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Assessment and Removal of Heavy Metal Ions from Jawaharlal Nehru Autonagar Industrial Effluents, Vijayawada, India: An Adsorption Study of CSM Activated Carbon.

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Abstract

Global industrialization has led to a significant increase in the release of hazardous and toxic metals into water bodies. These heavy metals pose a serious threat to human health and the environment (Vardhan et al., 2019). In particular, the Jawaharlal Nehru Autonagar Industrial Effluents in Vijayawada, India, have been identified as a major source of heavy metal pollution. The assessment and removal of heavy metal ions from these industrial effluents is crucial in order to minimize their detrimental effects on the surrounding ecosystem and protect the health of the local population (Jain & Reddy, 2022). Several studies have been conducted to examine the impact of heavy metal pollution in industrial effluents in Vijayawada. These studies have identified high levels of heavy metals such as Cadmium, Nickel, Lead, and Arsenic in the effluents, highlighting the need for effective assessment and removal strategies. Various methods have been proposed for the assessment and removal of heavy metal ions from industrial effluents in Vijayawada, India (Kumar & Dwivedi, 2021). Membrane filtration, reverse osmosis, chemical reduction, and adsorption are some of the conventional methods that have been used for the removal of heavy metals (Verma et al., 2021). While these conventional methods have been effective in removing heavy metal ions from aqueous industrial effluents but often generate secondary pollutants and can be costly (Singh et al., 2023). To address these limitations and provide low-cost solutions, innovative technologies such as hydrogel adsorption, activated carbon adsorption, and biological treatment methods have emerged as promising alternatives. These alternative methods offer cost-effective removal of heavy metal ions, especially from dilute solutions, and have shown high efficiency in treating contaminated industrial wastewater. The aim of this study was the assessment of the heavy metal ions contaminants of JNA industrial effluents and the adsorptive removal of ions present in high concentrations following the **Error! Bookmark not defined.** for the industrial effluents of India. 210 samples were collected from various outlets of the effluent stream flow from the JNA, Vijayawada, in three seasons during summer (April), rainy (August), and winter (December) 2022. The analysis results obtained indicate that some of the contaminants were above the acceptable limit of industrial wastewater as per **Error! Bookmark not defined.** India. However, heavy metals like Chromium ions (2.63 mg/L), lead (0.16 mg/L) and Nickel (1.75 mg/L) were found to be higher than the allowable level of Environmental pollutants (Environment protection rules, 1986) for industrial effluents for India. A novel biosorbent synthesized indigenously from Citrus Sinensis and Musa was used for the removal of Chromium, lead and Nickel from the wastewater effluent samples. This biosorbent successfully reduced the Chromium ion concentration in the wastewater sample from 2.093 to 1.252 mg/L at pH 6 in 1 h. Similarly, the concentration of lead reduced to 0.108 from 0.069 mg/L at pH 4, whereas Nickel ions were removed from 1.671 to 1.164 mg/L at pH 10 in 1 h. Treatment of wastewater through the synthesized biosorbent efficiently removed the high concentration ions and could potentially be applied to reduce the toxic effects of these contaminants on local public health.

Keywords: Industrial Effluent, Biosorbent; Adsorption, KOH, H_2SO_4, Activated Carbon, Citrus Sinensis, Musa.

Introduction

Waste is produced by human activity, and a lot of it ends up as wastewater in waterways. One of the main sources of pollution in the environment, affecting the quality of drinking water, soil, and aquatic environments, is industrial wastewater that finds its way into water sources. Various types of industrial wastewater are distinguished according to the industries and pollutants found in them. Every industrial zone produces a distinct set of pollutants. The rapid industrialization and urbanization of the world is leading to a growing concern regarding surface and groundwater contamination. Massive volumes of industrial waste are already being produced by the growth of already established industries as well as the creation of new ones. The textile, food, chemical, paper and pulp, leather and tannery, mining, metallurgy, and manufacturing products sectors are the main producers of industrial wastewater. The most often utilized waters across a range of industries are process, boiler feed, evaporative cooling, and irrigation of the area around the industrial facility.

