

Removal of Hexavalent Chromium from Sewage Produced by Small Scale Industries in Aligarh

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Abstract

In the present study, the adsorption potential of activated carbon for removal of (Cr^{+6}) ions from effluents of electroplating areas has been investigated by using the active compound onto the activated carbon surface under mild conditions. Hexavalent Chromium (Cr^{+6}) in the wastewater under analysis is higher than the permissible limits of World Health Organization (WHO), Bureau of Indian Standards (BIS) and Central Pollution Control Board (CPCB) at only one location Industrial Estate in Aligarh. The study involves batch experiments to investigate the effects of adsorbent dose, pH of solution and contact time on adsorption process and the evaluation of optimum conditions. In batch studies, the adsorption process has best fit to Freundlich isotherm. Freundlich adsorption isotherm model was applied to analyse adsorption data and was found to be applicable to this process. Finally, it can be concluded that activated carbon was more effective for the removal of (Cr^{+6}) ions from the wastewater.

Keywords: Heavy Metals, effluent from electroplating industry, adsorption, activated carbon

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INTRODUCTION

Heavy metals are elements those have atomic weights between 63.546 and 200.590 gram and a specific gravity greater than 4.0 i.e., at least 5 times that of water. They exist in water in colloidal, particulate and dissolved phases with their occurrence in water bodies being either of natural origin (e.g., eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e., solid waste disposal, industrial or domestic effluents, harbour channel dredging)^[1-4].

They constitute an ill-defined group of inorganic chemical hazards and those that are most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni).

Nowadays, there has been a growing concern with environmental protection. This can be achieved either by decreasing the afflux of pollutants or by their removal from the contaminated media. The former is feasible choice only for pollutants of anthropogenic origin, whereas the latter is unavoidable for those of natural origin. Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals at concentrations exceeding the local discharge limits. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, zinc and copper. The use of secondary treated wastewater, rather than raw effluent water, appears to have had few adverse physical, chemical, or biological effects on vegetables and fruits^[2-6].

This agrees with the findings of researchers in some other parts of the world.

Chromium (Cr)

Chromium is a chemical element in the periodic table that has the symbol Cr and atomic number 24. It is a steel-grey, lustrous, hard metal that takes a high polish and has a high melting point. Chromium is a metal, a naturally occurring element found in rock and soil as well as in the tissues of animals and plants^[5-7].

Forms of Chromium

For the purpose of evaluating health impact, it is important to distinguish between three forms of chromium:

Metal Chromium is used mainly for making steel and alloys. Little is known about the health effects of this form of chromium. However, there is no reason to believe that chromium (0) is a major cause for concern.

Chromium (III) is the form of chromium naturally found in the environment. It is used for brick lining for high-temperature industrial furnaces and for making alloys, chrome plating, dye manufacture, leather tanning and wood preserving. In air, most of the chromium is from man-made sources in the form of chromium (III). This form is also an essential nutrient. An intake of 50 to 200 µg of chromium (III) per day is recommended for adults. It is required for the body to utilize sugars, proteins and fat properly. Insufficient levels of chromium (III) may cause weight loss, impact growth, cause diabetes-like conditions and affect the nervous system^[8-12]. Chromium (III) appears to enhance sensitivity to insulin by facilitating the interaction of insulin with its receptor site. The main concern with the exposure to chromium (III) appears to be allergic reactions causing skin rashes as well as

redness and swelling of the skin in sensitive people.

Chromium (Cr⁺⁶) is released into the environment primarily as a result of industrial activity. High air levels (2 µg/m³) may cause irritation of nasal mucosa, nose bleeds, ulcers and holes in the nasal septum. Sensitive people may develop skin allergies similar to those caused by chromium (III). Very high doses if ingested may cause convulsion, liver or kidney damage, or even death. Such effects are observed only at high doses, which are not normally encountered in food or drinking water. The main cause for concern with chromium (Cr⁺⁶) is induction of lung cancer after long-term exposure to this toxicant. As chromium (Cr⁺⁶) is the most toxic of the three forms of chromium, the focus of the assessment is on this compound.

