filtration, flotation, electrocoagulation, adsorption, ion exchange, phytoremediation, and biofiltration, can be explored [69-73]. While acknowledging the limitations associated with some methods, **adsorption** emerges as a promising physico-chemical technique with widespread applicability in industries [74-79]. Many adsorbents have been widely employed to remove potentially toxic elements from wastewater in various industries. Several potential adsorbents reported in the literature [80-127], outlined in **Table A1** (see **Appendix A**), offer the opportunity for testing and implementation to address heavy metal pollution in the steel and paint industries. This recommendation opens avenues for future studies focusing on the exploration and optimization of adsorption-based methods as efficient and sustainable approaches for mitigating water pollution in industrial settings.

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Appendix A

Figure A1: Sampling points of steel industry.

Table A.1

List of promising adsorbents for the Heavy metals explored in this study.

Sl.	Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)	Author et al.
	Cd(II)		
1.	Poly(methacylic acid-co-maleic acid) grafted nanofibrillated cellulose	135	Maatar [80]
2.	Succinic anhydride modified CNC	150.2	Yu [81]
3.	Epichlorohydrin cross-linked carboxymethyl cellulose	150.6	Wei [82]
4.	Modified non-mercerized cellulose	164	Gurgel [83]
5.	Sodic form of succinic anhydride modified CNC (NaSCNC)	166.5	Yu [81]
6.	Modified sawdust	168	Geay [84]
7.	Succinate-bonded cellulose	185.2	Belhalfaoui [85]
8.	Sugarcane bagasse chemically modified with succinic anhydride	196	Karnitz [86]
9.	Mercerized nanocellulose	231.8	Hokkanen [87]
10.	Modified mercerized cellulose (cell 6)	250	Gurgel [83]
11.	Succinic anhydride (Carboxyl) Nanocellulose	259.7	Yu [81]
12.	Thiol functionalized polyacrylonitrile fibers	350.6	Deng [88]
13.	aminopropyltriethoxysilane (APS) modified microfibrillated cellulose	387.8	Hokkanen [89]
14.	mesoporous calcium silicate	437.4	Liu [90]
15.	chitosan beads	518	Rorrer [91]
16.	Polyvinyl alcohol /zeolite nanofibrous	838.7	Rad [92]
17.	Flowerlike MgO nanostructures	1500	Cao [93]
18.	Sawdust-derived cellulose nanocrystal	2207	Oyewo [94]

Sl.	Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)	Author et al.
		Cr(III)	
19.	cellulose and chitin nanofibers functionalized with carboxylate entities	58	Sehaqui [95]
20.	Cellulose bead	72.6	Liu[96]
21.	Wheat bran	93	Farajzadeh[97]
22.	Amidoximated cellulose	202.78	Saliba [98]
23.	nitrogen-doped magnetic carbon nanoparticles	638.51	Shin [99]
		Cr(VI)	
24.	Polypyrrole/Fe_2O_3 magnetic nanocomposite	208.8	Guajardo [100]
25.	Pine sawdust modified with epichlorohydrin and diethylenetriamine	238.6	Hao [101]
26.	Mosambi (Sweet lime) peel	250	Saha [102]
27.	Ti_3C_2Tx nanosheet	250	Ying [103]
28.	Triethylenetetramine modified $MnFe_2O_4$/cellulose	250	Ghanbarian [104]
29.	magnetic carbon nanocomposites	256.86	Qiu [105]
30.	Poly(amidoamine)-grafted cellulose nanofibril aerogel	377.36	Zhao [106]
31.	Poly(m-phenylenediamine)/bacterial cellulose composite	434.8	Yang [107]
32.	Poly(acryloyl hydrazide)-grafted cellulose nanocrystal	457.6	Park [108]
33.	Polyethyleneimine-crosslinked quaternized cellulose	490.3	Liang [109]
34.	Polypyrrole-bacterial cellulose nanofiber composites	555.6	Shao [110]

