

Full Length Research Paper

Adsorption of Heavy Metal Ions from Wastewater

¹Dhananjay Chaturvedi and ²Omprakash Sahu

¹Department of Chemical Engineering, IT GGV Bilaspur (CG), India

²Department of Chemical Engineering, KIOT, Wollo University, Kombolcha (SW), Ethiopia

Correspondence author Email:ops0121@gmail.com

Accepted 19th March, 2014

Water is a source of life and energy, although millions of people worldwide are suffering with the shortage of fresh and clean drinking water. Rapid pace of industrialization, population expansion, and unplanned urbanization have largely contributed to the severe water pollution and surrounding. The main sources of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. Adsorption process has been proven one of the best water treatment technologies around the world. Therefore attempt has been made to use the low cost method. The objective of present investigation shows that the agricultural by-products like bengal gram husk, tur dal husk, and tamarind husk can be used as an effective adsorbent for the treatment of wastewaters containing metals like chromium (VI), iron (III), nickel (II) and mercury (II). Adsorption dynamics, isotherms, pH effect and adsorbent dosage on the removal of metals for all the adsorbate were examined. In addition desorption of the metals from the loaded adsorbents was also carried out.

Keywords: Agriculture waste; bioadsorption; metal ions; organic; treatment

INTRODUCTION

All over the world industry is forced to diminish down to acceptable level contents of heavy metal in water and industrial waste waters. Many industrial wastewaters contain dissolved metals as a result of their manufacturing processes. Included among them are mercury, lead, cadmium, silver, copper and chromium (Abia et al., 2006). Wastewater treatment systems are designed to reduce metal contaminants to meet discharge requirements and achieve the water quality level needed for reuse and achieve the water quality level needed for reuse and recycling. As a result of improper treatment prior to discharge, many dissolved metals have been found in harmful concentrations in ground waters which are destined for potable drinking water (Chubar et al., 2004). In small quantities, certain heavy metals are nutritionally essentially for a healthy life, but large amounts of them may cause acute or chronic toxicity (poisoning). The metals most often linked to human poisoning have links to learning disabilities; cancer and death are typically caused by copper, nickel, cadmium, chrome, arsenic, lead and mercury (Horsfall et al., 2006). Many of these metals are required by human in trace amounts, but in larger, persistent dosages, these heavy metals become toxic when they

are not metabolized by the body and accumulate in the soft tissues (Gaballah et al., 2007). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage o blood composition, lungs, kidneys, liver, and other vital organs (Argun et. Al., 2007). Metals, a major category of globally-distributed pollutants, are natural elements that have been extracted from the earth and harnessed for human industry and products for millenia. Metals are notable for their wide environmental dispersion from such activity; their tendency to accumulate in select tissues of the human body; and their overall potential to be toxic even at relatively minor levels of exposure (Low et al., 2005). Today heavy are abundant in our drinking water, air and soil due to our increased use of these compounds. They are present in virtually every area of modern consumerism from construction materials to cosmetics, medicines to processed foods; fuel sources to agents of destruction; appliances to personal care products. It is very difficult for anyone to avoid exposure to any of the many harmful heavy metals that are so prevalent in our environment (Wafwoyo et al., 2009).

The effluent treatment in developing countries is expensive and major cost is associated with the

dependence on imported technologies and chemicals (Torres et al., 2006). The indigenous production of treatment techniques and chemicals locally, or use locally available non-conventional materials to treat pollutants seems to be the solution to the increasing problem of treatment of effluents (Saeed et al., 2010). In this regard, there has been a focus on the use of appropriate low cost technology for the treatment of wastewater in developing countries in recent years. Technically feasible and economically viable pre-treatment procedures with suitable biomaterials based on better understanding of the metal biosorbent mechanism(s) are gaining importance (Marshall et al., 2009). Activated carbon of agricultural waste products as low cost adsorbents has been reported till now. However, there is an additional cost involved in the processing of the agricultural wastes to convert the same to activated carbon, which is posing economic difficulties necessitating research on alternate adsorbents with equivalent potential of activated carbon.