Sources

The largest source of chromium in air is the combustion of fossil fuels (oil-based and coal-based). However, most of the chromium from this source is chromium (III). The largest sources of chromium (Cr⁺⁶) are chemical manufacturing processes. Chrome plating, steel welding and chromium (Cr⁺⁶) manufacturers and industrial users (textile industry, manufacturers of dyes and pigments etc.) can discharge chromium (Cr⁺⁶) waste into the waterways. The soil levels of chromium (Cr⁺⁶) are increased primarily by disposal of commercial products containing chromium, industrial waste containing chromium and by coal ash from electric utilities^[11-15].

Major Uses

Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, and in photography, and for chrome alloy

and chromium metal production, chrome plating, and corrosion control^[13-17].

ADSORPTION

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The molecules are attracted to the surface but do not enter the solid's minute spaces as in absorption.

Types of Adsorption

Depending upon the nature of forces that exist between adsorbate molecules and adsorbent, the adsorption can be classified into two types^[18-20]:

Physical Adsorption (physisorption)

If the force of attraction between adsorbate and adsorbent are Vander Waal's forces, the adsorption is referred to as physical adsorption, also known as Vander Waal's adsorption. In this, the force of attraction between the adsorbate and adsorbent are very weak, therefore it can be easily reversed by heating or by decreasing the pressure.

Chemical Adsorption (chemisorption)

If the force of attraction between adsorbate and adsorbent are almost of same strength as chemical bonds, the adsorption is referred to as chemical adsorption, also known as Langmuir adsorption. In this, the force of attraction is very strong; therefore adsorption cannot be reversed easily.

KINETIC STUDIES

Kinetic investigations are carried out to measure the rates of reaction under various experimental conditions; dye concentration, pH, temperature and time on the rates of reaction to attainment of equilibrium during the adsorption process.

Adsorption Kinetics

Result obtained during an adsorption test describes the performance of the adsorbent

and will yield valuable information if properly interpreted. Several mathematical relationships have been developed to describe the equilibrium distribution of solute between the solid and liquid phases and thus, aid in the interpretation of adsorption data. These relationships apply when the adsorption tests are conducted at constant temperature and are referred to as adsorption isotherms.

MATERIALS AND METHODS

Experimental Procedure

The wastewater was analysed for various parameters such as pH, alkalinity, total hardness, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), total solids, suspended solids and dissolved solids etc. The pH values were measured by the digital pH meter. Alkalinity, hardness and BOD were analysed by titrimetric methods. COD was analysed as per closed reflux technique and solids were determined from gravimetric methods. Commercially available granular activated carbon (Particle size = 300 mesh). To evaluate the potential of Activated Carbon to remove hexavalent chromium Cr^{+6} from wastewater, batch experiments were carried out^[17-20].

Wastewater Collecting Locations

The wastewater is collected from four locations in Aligarh. The wastewater sample has been collected separately for the heavy metal analysis^[21-23].

1. Nai Basti: Wastewater sample is taken from pond. The sample at this place contains heavy metals due to metal works in this area.
2. Upper Fort: The Wastewater sample is taken from main sewage. The soil at this place contains heavy metals due to the lock manufacturing in and around this area.
3. Industrial Estate: (Near exhibition ground). This is the industrial area of

Aligarh and the wastewater in this area is highly contains heavy metals.

4. Shahjamal: Wastewater in this area contains a significance amount of heavy metals because of industries in this area.

Batch Experiments

50 ml of wastewater has been taken in each 9 conical flasks. Adsorption has been performed in a set of three conical flasks (A1, A2 and A3) at room temperature ($27 \pm 1^\circ\text{C}$) for 24 hours contact time using mechanical shaker at fixed pH & variable dosing and at fixed dosing & variable pH.

The flasks were agitated in a mechanical shaker for 3 hours and left for 24 hours contact period. After the completion of adsorption, the suspension was filtered through Whatman filter paper (Qualitative circles 125 mm Φ , cat no. 1001125).