Sl.	Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)	Author et al.
35.	PPy-HNF membrane	839.3	Zhao [111]
36.	PEI modified CMCNF beads	1302.3	Kim [112]
37.	graphene sand composite	2859.38	Dubey [113]
		Cu(II)	
38.	Magnetic calcium alginate coated chitosan hydrochloride/Fe_3O_4 adsorbent	143.276	Yi [114]
39.	Polyethyleneimine-bacterial cellulose	148	Jin [115]
40.	Modified mercerized cellulose	153.9	Gurgel [83]
41.	Aminopropyltriethoxysilane modified microfibrillated cellulose	174.12	Hokkanen [89]
42.	Electrosterically stabilized nanocrystalline cellulose	185	Sheikhi[116]
43.	Amidoximated cellulose	238.93	Saliba[98]
44.	Wood sawdust	246.56	Saliba [117]
45.	Sodium alginate (SA)/polyvinyl alcohol (PVA)/graphene oxide (GO) hydrogel microsphere	247.16	Yi [118]
46.	TEMPO-oxidized cellulose nanofibers	303	Fiol[119]
47.	Cellulose extracted from the sisal fiber and cellulose-g-acrylic acid copolymer	328.53	Hajeeth[120]
48.	In situ TEMPO surface functionalization of nanocellulose membranes	374	Karim[121]
49.	Mesoporous calcium silicate	389.85	Liu[90]
50.	Coconut husk	443	Malik[122]
51.	Polyvinylpyrrolidone-reduced raphene oxide	1689	Zhang[123]
52.	magnetite nanorods	76.10	Karami[124]
		Fe(III)	
53.	Sludge nanocrystals nanocellulose	6.3	Liu[125]

Sl.	Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)	Author et al.
54.	natural byproduct wood pulp	6.69	Abdel-Aal[126]
55.	TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidized cellulose nanofibers	70	Georgouvelas[127]
56.	Phosphorylated cellulose nanocrystals from sludge	114	Liu[125]
57.	Poly(methacylic acid-co-maleic acid) grafted nanofibrillated cellulose	117	Maatar[80]
58.	Aminopropyltriethoxysilane modified microfibrillated cellulose	154.36	Hokkanen[89]
59.	Wood sawdust	187.82	Saliba[117]
60.	Porous cellulose carrier modified with polyethyleneimine	276.45	Hajeeth[120]
61.	Mesoporous calcium silicate	278.35	Liu[90]
62.	Polyvinyl alcohol /zeolite nanofibrous	342.8	Rad[92]
63.	Coconut husk	404.5	Malik[122]
64.	Nitrogen-doped magnetic carbon nanoparticles	473.07	Shin[99]
65.	Sawdust-derived cellulose nanocrystal	956.6	Oyewo[94]

Appendix B

The assessment of data sheets for heavy metals was conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany). Limited sample data is presented here, and comprehensive data are available on request.

