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Assessment of chromium biosorption by Saw Dust from groundwater in Delhi Region

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ABSTRACT

Water is a valuable and indispensable resource for life support. It finds use in many areas like water supply and sanitation, energy production, habitat for aquatic life, navigation, agriculture, etc. The groundwater in some pockets the Delhi region, India, has significant quality problems due to contamination with harmful elements such as fluoride, nitrate, heavy metals i.e., chromium, lead and cadmium, etc. The study aimed to evaluate the removal efficiency of hexavalent chromium from the synthetic solution using pre-treated sawdust as biosorbent. The individual effect of different operating parameters namely solution pH (2.0 to 12.0), biosorbent dosage (0.2 to 2.5g) adsorbate dosage (10 to 60 mg/l) on the biosorption process was evaluated. The biosorption process was found dependent on solution pH, contact time, biosorbent dose, adsorbate dose and temperature. The optimal conditions for the biosorption of 20 mg/l Chromium (VI) were found at 2<pH>10, 2 g of biomass amount and 30 mins of equilibrium time. More than 99 % Cr (VI) was removed from all input parameters. The results indicate that sawdust, waste of wood is an attractive biosorbent for eliminating hexavalent chromium from the groundwater.

***Key words** : Biosorption, Chromium, Groundwater, Heavy Metal and Saw Dust*

Introduction

Groundwater is a valuable resource available for mankind catering to their industrial, agricultural and domestic needs. Seepage of untreated effluents released from the industries on open land increases the concentration of pollutants in the groundwater.

Anthropological activities such as agricultural, industrial activities the groundwater quality. Delhi is the third-largest metropolitan city of the country and also the third leading densely inhabited city. River Yamuna (surface water) and groundwater are two sources of water supply Delhi (Singh, 2010).

Environmental pollution of heavy metals has become of great concern due to the adverse effects. The traces of fluoride, nitrate and heavy metals like chromium, lead and cadmium in the groundwater have been reported above the prescribed limits in Northwest, South and East of Delhi. In Delhi, the issue of water shortage seriously dominates (Singh, 2010). Water degradation caused by anthropological activities such as agricultural and industrial etc. contributes to a high degree of pressure on the quality of groundwater.

Chromium is a hazardous environmental pollutant and is present in wastewaters from various industrial activities (Sen *et al.,* 2010). It exists inthe oxidation states from -(II) to +(VI). The most common forms are chromium (0), trivalent [or chromium (III)], and hexavalent [or chromium (VI)]. The metal chromium, which is chromium (0) form, is a steel-grey solid with a high melting point. It is mainly used for making steel and other alloys.

Hexavalent and trivalent chromium have different properties. Trivalent chromium or chromium (III), in the form of chromium is essential to human health, whereas hexavalent chromium, or chromium (VI), is a toxic form. Chromium compound is generated from the chemical industries. Chromium (III) and chromium (VI) forms are used in chrome plating industries, dye and pigments manufacturing, leather tanning and wood preserving (Chua, 1998). Trivalent Cr adsorbs intensely to the surface of soil particles anddoes not leach out into the groundwater. Hexavalent Chromium may reduce to trivalent Chromium only into the upper layer of soil and the rate of reduction depends on the pH and humicacid content of the soil.

Heavy metals need to be treated from polluted wastewater to meet the regulatory discharge norms. Chemical precipitation, reverse osmosis, ion exchange, and electrochemical deposition are typical conventional treatment methods (Meena *et al.,* 2005; Barkat, 2011). Though several disadvantages are associated with the conventional methods. Chemical precipitation requires a large number and amount of chemicals and produces large amount of sludge with environmental implications of its disposal (Aziz *et al.,* 2008). In ion-exchange method handling of concentrated metal solution is a concern. Ion exchange resins easily get fouled by organics compounds and other solids in the treated water (Barakat, 2011).

The Biosorption technique has been employed as a promising cost-effective clean-up biotechnology. Biosorption may be simply defined as the removal of substances (organic matter, dyes, heavy metals etc.) from solution by biological material. The biosorbents are categorized under different categories such as microorganisms like bacteria, yeast, fungi, algae; agricultural by-products like bran of rice, sugarcane bagasse, rice husk, wheat, weeds, fruit wastes etc. and other polysaccharide materials. Many biosorbents, irrespective of their source have shown efficiency in metal removal. Researchers have studied the biosorption potential of different biosorbent materials for metal removal (Babel and Kurniawan, 2004; Monji, 2004; Dubey and Gopal, 2007; Ngah and Hanafiah, 2008; Pehlivan and Altun, 2008; Anandkumar and Mandal, 2009; Menon *et al.,* 2009; Singh, 2009; Chen *et al.,* 2010; K. Singh, S. H. Hasan, M Talat; Wang *et al.,* 2010; Hegazi, 2013).