Chemicals and heavy and trace metal pollution in the environment are caused by industrial waste, which is one of the biggest health hazards in industrial cities. Large volumes of slag are created during industrial metallurgical processing, and this slag can contribute significantly to heavy metal contamination in water supplies. Because of the different chemicals that industries release into the environment, industrial contamination directly affects health. These substances have detrimental effects on human blood, heart, kidneys, liver, and reproductive organs when they are present in excess of a certain threshold. Therefore, it is essential to monitor heavy metal concentrations to make sure they stay within allowable bounds in order to preserve the environment and avoid contamination. Samples of industrial waste are gathered and examined in compliance with all relevant laws and regulations.

Water quality around the world is at risk from industrial wastewater. However, because industrial waste is dumped directly without any special treatment in developing nations like India, the situation is worse. India's water quality is declining for a number of reasons, including runoff from agriculture and industry and wastewater. Many industries, including textile, sugar processing, metal, chemicals, dyeing, pesticides, pharmaceuticals, and leather, are responsible for the majority of pollution to ground and surface waters. Rivers become contaminated when industrial and municipal wastewater are carried into them through canals and drains. The main contaminants in rivers that make the water unfit for drinking and other household uses are nitrates, sulfates, and toxic metal ions. The Krishna River has been seriously contaminated as a result of the inappropriate handling of industrial wastewater.

With a population of over 2.3 million, Vijayawada is the city in India that is growing the fastest. Textiles, paints, glass, bricks, rubber, pigments, cosmetics, medicines, ceramics, and other chemical products are all manufactured in Vijayawada. Due to the large volumes of wastewater produced by each of these industries, industrial wastewater is one of Vijayawada's top environmental problems. The primary cause of contamination in the groundwater and water quality of the Krishna River in Vijayawada is human activity, including domestic, industrial, and agricultural water use, as well as the untreated discharge of drain water into the river. Lack of canal water is a major cause of wastewater production, especially in areas close to industrial facilities. Due to haphazard urbanization and inadequate planning for industrial development, the city is currently facing several environmental problems. Little thorough research has been done up to this point on the evaluation and mitigation of the industrial wastewater in Vijayawada. This means that a thorough examination of the industrial wastewater profile throughout Vijayawada's industrial area is required.

An efficient, economical, and ecologically friendly way to eliminate harmful heavy metals from wastewater that contaminates aquatic and groundwater systems is to treat it with biosorbents. Consequently, an effort was undertaken to ascertain the chemical and heavy metal composition of the industrial wastewater in Vijayawada. Subsequently, we synthesized an economical and sustainable biosorbent to eliminate the high concentrations of ions.

2. Materials and Methods

2.1. Study Area

Jawaharlal Nehru Autonagar founded approximately fifty-two years ago, Autonagar is gradually losing its charm as a result of the unhygienic environment and increasing pollution. Approximately 1,200 major and minor industries are located in the industrial estate, which is well-known for truck body building, tyre re-bottoming, engine repair, and other automotive-related electronic works. In the region, there are about 1.5 lakh workers across a range of industries. Although the industrial estate brings in about Rs 600 crore in revenue each year, there has long been an issue with sanitation. Plastics and hazardous industrial waste have long since clogged the primary inundation drain that runs through the industrial estate, creating a terrible stench. In Autonagar, most of the drains are in poor condition. Because authorities have disregarded desilting work for years, nearly all of them are likewise blocked. These drains are receiving industrial chemical waste emissions, which could be harmful to human health..

Figure 1. Map of Vijayawada (Sample Collection Area Taken Via Google Maps)

2.2. Samples Collection and Preservation

Sewage samples were collected in different seasons at various outlets, they were named, as shown in table 1. For illustration, SO1S1 is sewage sample 1 collected at outlet 1 in summer. 210 samples were collected overall, as 70 samples in the summer followed by other two seasons (10 at each outlet of 7 streams). High quality polyethylene bottles with tight caps were utilized to store the samples. Prior to usage, the bottles underwent a cleaning process using distilled water and were later rinsed with 10% (v/v) nitric acid overnight. The samples were filtered using Whatmann filter paper number 42. Subsequently, the samples were promptly transferred to the laboratory in iceboxes and kept in an incubator at a temperature of 20°C, and subsequently analyzed.