The heavy metals have proven to be hazardous not only for human life, but also to the aquatic flora and fauna, requiring remediation of the heavy metals through biosorption using low cost adsorbents (Robert and Barbati, 2012). Keeping these environmental, ecological and societal health issues in view, it is considered necessary to attempt and provide an easy, feasible, economical and reliable method for the removal of heavy metals (Babarinde et al., 2008). Hence, adsorption by locally available, environmentally-friendly and cost effective adsorbents have been explored and exploited (Marshall and Johns, 1996). The objective of the present research is to find out the adsorption capacity of the four husks namely Tur dal (*Cajanus cajan*) husk (TDH); bengal gram husk (BGH), seed coat of *Cicer arietinum*; coffee (*Coffea arabica*) husk (CH) and tamarind (*Tamarindus indica*) pod shells (TH) for the removal of heavy metals from aqueous solutions so as to facilitate comparison with other adsorbents and provide a sound basis for further modification of the adsorbent to improve its efficiency. The four adsorbents chosen for the present study is available in plenty in tropical regions. Adsorption properties of these adsorbents have not yet been reported in literature. The adsorbents in the present study were tested for their adsorption capacity on the four heavy metals namely chromium (VI), iron (III), mercury (II) and nickel (II). Exploratory studies reveal that lakes of Bangalore are contaminated with heavy metals chromium (VI), iron (III), mercury (II) and nickel (II).

MATERIAL AND METHODS

MATERIAL

Raw Water

The synthetic water generated in lab, all the chemicals

and reagents used were of A. R. grade and were obtained from E. Merck, India.

Adsorbent

The adsorbent material Bengal gram husk (BGH); Turdal husk (TDH); Coffee husk (CH) and tamarind husk (TH) are arranged from local area.

METHOD

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, agitation time and pH. Solution containing adsorbate and adsorbent was taken in 250 mL capacity beakers and agitated at 150 rpm in a mechanical shaker at predetermined time intervals. The adsorbate was decanted and separated from the adsorbent using Whatman No.1 filter paper. To avoid the adsorption of adsorbate on the container walls, the containers were pretreated with the respective adsorbate for 24 hours.

Effect of agitation time

For the determination of rate of metal biosorption by BGH, TDH, TH and CH from 100 ml (at 10, 20, 50, 100 mgL⁻¹), the supernatant was analysed for residual metal at different time intervals. The pH and the adsorbent dosage was kept constant, which varied according to the adsorbent and adsorbate under consideration.

Effect of adsorbent dosage

The effect of adsorbent dosage i.e., the amount of the four husks on the adsorption of metals was studied at different dosages ranging from 1 to 40 g/l with varied metal concentrations of 10, 20, 50 and 100 mg/L. The equilibrium time and the pH were kept constant depending on the metal under consideration.

pH effect

To determine the effect of pH on the adsorption of metal solutions (100 mL) of different concentration ranges (0-100 mgL⁻¹) were adjusted to desired pH values and mixed with known weight of adsorbent and agitated at preset equilibrium time. The equilibrium time and adsorbent dosage varied with the metal and adsorbent under consideration.

Desorption studies

After adsorption, the adsorbate – loaded adsorbent

Were separated from the solution by centrifugation and the supernatant was drained out. The adsorbent was gently washed with water to remove any unabsorbed adsorbate. Regeneration of adsorbate from the adsorbate – laden adsorbent was carried out using the desorbing media – distilled water at pH ranges 4.0 to 12.0 using dilute solutions of NaOH and HCl. Then they were agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution was separated and analyzed for the residual heavy metals.