The objective of the study is to assess the biosorption potential of sawdust/wood dust for removal of hexavalent chromium metal from the synthetic water using biosorption technique, utilizing sawdust as a biosorbent in the batch systems.

Materials and Methods

Groundwater samples were collected from 25 locations distributed throughout the NCT Delhi (Fig. 1). The physicochemical parameters and heavy metals were analyzed. In addition, data on groundwater quality available with Central Ground Water Board has also been referred. Out of 25 sampling points, 22 were collected from hand pump/bore well extraction, (W12 and W15) were wastewater samples of an electroplating industry and W14 was sourced from RO, drinking water depicted below.

Sawdust or wood dust was used for removal of Chromium VI for this study, as these are available abundantly and also being low-cost biosorbents.

Preparation of biosorbent

Sawdust or wood dust is a waste residual of carpentry activities, sawing, drilling and sanding or a byproduct from agro-waste was used as biosorbent.

Pre-treatment of biosorbent

Sawdust (biosorbent) was pretreated with boiling

Fig. 1. Local map of NCT Delhi

water and dried in the air to get rid of other contaminants present in it. Bio sorbent was sieved by sieving (425-micron size) to get desired particle size (Fig. 2).

Fig. 2. Image of dried biosorbent

Preparation of solution reagents

Chromium solution: To make the solution of desired concentration ranging from 10 to 60 mg l^{-1}, an available approved reference material solution of Cr (VI) (1000 mg / l) was taken for dilution and was kept in bottles for use in biosorption studies.

Diphenylcarbazide solution: In 50 mL acetone 250 mg 1,5-diphenylcarbazide was dissolved and stored in a brown bottle. On discolouration discarded the solution. Effect of solution pH (2.0 to 12.0), biosorbent dosage (0.2 to 2.5g) and adsorbate dosage (10 to 60 mg/l) on the biosorption process were evaluated. All the experiments were carried out in doublets.

Table 1. Parameters for measurement of a standard curve

Parameter	**Hexavalent Chromium**	
Date of Calibration:	20.04.2018	
Instrument:	PRPL/EQ/040	
Wavelength:	540nm	
Standard Curve Values:		
S.No.	Concentration	Absorbance
1	0.062	0.2
2	0.113	0.4
3	0.172	0.6
4	0.232	0.8
5	0.293	1

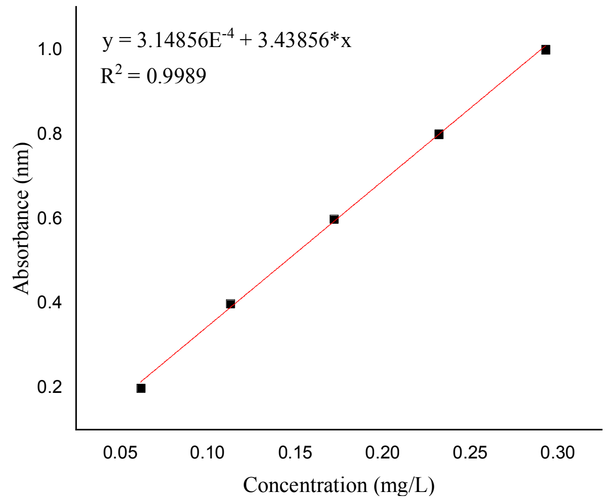

Fig. 3. Calibration curve for hexavalent chromium

The calibration curve (Fig. 3 and Table 2) was prepared by using a standard solution of potassium dichromate (Table 1).

Table 2. Formula used for calculation of chromium concentration

Blank Absorbance	0.039
Intercept of Curve	0.0003
Slope of Curve	3.4386
Formula for Calculation	[Absorbance × slope] + [Intercept]

The difference in Cr (VI) concentration pre and post biosorption was taken into consideration to calculate the percentage biosorption of Cr (VI) on sawdust and it was stated by Eq. (1):

$$\text{Biosorption of sawdust (\%)} = \frac{(C0-Ce)}{C0} \times 100 \quad .. (1)$$

The amounts of Cr biosorbed onto sawdust were calculated using Eq. (2):

$$q_e = \frac{(C0-Ce)}{W} \times V \quad .. (2)$$

Where C_0 is the initial concentration (mg/L), C_e is Cr concentration in solution at a given time (mg/L), W is the sawdust weight (g) and V is the volume of CRM solution (L).

Results and Discussion

After performing a screening test of the collected samples, Cr was found above the prescribed limits at all the locations. Removal of Cr was done with the help of a very cost-effective technique, i.e. biosorption by using sawdust. Few batch studies were observed to set the operational conditions for optimum removal of chromium from a solution.