Table 1. Identification of Sewage Samples Collected In Different Seasons

Season	Outlet	Samples									
Summer	1	SO_1S_1	SO_1S_2	SO_1S_3	SO_1S_4	SO_1S_5	SO_1S_6	SO_1S_7	SO_1S_8	SO_1S_9	SO_1S_{10}
	2	SO_2S_1	SO_2S_2	SO_2S_3	SO_2S_4	SO_2S_5	SO_2S_6	SO_2S_7	SO_2S_8	SO_2S_9	SO_2S_{10}
	3	SO_3S_1	SO_3S_2	SO_3S_3	SO_3S_4	SO_3S_5	SO_3S_6	SO_3S_7	SO_3S_8	SO_3S_9	SO_3S_{10}
	4	SO_4S_1	SO_4S_2	SO_4S_3	SO_4S_4	SO_4S_5	SO_4S_6	SO_4S_7	SO_4S_8	SO_4S_9	SO_4S_{10}
	5	SO_5S_1	SO_5S_2	SO_5S_3	SO_5S_4	SO_5S_5	SO_5S_6	SO_5S_7	SO_5S_8	SO_5S_9	SO_5S_{10}
	6	SO_6S_1	SO_6S_2	SO_6S_3	SO_6S_4	SO_6S_5	SO_6S_6	SO_6S_7	SO_6S_8	SO_6S_9	SO_6S_{10}
	7	SO_7S_1	SO_7S_2	SO_7S_3	SO_7S_4	SO_7S_5	SO_7S_6	SO_7S_7	SO_7S_8	SO_7S_9	SO_7S_{10}

Rainy	1	RO_1S_1	RO_1S_2	RO_1S_3	RO_1S_4	RO_1S_5	RO_1S_6	RO_1S_7	RO_1S_8	RO_1S_9	RO_1S_{10}
	2	RO_2S_1	RO_2S_2	RO_2S_3	RO_2S_4	RO_2S_5	RO_2S_6	RO_2S_7	RO_2S_8	RO_2S_9	RO_2S_{10}
	3	RO_3S_1	RO_3S_2	RO_3S_3	RO_3S_4	RO_3S_5	RO_3S_6	RO_3S_7	RO_3S_8	RO_3S_9	RO_3S_{10}
	4	RO_4S_1	RO_4S_2	RO_4S_3	RO_4S_4	RO_4S_5	RO_4S_6	RO_4S_7	RO_4S_8	RO_4S_9	RO_4S_{10}
	5	RO_5S_1	RO_5S_2	RO_5S_3	RO_5S_4	RO_5S_5	RO_5S_6	RO_5S_7	RO_5S_8	RO_5S_9	RO_5S_{10}
	6	RO_6S_1	RO_6S_2	RO_6S_3	RO_6S_4	RO_6S_5	RO_6S_6	RO_6S_7	RO_6S_8	RO_6S_9	RO_6S_{10}
	7	RO_7S_1	RO_7S_2	RO_7S_3	RO_7S_4	RO_7S_5	RO_7S_6	RO_7S_7	RO_7S_8	RO_7S_9	RO_7S_{10}
Winter	1	WO_1S_1	WO_1S_2	WO_1S_3	WO_1S_4	WO_1S_5	WO_1S_6	WO_1S_7	WO_1S_8	WO_1S_9	WO_1S_{10}
	2	WO_2S_1	WO_2S_2	WO_2S_3	WO_2S_4	WO_2S_5	WO_2S_6	WO_2S_7	WO_2S_8	WO_2S_9	WO_2S_{10}
	3	WO_3S_1	WO_3S_2	WO_3S_3	WO_3S_4	WO_3S_5	WO_3S_6	WO_3S_7	WO_3S_8	WO_3S_9	WO_3S_{10}
	4	WO_4S_1	WO_4S_2	WO_4S_3	WO_4S_4	WO_4S_5	WO_4S_6	WO_4S_7	WO_4S_8	WO_4S_9	WO_4S_{10}
	5	WO_5S_1	WO_5S_2	WO_5S_3	WO_5S_4	WO_5S_5	WO_5S_6	WO_5S_7	WO_5S_8	WO_5S_9	WO_5S_{10}
	6	WO_6S_1	WO_6S_2	WO_6S_3	WO_6S_4	WO_6S_5	WO_6S_6	WO_6S_7	WO_6S_8	WO_6S_9	WO_6S_{10}
	7	WO_7S_1	WO_7S_2	WO_7S_3	WO_7S_4	WO_7S_5	WO_7S_6	WO_7S_7	WO_7S_8	WO_7S_9	WO_7S_{10}