Analytical

A pH meter (model no. SN 95010006684, Hach Co., USA) was used to measure the pH of solutions. The surface area of the adsorbent was measured by a surface area analyser (Model QS-7; Quantasorb Surface Area Analyser). IR spectra of the sample were recorded on an infrared spectrophotometer (FTIR Perkin Elmer 1600). The constituents of the prepared adsorbent were analysed following the standard methods of chemical analysis (Vogel, 1989). The absorbance measurements were recorded on a Du-6, UV±VIS spectrophotometer. The Remi centrifuge machine (model no. R 24, India) was used for centrifugation purposes. The concentration of metal ion was determined by gas chromatography (model Hewlett Packard, 5890A).

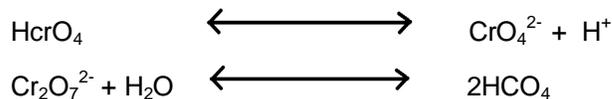
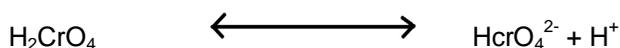
RESULTS AND DISCUSSION

Effect of pH on the adsorption of metal ions

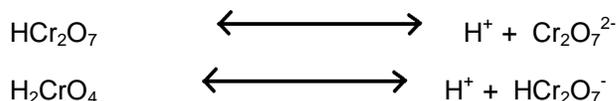
The effect of the pH on the adsorption of heavy metal was carried out for 90min time and 2.5g/l of dosing. The graphical representation effect of pH is shown in Fig. 1 (a)-(d).

Chromium

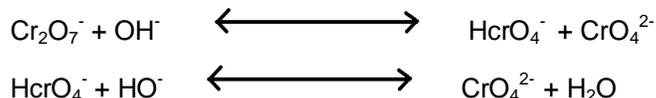
The maximums 95.4% of adsorption was found for Bengal gram (BGH) at pH 1, which shown in Fig. 1(a). With the increase in pH the adsorptions was decreases. Turdal husk (TDH) shows 93.7% of adsorption at pH 3, coffee husk (CF) shows 90% of adsorption at pH 3 and Tamarind husk (TH) shows maximum adsorption 89% at pH 5. It was observed that amount of chromium adsorbed decreased with increase in pH. But the amount adsorbed increased with increase in initial chromium concentration. Chromium exhibits different types of pH dependent Equilibria in aqueous solutions (Sawalha et al., 2007). The most important of which are the following:



In acidic solutions, the equilibrium is as follows:



The equilibrium in alkaline pH is given

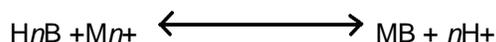


The only species that can exist in solution, above pH 8.0 is CrO_4^{2-} . As the pH is shifted, the equilibrium will also shift; in the pH range 2-6, HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, 115 ions are in equilibrium. At still lower pH (pH <2.0) values, $\text{Cr}_3\text{O}_{10}^{3-}$ – and CO_4H_{13} species are formed. Thus the formation of more polymerized chromium oxide species occurs with the decrease in solution pH. In highly acidic media, the adsorbent surfaces are highly protonated and favour the uptake of Cr (VI) in the anionic form HCrO_4^- . The removal of Cr (VI) by carbonaceous materials such as saw dust, sugar beet, sugar beet pulp, sugarcane bagasse and maize cob at an optimum pH 2.0 .

Nickel (II)

The maximum 98% adsorbent was shown by coffee husk(CH) at pH 3. The 96% adsorbent at pH 5 by Tamarind husk, 93.7% at pH 3 by (TDH) and 87% at pH 1bt BGH. Adsorption is high at pH 3.0 and decreases as the pH increases or decreases. At low pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the metal cations, pH affects both cell surface metal binding sites and metal chemistry in water (Kadirvelu et al., 2010). At low pH values, the functional groups of the biosorbent are closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions. With increasing pH, more functional groups such as amino and carbonyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the surface of adsorbent . The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complex (Villaescusa et al., 2004).