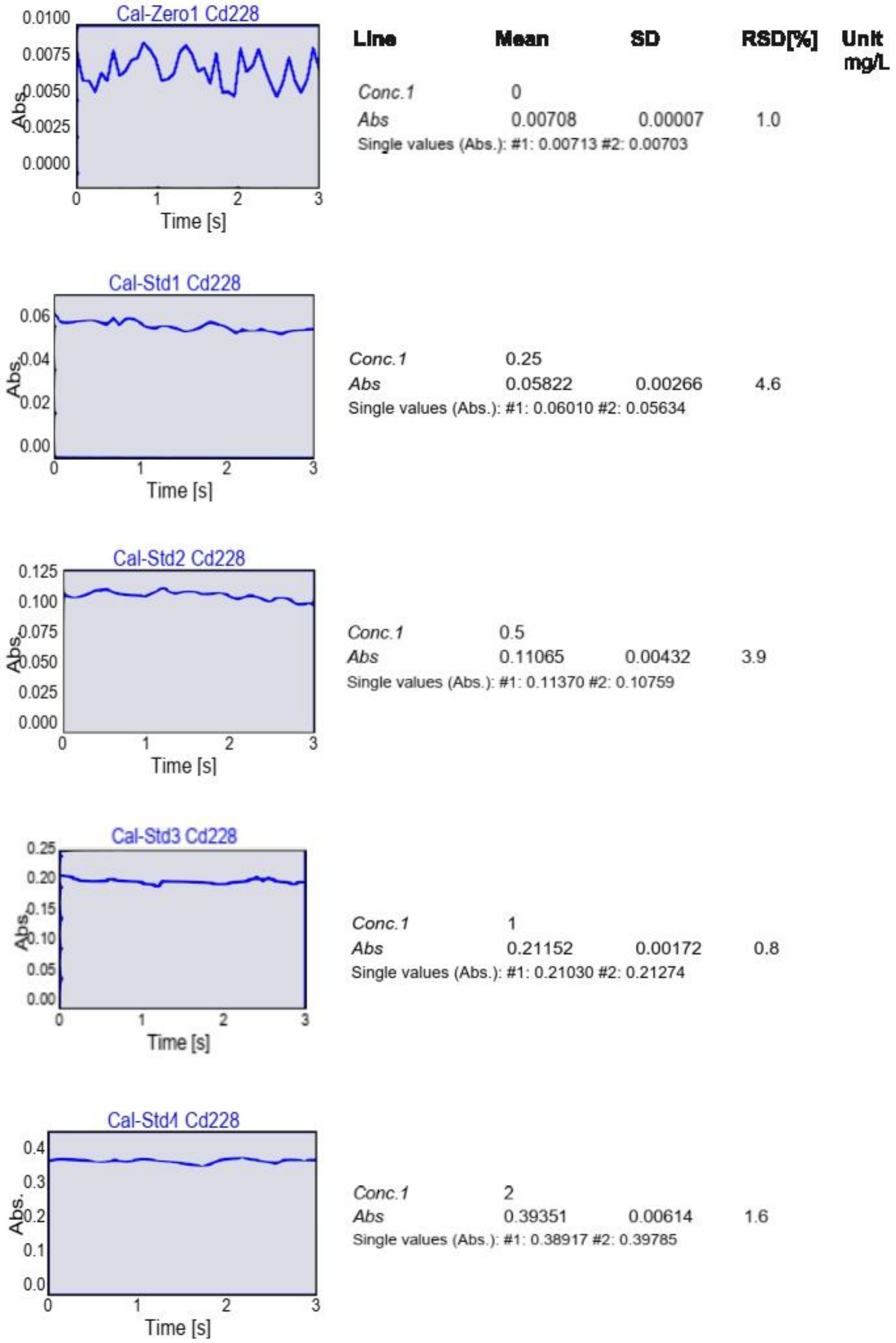
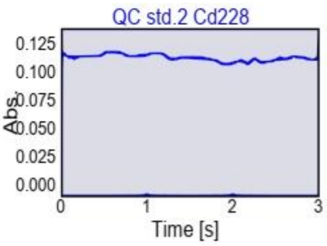
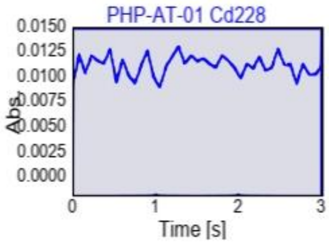


Fig. B (continued). The assessment of data sheets for heavy metals conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany).



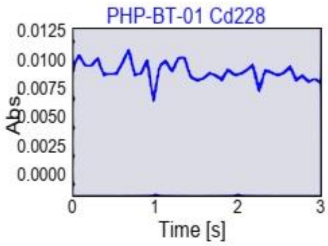
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	0.5686	0.0027	0.5	
Abs	0.12118	0.00052	0.4	

Single values (Abs.): #1: 0.12155 #2: 0.12081



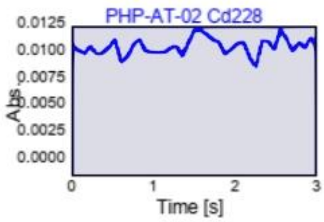
Conc.1	0.0047	0.0022	47.2
Conc.2	0.0047	0.0022	47.2
Abs	0.01229	0.00043	3.5

Single values (Abs.): #1: 0.01199 #2: 0.01260



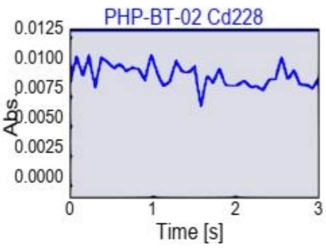
Conc.1	-0.0081	0.0003	3.2
Conc.2	-0.0081	0.0003	3.2
Abs	0.00983	0.00005	0.5