The filtrate of each 9 conical flasks and one sample of wastewater has been taken and was analysed to evaluate the concentration of hexavalent chromium (Cr^{+6}) in the treated water and wastewater by spectrophotometer. Similarly, for different wastewater, 50 ml of wastewater has been taken in each 9 conical flasks and experimental procedures were carried out as mentioned above^[18-22].

Effect of Various Adsorbent Doses on Cr^{+6} Removal

To study the effect of various adsorbent doses on Cr^{+6} removal, suitable doses of AC ranging from 25 to 400 mg were added to 50 ml wastewater sample at fixed pH.

The initial pH of wastewater before addition of the adsorbent was measured. NaiBasti, UpperFort, Industrial Estate, Shahjamal had a pH of 7.80, 7.03, 7.68 and 7.22 respectively. The final concentration of Cr^{+6} in the treated wastewater was determined after 24 hours contact time. Thus, the amount of Cr^{+6}

adsorbed on various adsorbent doses has been determined^[22-23].

Effect of pH on Cr^{+6} Removal

To study the effect of various pH on Cr^{+6} removal, the pH was adjusted by 0.1 N H_2SO_4 and 0.1 N NaOH solution depending upon acidity or alkalinity. Contact time has been kept 24 hours at varying pH and fixed doses.

Experiments were done at room temperature ($27 \pm 1^\circ\text{C}$). The pH of wastewater was adjusted to 2, 4 and 6 by 0.1 N H_2SO_4 respectively for each sample of 4 different areas.

Effect of Contact Time on Cr^{+6}

Removals

To study the effect of contact time on Cr^{+6} removal from the wastewater, 25 to 400 mg adsorbent doses AC were added to each 50 ml wastewater sample of respective areas.

The pH of wastewater was adjusted to 2, 4 and 6 by 0.1 N H_2SO_4 respectively. Contact time was varied from 3 to 24 hours and the final concentrations of Cr^{+6} in the treated wastewater were determined.

RESULT AND DISCUSSION

Waste Water Analysis

In table initially concentration of Hexavalent Chromium Cr^{+6} is very high. The permissible limit according to BIS and CPCB is 0.05 mg/l for drinking purposes and effluent discharge limit is 2 mg/l for industry.

According to the tests performed, Cr^{+6} exceed the limit of only one location. The effect of various adsorbent doses on Cr^{+6} removals from wastewater is represented through Tables and Graphs performed at 3 to 24 hours contact time, room temperature ($27 \pm 1^\circ\text{C}$).

Table 1: Characteristics of Raw Electroplating Wastewater.

S. No.	Parameters	Results			
		Industrial Estate	Shahjamal	Nai Basti	Upper Fort
1	pH	7.68	7.22	7.80	7.03
2	Alkalinity (mg/l as CaCO ₃)	568	436	464	584
3	Suspended Solid (mg/l)	<u>1000</u>	400	200	<u>800</u>
4	Dissolved Solid (mg/l)	1600	1500	1200	1400
5	BOD ₅ at 20°C (mg/l)	108	114	153	159
6	Total Hardness (mg/l as CaCO ₃)	192	224	104	200
7	Total solids (mg/l)	2600	2000	1400	2200
8	COD (mg/l)	<u>1312</u>	<u>736</u>	<u>896</u>	<u>2344</u>

(Underline shows exceed the discharge limit according to the BIS and CPCB)

Batch Study for the Treatment of Wastewater by Adsorption

Table 2: Initial Concentration of Hexavalent Chromium Cr⁺⁶ at All Samples Locations.

Industrial Estate	Shahjamal	Nai Basti	Upper Fort
7.24 mg/l	0.21 mg/l	0.35 mg/l	0.325 mg/l

Effect of Various Adsorbent Dosages on Cr⁺⁶ Removal

Figure 1 to 4 depicts the variation of Cr⁺⁶ removals for variable dosage at 3, 6 and 24 hours contact time. The results indicate an increase in percent of Cr⁺⁶ removals with an increasing adsorbent dose up to certain limit (around 100 mg/50 ml of sample) and beyond that a less constant removal is observed. The maximum (69.06%) removal of Cr⁺⁶ have been

observed at dose of 400 mg/50 ml and the minimum (45.16%) at dose of 100 mg/50 ml in 24 hours. These Figures show the variation of Cr⁺⁶ removals for variable dosage at 3 and 6 hours contact time. The maximum (12.15%) and (34.8%) removal of Cr⁺⁶ has been observed at dose 400 mg/50 ml and beyond that a little change in removal is observed and the minimum (3.59%) and (21.54%) at dose of 100 mg/50 ml.