2.3. Material & Instrumental Details

The samples were analyzed using UV-Spectrophotometer to assess the heavy metal ions present in JNA industrial effluents. The results of the study revealed significant concentrations of heavy metal ions including Chromium, Lead, Mercury, Zinc, Nickel and Copper in the industrial effluents as well as in the groundwater of the surrounding areas. The presence of excessive heavy metal levels in drinking water, surpassing the thresholds established by numerous esteemed national and international bodies, gives rise to a multitude of acute and chronic ailments.

For chemical modification, the aforementioned carbonaceous material was treated with H2SO4 and KOH. 120 g of each sample were manually stirred with a glass stirrer in a 250 ml beaker containing 100 ml of standard H2SO4 and KOH solutions at concentrations of 0.5, 1.0, and 1.5 M. The samples were then allowed to stand at room temperature for activation. The samples were repeatedly cleaned with distilled water after activation in order to get rid of any extra H2SO4 and KOH compounds. The final products were created by drying the cleaned samples for four hours at 110°C. Testing for characteristics like contact time, initial ion concentration, particle size, and dosage in compliance with the 1987 ASTM standard allowed for a thorough characterization of the produced adsorbent. It was taken to the lab, where it was promptly broken down after being meticulously sealed in a plastic container. Next, the effect of treatment parameters on the developed adsorbent's adsorption capacity was examined. These parameters included adsorbent dose, contact time, and particle size.

Figure 2. Chemical Activator

Figure 3. Charcoal Mixed with Activator

2.4. Preparation of Biosorbent

Citrus Sinensis & Musa, a novel biosorbent, was employed to eliminate pollutants at high concentrations. The banana and orange were stripped of their outer layer, cleaned of any dirt with distilled water, and oven dried until their weight was constant. It was ground into a powder using a blender after it had dried. After carbonization, the resultant powder was activated. By adjusting the temperature (350, 400, 450, and 500°C) and carbonization time (30, 60, and 90 minutes) in a porcelain crucible that was placed in an electric muffle furnace and then cooled to room temperature, the charcoal was prepared by carbonizing it at 450°C for one hour. The selected temperature and duration (450°C for 1 hour) produced the best characterization.

2.5. Adsorption Activity

The high concentrations of pollutants were removed from the CS&M activated carbon using the batch adsorption technique. HNO3 and sodium hydroxide (1 M) were mixed in equal parts to create a stock solution. In order to maintain the pH of the sample solutions throughout the experiment, a 0.1 M HNO3/NaOH solution was made from the stock solution. At different pH values—2, 4, 6, 8, 10, and 12—the adsorptive removal of ions was carried out using 50 mL of industrial wastewater in 200 mL Erlenmeyer flasks. Using a 0.1 M HNO3/NaOH solution and a pH meter, the flasks' pH was changed. The pH was measured at room temperature. Following the addition of different amounts of biosorbent to the flask, an orbital shaker was used to shake the resulting suspensions for 12 hours at 110 rpm. To determine the final concentration of the adsorbate species, the suspension was filtered through Whatman filter paper using a spectrophotometer, conductivity meter, and colorimeter.

The same methodology as the pH study previously discussed was used to examine the effect of contact time; however, the suspension was shaken for fixed pH intervals of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes. In both scenarios, the amount of adsorbate adsorbed per unit mass of CS&M activated carbon was calculated using the formula $q = (Ci - Cf)\ V/W \times 1000$. In this case, W is the weight of the adsorbent (gm), Ci stands for the initial concentrations, Cf for the final concentrations (mg/L), and q for the amount of adsorbent adsorbed (mg/gm).

3. Results and Discussion

3.1. Analysis of Samples

The measured concentrations of pollutatnts present in industrial sewage are summarized in table 3.