Single values (Abs.): #1: 0.00987 #2: 0.00980



Conc.1	-0.0006	0.0016	277.8
Conc.2	-0.0006	0.0016	277.8
Abs	0.01128	0.00030	2.7

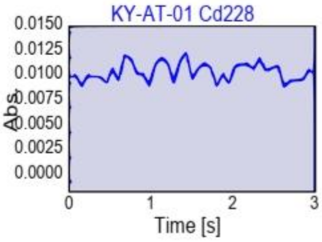
Single values (Abs.): #1: 0.01107 #2: 0.01150



Conc.1	-0.0108	0.0002	1.8
Conc.2	-0.0108	0.0002	1.8
Abs	0.00930	0.00004	0.4

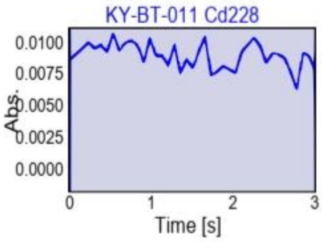
Single values (Abs.): #1: 0.00932 #2: 0.00927

Fig. B (continued). The assessment of data sheets for heavy metals conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany).



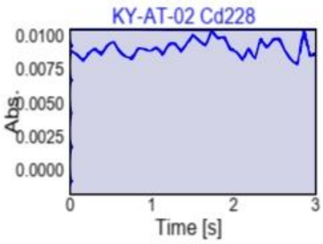
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	-0.0009	0.0009	103.1	
Conc.2	-0.0009	0.0009	103.1	
Abs	0.01122	0.00018	1.6	

Single values (Abs.): #1: 0.01109 #2: 0.01134



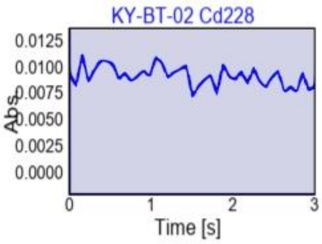
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	-0.0109	0.0034	30.8	
Conc.2	-0.0109	0.0034	30.8	
Abs	0.00928	0.00065	7.0	

Single values (Abs.): #1: 0.00974 #2: 0.00883



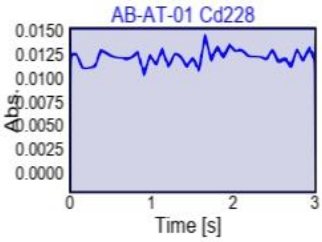
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	-0.0091	0.0016	17.6	
Conc.2	-0.0091	0.0016	17.6	
Abs	0.00963	0.00031	3.2	

Single values (Abs.): #1: 0.00985 #2: 0.00941



Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	-0.0075	0.0010	13.1	
Conc.2	-0.0075	0.0010	13.1	
Abs	0.00994	0.00019	1.9	

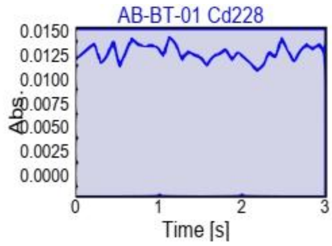
Single values (Abs.): #1: 0.01008 #2: 0.00981



Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	0.0105	0.0005	4.9	
Conc.2	0.0105	0.0005	4.9	
Abs	0.01341	0.00010	0.7	

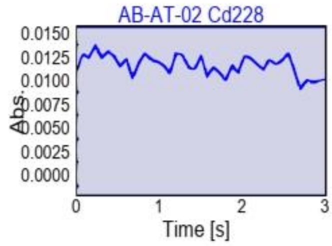
Single values (Abs.): #1: 0.01334 #2: 0.01348

Fig. B (continued). The assessment of data sheets for heavy metals conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany).