The reaction of nickel ions in the solution with the biomass can be described by the following equilibrium:



Where M represents the metal, n its charge and B the biosorptive active centers . According to reaction, the pH should influence the metal ions biosorption because of

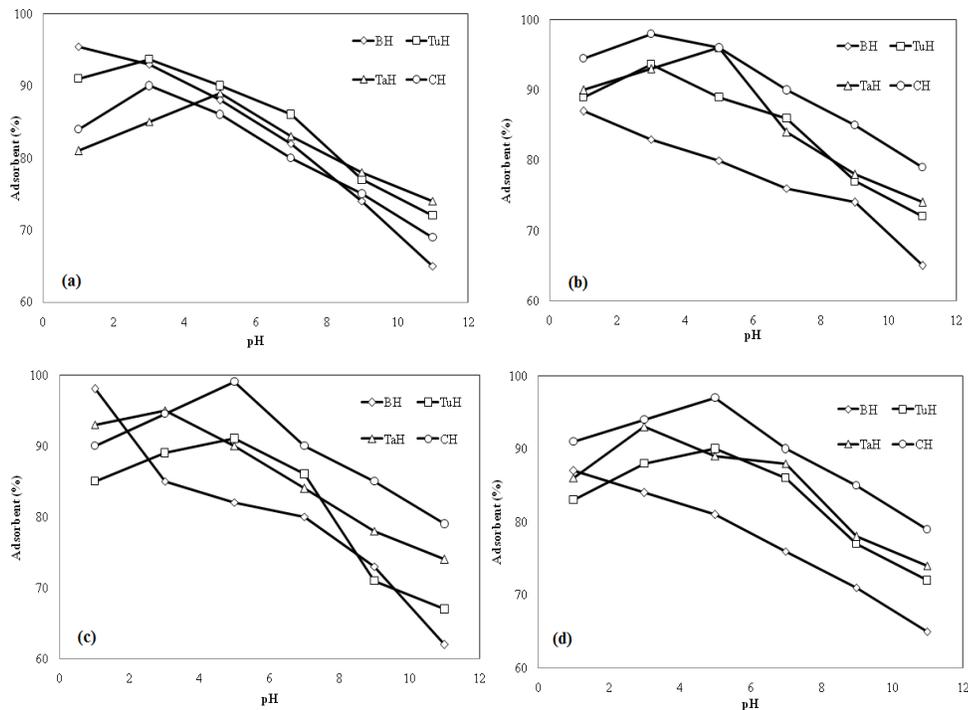


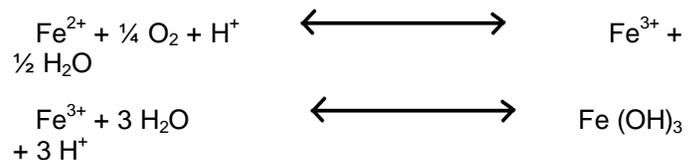
Figure 1. Effect of pH on heavy metal adsorption by (a)BGH, (b) TDH, (c)TH and (d) CH at 2.5g/l dosing and 90 min contact time.

the competition between the metal and H⁺ ions for the active biosorption sites.

Iron (III)

The maximum 95% adsorbent shown by coffee husk (CF) at pH 5. BGH shows 98% of adsorbent at pH 1, TH 95% of adsorbent at pH 3 and TDH shows 91% of adsorbent at pH 5. This is graphically represented in Fig. 1(c). It was found that adsorbent was good at when solution is acidic nature. The initial adsorption rates increased with increasing initial pH up to optimum pH values. At higher pH values, Fe (III) precipitated because of the high concentration of OH ions in the adsorption medium and so adsorption experiments at pH>3 could not be performed. The percentage of Ferric ions adsorbed at pH 2.5 decreased with increasing metal concentration, but the amount of metal ion adsorbed increased with increase in initial iron concentration. Iron typically enters water bodies in the form of ferrous iron (Fe²⁺), which can be oxidised to ferric iron (Fe³⁺) by the oxygen dissolved in water. The rate of oxidation reaction depends primarily on the pH and on the level of dissolved oxygen in water (DO). At pH <4 and are relatively low dissolved oxygen, the oxidation process to ferric iron is very slow. At pH>4, however Fe²⁺ ions oxidise quickly to Fe³⁺ ions which then react with water producing ferric hydroxide precipitate and acidity (Nam-

asivayam and Ranganathan, 2005).