Table 2. Statistical Information about the Levels of Pollutants in the Industrial Effluents from JNA Industrial Area.

Sample	Parameter	Cr	Pb	Hg	Zn	Ni	Cu	BOD	COD	TSS
Sewage (N=210)	Min	1.812	0.088	0.002	3.128	1.575	0.025	69.00	84.00	38.00
	Max	2.632	0.164	0.010	5.846	1.747	1.007	79.00	91.00	48.00
	Mean	2.093	0.107	0.006	4.332	1.671	0.492	75.28	87.28	44.28
	Standard deviation	0.198	0.017	0.002	0.648	0.032	0.247	73.58	85.57	42.60
	% RSD	0.095	0.160	0.333	0.149	0.019	0.503	0.977	0.980	0.962

3.2. Heavy metal concentrations vs Indian standard values

In general, the concentrations of Cr, Pb, Hg, Zn, Ni, and Cu in industrial effluents are typically below the pollution standards set by the **Error! Bookmark not defined.**. However, it has been observed that the levels of Cr, Pb, Zn, and Ni in JNA exceed these pollution standards, as shown in Figure 4.

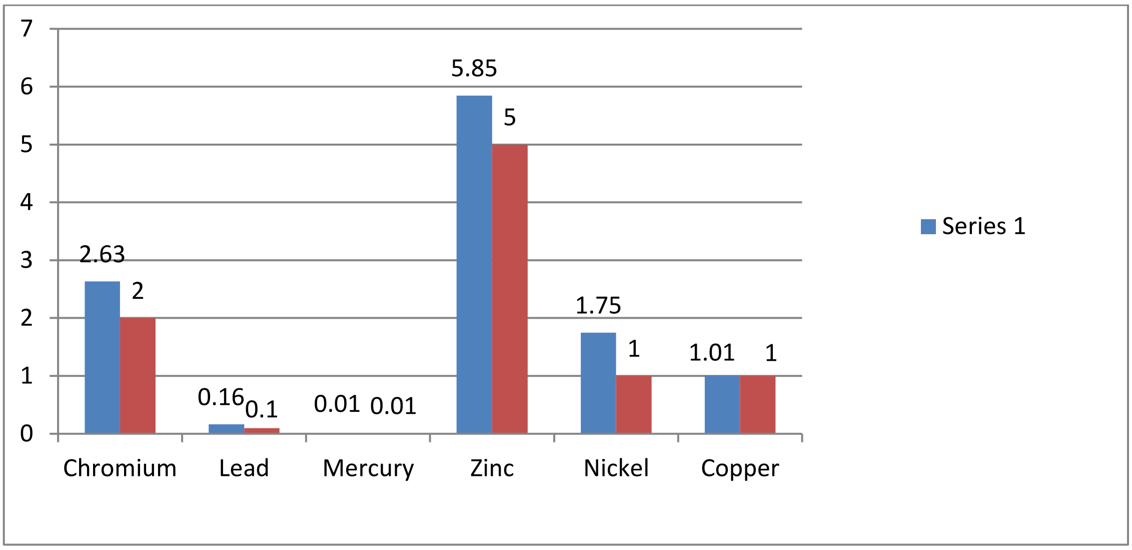

Figure 4. Concentration (mg/L of Cr, Pb, Hg, Zn, Ni, and Cu).

3.3. Effect of pH

The contaminants found in JNA industrial wastewater samples were subjected to a 12-hour pH study at room temperature. The contaminants included chromium (2.63 mg/L), lead (0.16 mg/L), mercury (0.01 mg/L), zinc (5.85 mg/L), nickel (1.75 mg/L), and copper (1.01 mg/L). At pH values between 2 and 8, all metal ions were totally eliminated. Table 3 displays the findings of the pH analysis for the pollutants, including TSS, BOD and COD found in wastewater samples that were left at room temperature for 12 hours. The results are displayed graphically in Figure 5.