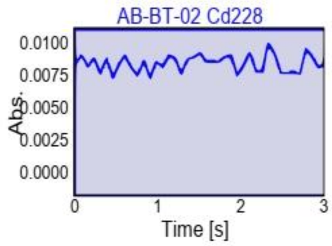
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	0.0120	0.0007	5.9	
Conc.2	0.0120	0.0007	5.9	
Abs	0.01371	0.00014	1.0	

Single values (Abs.): #1: 0.01381 #2: 0.01361



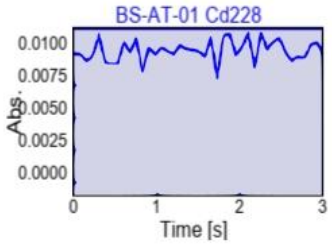
Conc.1	0.0058	0.0021	35.9
Conc.2	0.0058	0.0021	35.9
Abs	0.01251	0.00040	3.2

Single values (Abs.): #1: 0.01279 #2: 0.01222



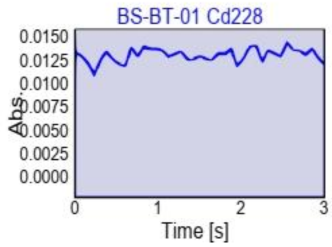
Conc.1	-0.0110	0.0006	5.2
Conc.2	-0.0110	0.0006	5.2
Abs	0.00927	0.00011	1.2

Single values (Abs.): #1: 0.00919 #2: 0.00935



Conc.1	-0.0057	0.0006	9.9
Conc.2	-0.0057	0.0006	9.9
Abs	0.01028	0.00011	1.1

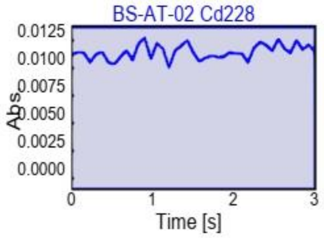
Single values (Abs.): #1: 0.01021 #2: 0.01036



Conc.1	0.0105	0.0051	48.5
Conc.2	0.0105	0.0051	48.5
Abs	0.01342	0.00099	7.3

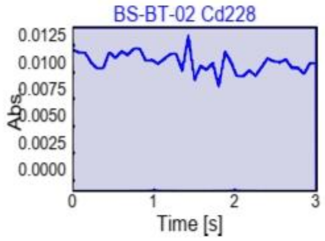
Single values (Abs.): #1: 0.01412 #2: 0.01272

Fig. B (continued). The assessment of data sheets for heavy metals conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany).



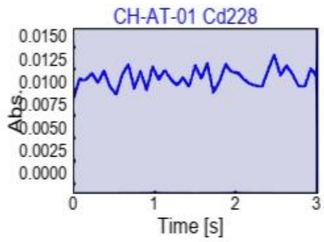
Line	Mean	SD	RSD[%]	Unit mg/L
Conc.1	0.0013	0.0014	104.4	
Conc.2	0.0013	0.0014	104.4	
Abs	0.01164	0.00026	2.3	

Single values (Abs.): #1: 0.01146 #2: 0.01183



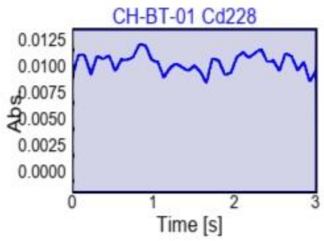
Conc.1	-0.0036	0.0017	48.0
Conc.2	-0.0036	0.0017	48.0
Abs	0.01069	0.00034	3.2

Single values (Abs.): #1: 0.01093 #2: 0.01045



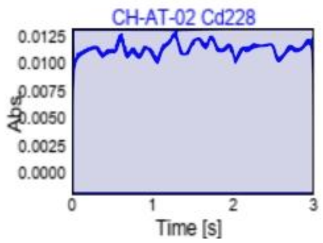
Conc.1	0.0016	0.0008	50.4
Conc.2	0.0016	0.0008	50.4
Abs	0.01170	0.00016	1.3

Single values (Abs.): #1: 0.01159 #2: 0.01181



Conc.1	-0.0020	0.0021	103.8
Conc.2	-0.0020	0.0021	103.8
Abs	0.01100	0.00040	3.7

Single values (Abs.): #1: 0.01129 #2: 0.01071



Conc.1	0.0050	0.0011	22.8
Conc.2	0.0050	0.0011	22.8
Abs	0.01235	0.00022	1.8

Single values (Abs.): #1: 0.01219 #2: 0.01250

Fig. B (continued). The assessment of data sheets for heavy metals conducted using ASPECT CS 2.1.2.0 software (contrAA 700, Analytik Jena, Germany).