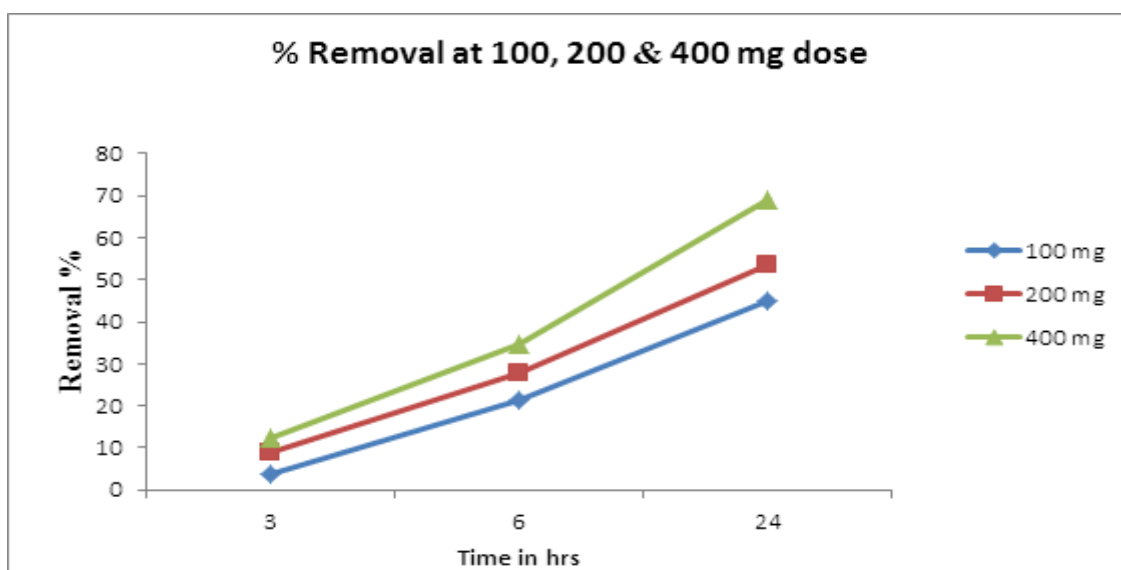


Fig 1: Effect of Adsorbent and Contact Time at Industrial Estate.