Table 3. Concentrations of BOD, COD, and TSS Adsorption in Industrial Wastewater Samples at Various pH Levels

pH	BOD		COD		TSS	
	Concentration (mg/L)	Adsorption (mg/gm)	Concentration (mg/L)	Adsorption (mg/gm)	Concentration (mg/L)	Adsorption (mg/gm)
2	72	1	70	9	44	3
4	65	4.5	61	13.5	40	3.5
6	60	7	55	16.5	37	5
8	58	8	50	19	33	7
10	55	9.5	47	20.5	29	9
12	55	9.5	45	21.5	29	9

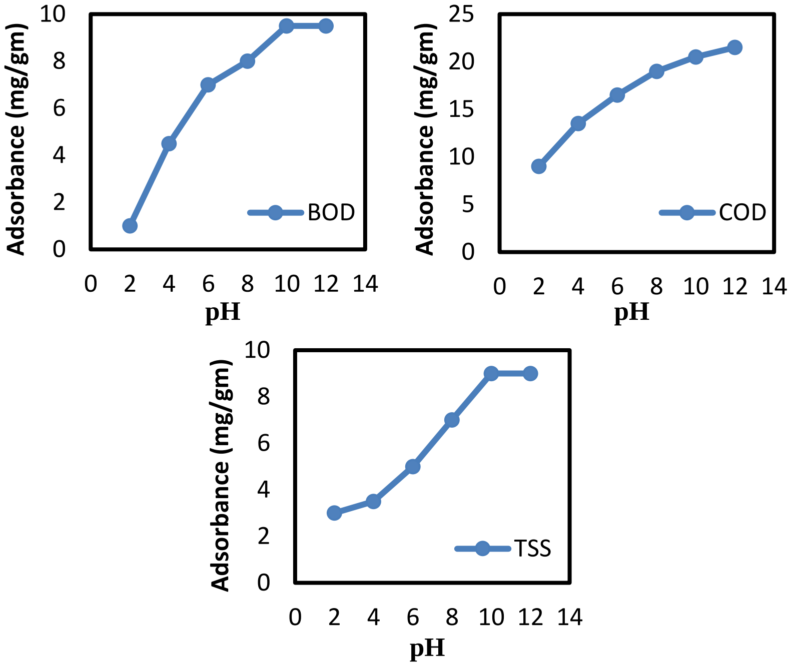

Figure 5. Concentrations of BOD, COD, and TSS Adsorption (mg/gm) at Various pH

BOD, COD, and TSS ion concentrations were initially 79 mg/L, 91 mg/L, and 48 mg/L, respectively. During the batch adsorption process, the concentration of these ions in the wastewater dropped, as shown by the adsorptive removal of these ions at various pH values. At pH 10, the biosorbent was able to reduce BOD to a maximum of 55 mg/L at room temperature in 12 hours (Table 4). The COD concentration decreased in 12 hours at pH 12 from 91 to 45 mg/L at room temperature during the adsorption process, indicating good biosorbent activity. According to Table 4's analysis results, the TSS concentration decreased from 48–29 mg/L at room temperature and pH 10 in a 12-hour batch adsorbent experiment.

3.4. Effect of Contact Time

By keeping the ideal pH at room temperature for five to sixty minutes, the impact of contact time was investigated for contaminants such as lead (0.16 mg/L), chromium (2.63 mg/L), zinc (5.85 mg/L), mercury (0.01 mg/L), copper (1.01 mg/L) and nickel (1.75 mg/L) present in JNA industrial wastewater samples. The impact of contact time showed that within the first 45 minutes, all metal ions were totally eliminated in the ideal pH ranges. The impact of contact time on the contaminants is depicted in Figure 6, which are listed in detail in Table 4 and include BOD (pH-10), COD (pH-12), and TSS (pH-10) detected after 60 minutes at room temperature in the wastewater samples.

Table 4. Adsorption Concentrations of BOD, COD and TSS in the Industrial Wastewater Samples at Different Time Intervals.