Mercury (II)

The maximum adsorbent 97% shown by coffee husk at optimum pH 5 as compared to other husks. TH, TDH and BGH show 93%, 90% and 87% of adsorbent at pH 3, 5 and 1. The percentage and the amount of mercury adsorbed decrease with increase in pH. It is expected that the adsorption of metals increase at low pH values because of competition for binding sites between cations and protons, while at pH higher than 7, hydroxo species of the metals can be formed and do not bind to the adsorption sites on the surface of the adsorbent (Namasivayam and Kadirvelu, 1999). Several other researchers have already reported a strong dependency of heavy metal biosorption on pH (Jeon and Park, 2005) Figure 1.

Effect of Dose

The effect of dose on adsorbent was carried out at

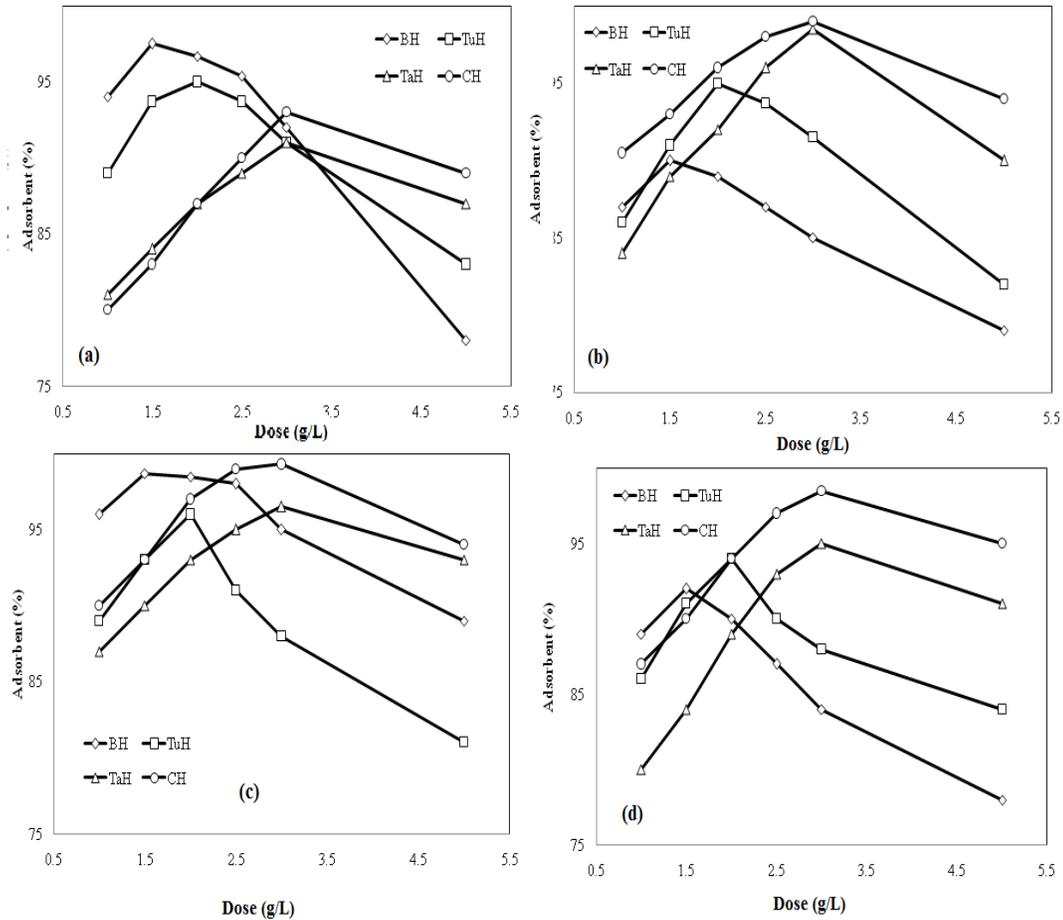


Figure 2. Effect of dose on heavy metal adsorption by (a)BGH, (b) TDH, (c)TH and (d) CH at optimum pH and 90 min contact time.