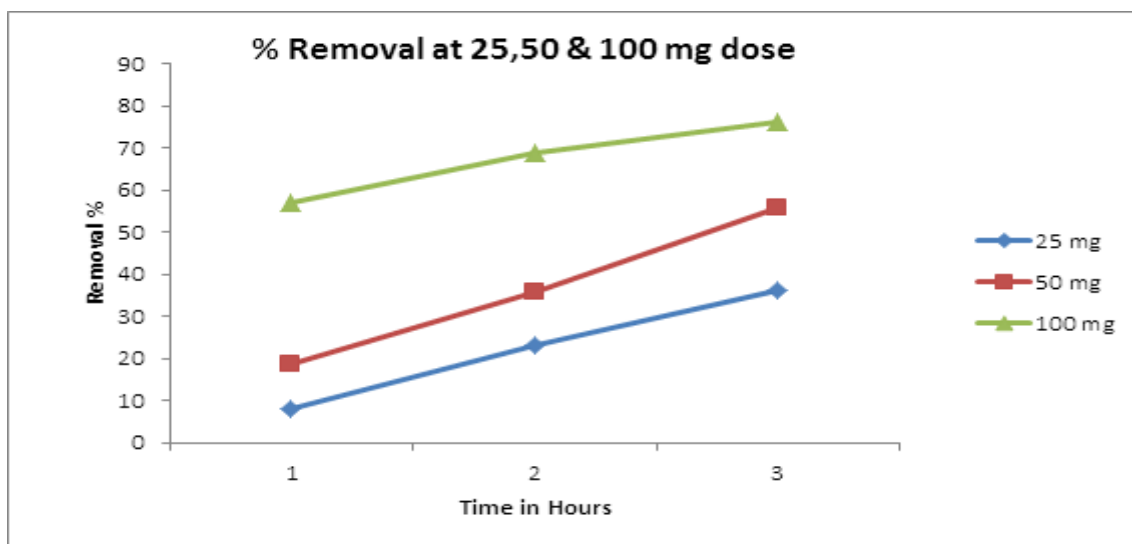


Fig. 2: Effect of Adsorbent and Contact Time at Shahjamaal.

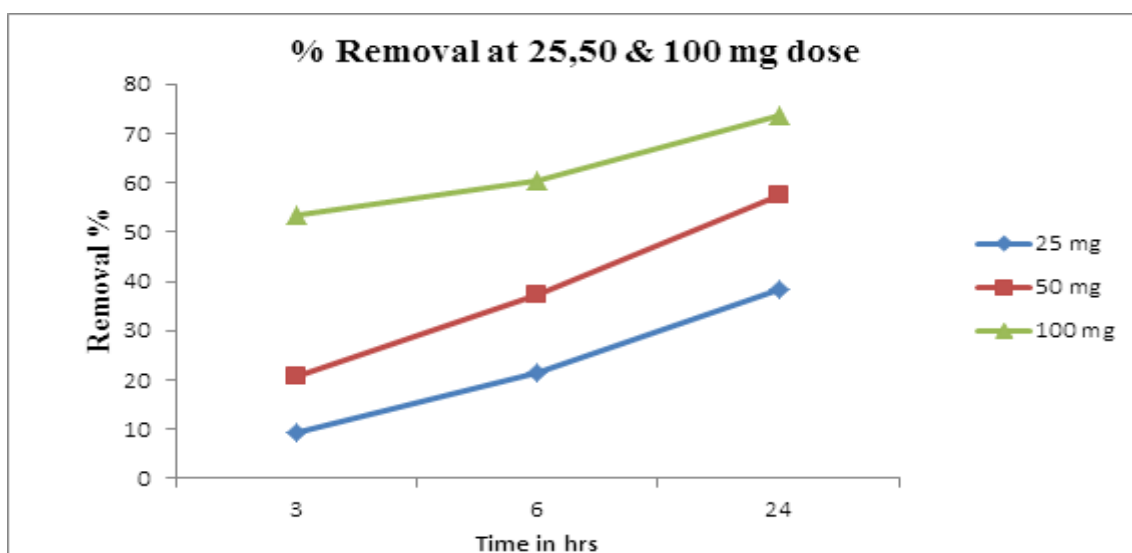


Fig. 3: Effect of Adsorbent and Contact Time at Upper Fort.