Time		5	10	15	20	25	30	35	40	45	50	55	60
BOD	Concentration (mg/L)	70	65	60	56	53	52	48	46	43	42	41	41
	Adsorption (mg/gm)	2	4.5	7	9	10.5	11	13	14	15.5	16	16.5	16.5
COD	Concentration (mg/L)	79	71	63	55	52	49	46	44	42	41	41	40
	Adsorption (mg/gm)	4.5	8.5	12.5	16.5	18	19.5	21	22	23	23	23.5	24
TSS	Concentration (mg/L)	42	37	37	33	28	25	25	23	23	22	22	21
	Adsorption (mg/gm)	2.5	5	5	7	9.5	11	11	12	12	12.5	12.5	13

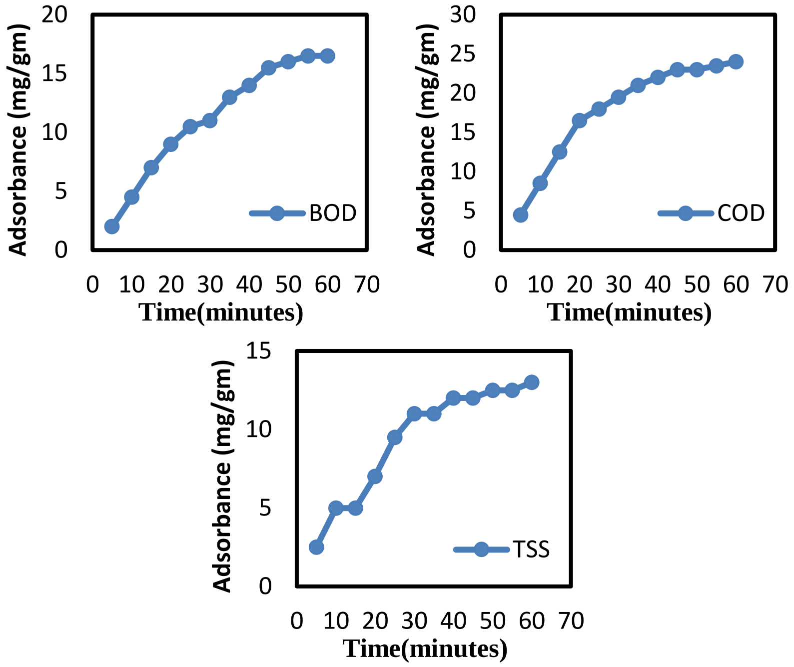

Figure 6. Concentrations of BOD (Ph-10), COD (Ph-12), TSS (Ph-10), and Chlorides Ions (Ph-10) Adsorption at Various Time Intervals (Mg/Gm)

The initial ion concentration was noted prior to measuring adsorptive activity at a particular pH. According to Table 4, the results of the contact time analysis that was produced at room temperature during the batch adsorption process showed that, at the sample's ideal pH of 10, the BOD concentration from wastewater dropped from 74 to 41 mg/L in 55 minutes. For COD, the concentration decreased from 88 to 40 mg/L at room temperature in 60 minutes at the sample's optimal pH of 12. In a similar vein, a reduction in TSS was noted from 41 to 21 mg/L after 60 minutes of contact time with the biosorbent. Adsorption occurred at room temperature while maintaining the ideal pH of 10 (Table 4).

4. Conclusions

The evaluation of the chemicals and heavy metals from the industrial wastewater of the Indian city of Vijayawada served as the basis for the study. The city's industrial center has heavily contaminated the water supplies. The majority of the contaminants were found to be below the allowable limit of environmental pollutants, according to the analysis results (Environment protection rules, 1986). Only three pollutants were discovered to be higher: nickel (1.75 mg/L), lead (0.16 mg/L), and chromium ions (2.63 mg/L). In wastewater effluent samples, heavy metals, BOD, COD, TDS, and TSS were removed using a novel biosorbent made from Citrus Sinensis & Musa. Within the first 45 minutes, this biosorbent effectively eliminated all metal ions within the ideal pH ranges. In a similar vein, at pH 4, TDS concentration dropped from 6295 mg/L to 3395 mg/L, while at pH 10, BOD dropped from 79 to 55 mg/L at room temperature in 12 hours. In just 12 hours, the COD concentration at pH 12 decreased from 91 to 45 mg/L at room temperature. In just 12 hours, the TSS concentration at room temperature and pH 10 decreased from 48 to 29 mg/L. Based on the study's findings, this biosorbent may be utilized to treat industrial wastewater that has high levels of BOD, COD, TDS, and TSS before it is released into the environment. This will help to lessen the harmful effects of these contaminants on the public's health in the area.

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