optimum pH for 90 min. The variations of dose from 1g/L to 5g/L are graphically represented in Figure 2 (a)-(d). In Figure 2(a) adsorption of Cr(IV) with BGH(pH 1), TDH (pH 3), TH (pH 5), and CH (pH 3) was carried out. It was found that BH show maximum adsorption 97.5% at 1.5g/L dosing. TH shows minimum 91% adsorption at 3g/L of dosing, TDH and CH shows 95%, 91% adsorptions at 2 and 3g/L of dosing. For the adsorption of Ni (Fig. 2(b)) maximum 99% was shown by CH at 3g/L, 88.5% TH at 3g/L, TDH 95% at 2g/L and BGH 90% at 1.5g/l dosing. In the adsorption of Fe (Fig. 2(c)) maximum 99.3% shown by CH at 3g/L, 98.7% BH at 1.5g/L 96.5% TH at 3g/L, and 96% TDH at 2g/L dosing. In Fig. 2(d) the maximum 98.5%adsorption is shown by CH at 3g/L, 95% at 3g/L by TH, 94% at 2g/L and 92% at 1.5 g/L respectively. It was observed that CH show good efficiency for all heavy metal at acidic nature of sample. The results revealed that the increasing adsorbent dosage with increases the percent removal and reached a constant value after a particular dosage of adsorbent for all the dyes studied. The removal efficiency of the ion were increases with increase in carbon concentration is

due to the greater surface area with more functional groups consequent to the increase in the number of carbon particles with more number of exchangeable sites for adsorption and saturation occurs as a result of non availability of exchangeable sites on the adsorbent (Dubey and Gopal, 2006).

Effect of contact time

The effect of contact time was carried out at optimum pH and optimum dose for 30 upto 180 min contact time which shown in Figure 3(a)- (d). From the Fig. 3(a) the maximum 98% adsorption of Cr shown by CH at 120min, 95.4% at 150min by BGH, 95% at 60min TDH and 91% at 90min TH respectively. In the Fig. 3(b) the maximum 99.5% of Ni adsorption was shown by CH at 120min, 98.5% at 90min by TH, 97.5% at 60min by TDH and 96% at 150min by BGH. The maximum adsorption of iron (Fe) 99.5% was shown by BGH and CH at 150min and 120. TH shows 96.% at 90min and TDH shows 91% at 60 min. In Fig. 3(d) maximum 99.3% at 120min