Influence on solution pH

One of the most critical parameters to be taken into account during the biosorption of metal ions from aqueous solutions is solution pH. The effect of pH of the chromium solution, on the biosorption was studied at pH ranging from 2, 4, 6, 8, 10 and 12 for 30 mins. Fig. 4 indicates the uptake capacity of chromium by sawdust.

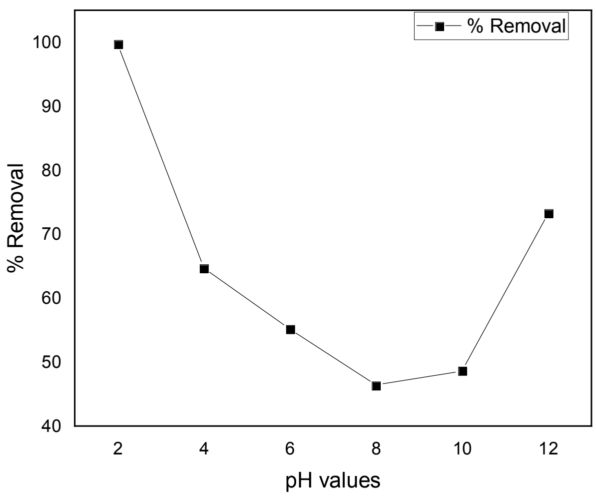

Fig. 4. Effect of solution pH on removal of chromium

Earlier works have also reported similar behaviour using other adsorbents e.g. at pH 2, the dominant form of Cr (VI) is $HC_rO_4^-$ whereas at higher pH the other forms of Cr (VI), i.e. CrO_4^{2-} or $Cr_2O_7^{2-}$ predominate. The adsorption was observed high at lower pH. The strong electrostatic attraction between positively charged surface groups and $HCrO_4^-$ can be attributed to the observed greater adsorption at lower pH. A decrease in adsorption above pH6 can be recognized to the competitive adsorption of CrO_4^{2-} and OH^- ions (Rai *et al.,* 2016). This indicates that the uptake activity of chromium decreased between pH range 2-10 and then increased at pH 12. At higher acidic and alkaline conditions, Cr showed active biosorption.

Effects of contact time and concentration of chromium on biosorption

With an increase in agitation time amount of chromium adsorbed increased and reached equilibrium within 30-45 mins. The biosorption of Cr (VI) as a function of time in terms of contact and initial concentration of metal ion onto sawdust is shown in Fig. 5. Results showed 98.98% adsorption of chromium in 30 mins. Initially, all the active sites on the adsorbent are empty, so adsorption continues at a higher pace and desorption at a comparatively lower rate, with the net effect of adsorption increasing more rapidly. As the active sites are occupied, the adsorption and desorption rates tend to remain the same and the degree of adsorption decreases to become almost constant in equilibrium (Rai *et al.,* 2016).

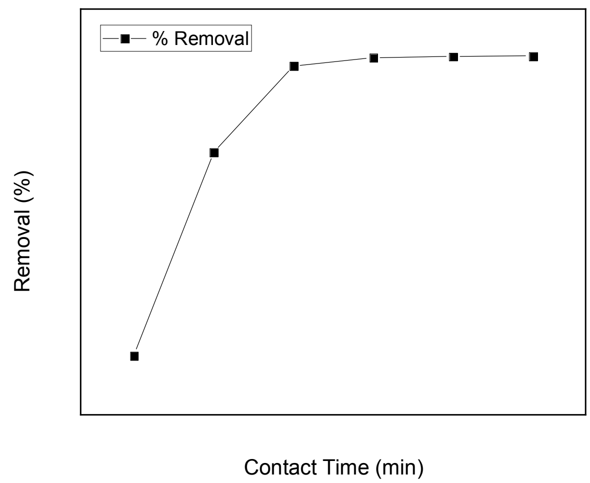

Fig. 5. Effect of contact time on removal of chromium

Effect of temperature

The effect of temperature on the kinetics of chro-

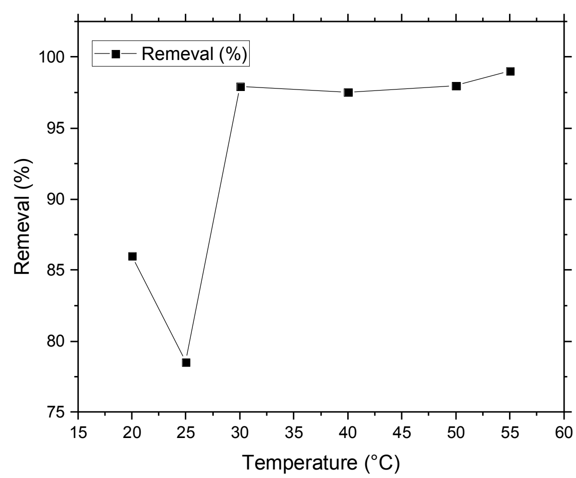

Fig. 6. Effect of temperature on removal of chromium

mium sorption through sawdust was determined by varying the temperature from 20 ° C to 55 ° C, as shown in Fig. 6. Spirulina sp. show that by percent sorption increased with increase in temperature up to 40°C (Rezaei, 2016).