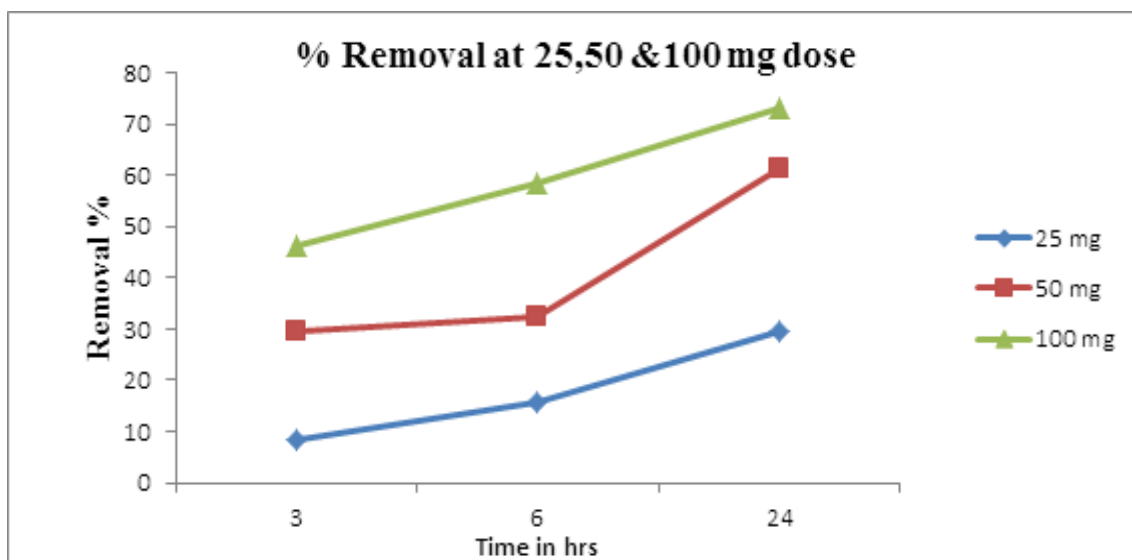


Fig. 4: Effect of Adsorbent and Contact Time at Nai Basti.

Effect of pH on Cr⁺⁶ Removal

These Figures 5 to 8 show the variation of Cr⁺⁶ removal for variable pH at 2, 4 and 6 at different contact time 3, 6 and 24 hours and at fixed dose of 200 mg/50 ml in Industrial Estate area and 50 mg/50 ml for

other areas. The maximum adsorption (55.24%), (66.67%) and (93.67%) of Cr⁺⁶ was obtained at a pH of 2 and the minimum adsorption (15.05%), (27.07%) and (32.04%) at pH of 6. The adsorption decreased with increase in pH value.

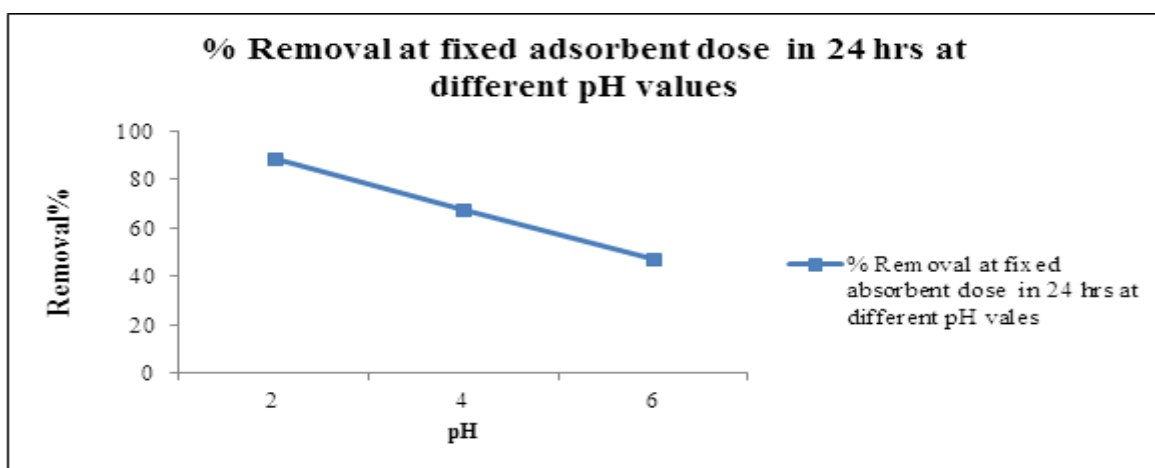


Fig. 5: Effect of pH on Adsorbent Dose at Industrial Estate.

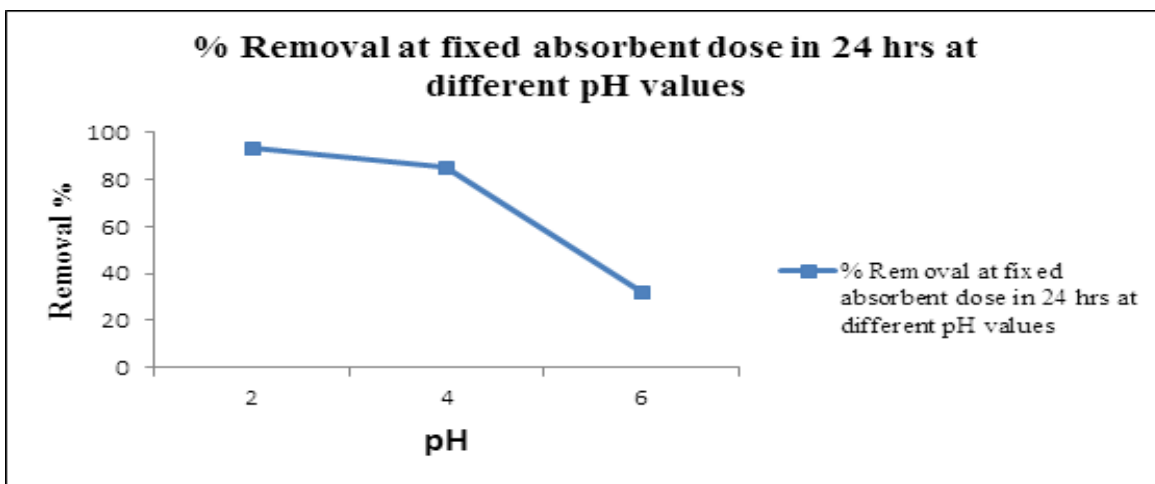


Fig. 6: Effect of pH on Adsorbent Dose at Shahjamal.

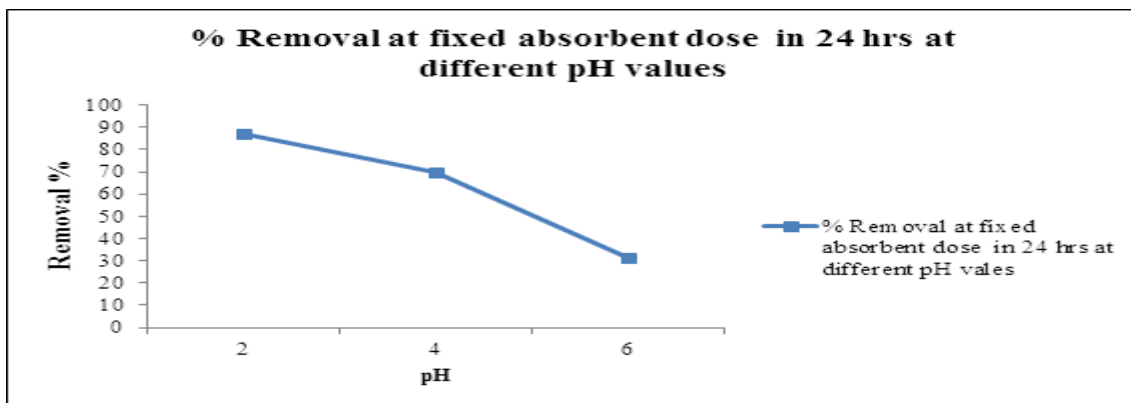


Fig. 7: Effect of pH on Adsorbent Dose at Upper Fort.