Effect of biosorbent dosage

The bio sorbent dose has also been shown to be an important parameter during biosorption studies, as it initially specifies the prospective material to adsorb metal ions for a given concentration of the solution. The effect of the quantity of sawdust on chromium acceptance is shown in Fig. 7. Adsorbent dose when high, there are not enough Cr (VI) in the solution to engage the active sites and hence forward the adsorption tends to become constant (Simha *et al.*, 2016).

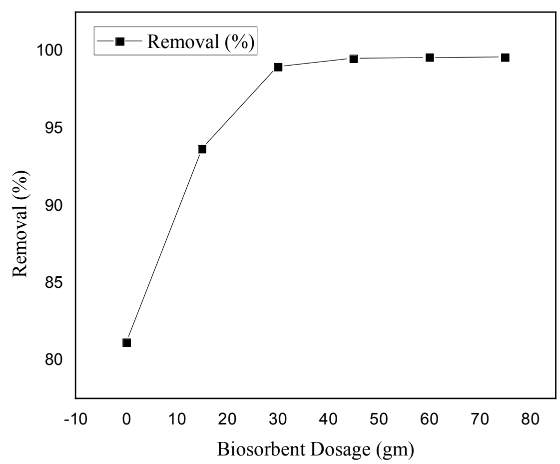

Fig. 7. Effect of biosorbent dosage on removal of chromium

Effect of dosage of adsorbate

Effect of adsorbate dosage on the kinetics of chromium sorption by sawdust was determined by varying the dosage from 10 mg/l to 60 mg/l. Initially, the acceptance of Cr (VI) increased with increasing Cr (VI) concentration after that it gradually reduced as the concentrations increases and finally became constant (Fig. 8). Active sites of the adsorbent surface get engaged and ultimately establish a form of dynamic equilibrium after a firm level of increase in initial Cr (VI) concentration, amid the procedures of adsorption and desorption (Rai *et al.*, 2016).

It was observed that more than 99 % Cr (VI) was removed from all input parameters in process of biosorption by sawdust (Table 3).

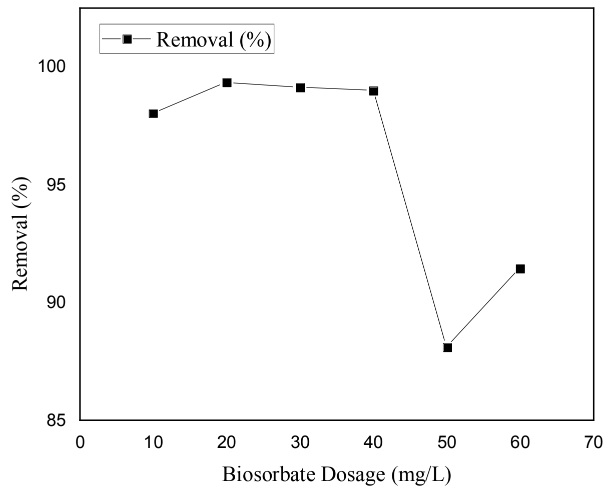

Fig. 8. Effect of adsorbate dosage on removal of chromium

Table 3. Maximum removal of Cr (VI) from different parameters

Parameter	Removal of Cr (VI) (%)
pH	99.74
Contact time (Mins.)	99.6
Temperature (°C)	99.02
Biosorbent dose (g)	99.69
Biosorbate amount (mg/l)	99.34

Conclusion

Through the present study, it was observed that the ground water quality of some areas in the Delhi region is contaminated with chromium. Sawdust as a biosorbent was found as cost-effective and environmental friendly option for the removal of hexavalent chromium from groundwater. Therefore sawdust which has high porosity and surface area may be considered as a potential biosorbent in the treatment of hexavalent chromium.

The percentage removal of Chromium (VI) from synthetically prepared aqueous solutions was examined by sawdust. The biosorption of Chromium (VI) was found to be dependent on solution pH, contact time, biosorbent dose, adsorbate dose and temperature. Optimum conditions for the biosorption of 20 mg/l Chromium (VI) were found at 2<pH>10, 2 g of biomass dose and 30 mins of equilibrium time. More than 99 % Cr (VI) was removed from all input parameters. The results indicate that waste of wood (like sawdust) is an attractive biosorbent for removing hexavalent chromium from the wastewater/ groundwater.

Conflict of Interest statement

The authors declare that they have no conflict of interest.

Acknowledgments

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Data Availability Statement

All data, models, and code generated or used during the study appear in the submitted article.

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