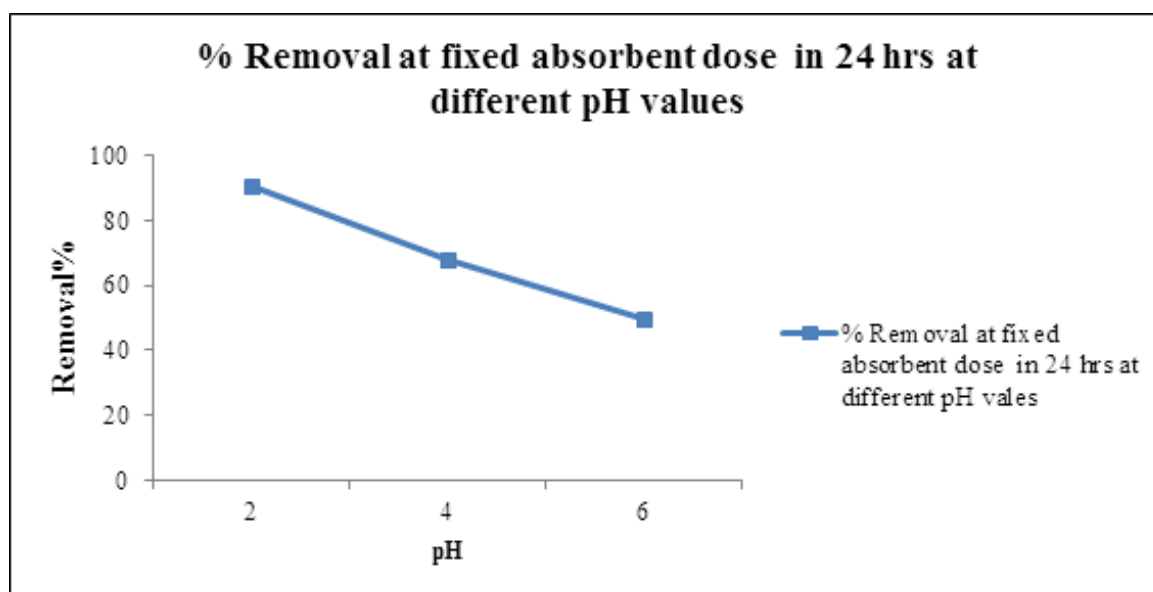


Fig. 8: Effect of pH on Adsorbent Dose at Nai Basti.

Effect of Contact Time on Cr⁺⁶ Removal

The response of contact time on Cr⁺⁶ removal is presented through Tables and Figures. The observations reveal that the percentage Cr⁺⁶ removal increases with the increase in the contact time. About 90% Cr⁺⁶ removal was observed after a contact time of 24 hours. On further increasing the contact time to more than 24 hours, more or less the same efficiency was achieved. It was interesting to note that even at a low contact time of 3 hours and pH 2, the adsorbent demonstrates a chromium removal of about 58.95% at fixed adsorbent dose in table.

CONCLUSION

1. The presence of heavy metals in wastewater of electroplating areas can affect the quality of food, groundwater, micro-organisms activity, plant growth etc.
2. Wastewater characteristic of different locations shows the some values are within the permissible limit or some values are not in limit according to the BIS and CPCB.
3. The difference in between their values of four different locations Industrial Estate, Shahjamal, Upper Fort and Nai

Basti are differences is highly in between Total Hardness and COD.

4. However there is an undesirable immobilization of these toxic and unwanted heavy metals into the groundwater.
5. The effluent if any type containing heavy metal practice to treated before disposing it to prevent ground water contamination.
6. The hexavalent chromium Cr⁺⁶ in industrial wastewater collected from four locations iscontaining initially concentration 7.24, 0.21, 0.325 and 0.35 mg/l respectively. Highly contaminated than the permissible limit. The concentration hexavalent chromium Cr⁺⁶ is high in Industrial Estate 7.24 mg/l wastewater and low in Shahjamal 0.21 mg/l wastewater.
7. The removal of Cr⁺⁶ is doing by Activated Carbon, The adsorption percentages of Cr⁺⁶ ions increased sharply by increasing adsorbent dose in our study as shown in figures. It works very effectively.
8. In Batch experiments showed that the solution pH strongly influenced the biosorptive capacity of the biomass. Maximum removal efficiency of Cr⁺⁶

ions achieved at pH 2 and minimum at pH 6.

9. A contact time of 3,6 and 24 hours for adsorption is sufficient for about 70 to 90% Cr⁺⁶ removal from the wastewater sample by using Activated Carbon for treatment of wastewater.
10. It was interesting to note that even at a low contact time, the adsorbent demonstrates a chromium removal of about 58.98% at pH 2 at fixed adsorbent dose. The adsorption decreased with an increase or decrease in pH in Table 1.
11. The adsorption capacity of the material for chromium is encouraging and needs further investigation and standardization Data obtained during presented study may be quite helpful in designing and studying performance of full scale adsorber for the treatment of industrial wastewater containing chromium and heavy metals also.

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