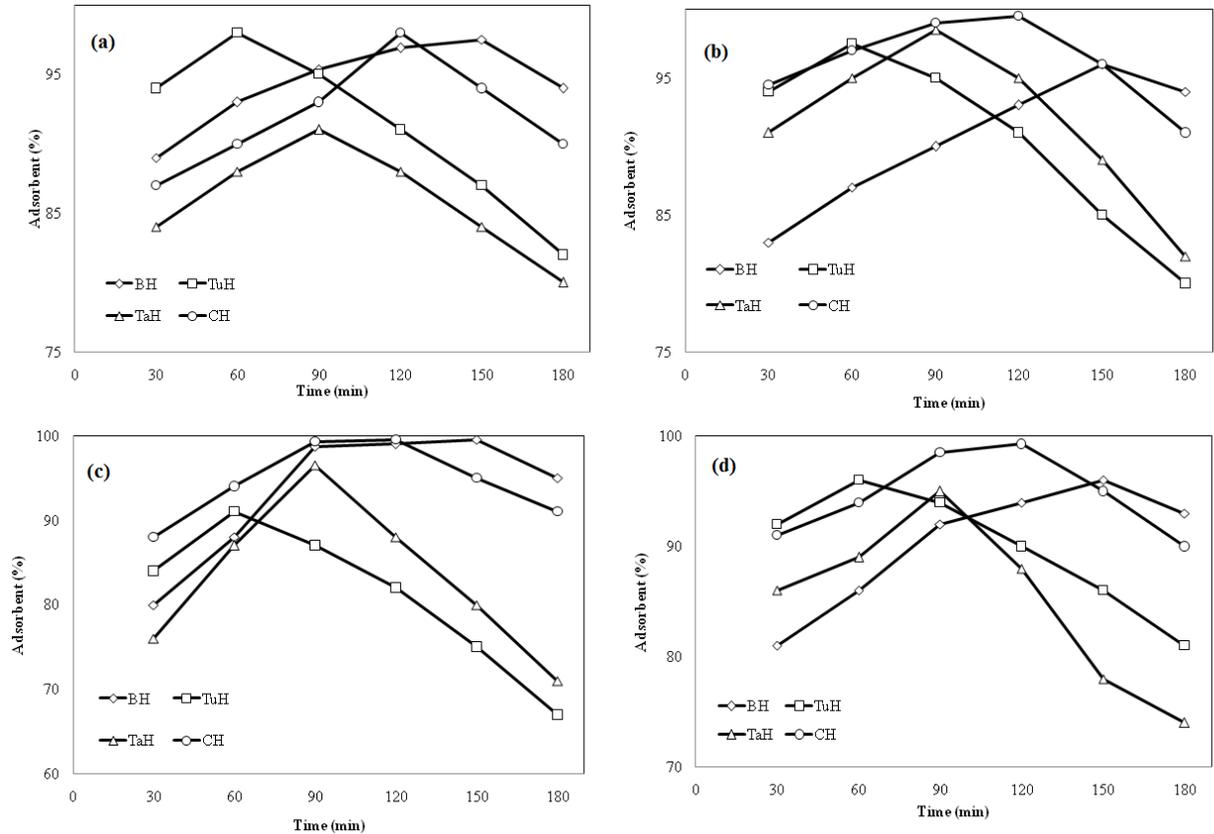


Figure 3. Effect of contact time on heavy metal adsorption by (a)BGH, (b) TDH, (c)TH and (d) CH at optimum pH and dose.

shows by CH, 96% of adsorption shown by TDH and BGH at 60 and 150 min, and 95% at 90 min by TH. It was found that coffee husk shows good efficiency for all heavy metals. It is due to the possible monolayer coverage of heavy metal on the surface of the adsorbent. The extent of biosorption was limited by metal concentration at high adsorbent concentrations. At constant initial metal concentrations, the biosorbent concentration should be low to maximize solid phase metal ion concentration at equilibrium. The results in the present study are in agreement with literature reports indicating lower biosorbed metal concentrations (q) at high adsorbent concentrations (Esteghlalian et al., 1997). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption increases by increasing the adsorbent dose.

Isotherm study

Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses have been treated by Langmuir and Freundlich (Fr) isotherms, two widely used models. The Langmuir isotherm model is based on

the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. Langmuir isotherms were obtained by agitating the adsorbent of fixed dose and the adsorbate solution of different concentrations for a contact time greater than equilibrium time. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$q = \frac{q_{\max} b C_{\text{eq}}}{1 + b C_{\text{eq}}}$$

where q is milligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metal residual concentration in solution; q_{\max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates. When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$\frac{C_{\text{eq}}}{q} = \frac{1}{q_{\max} b} + \frac{C_{\text{eq}}}{q_{\max}}$$

Thus a plot of C_{eq}/q vs C_{eq} should be linear if Langmuir adsorption were operative, permitting calculation of q_{\max} . The Langmuir isotherm model was followed by all the

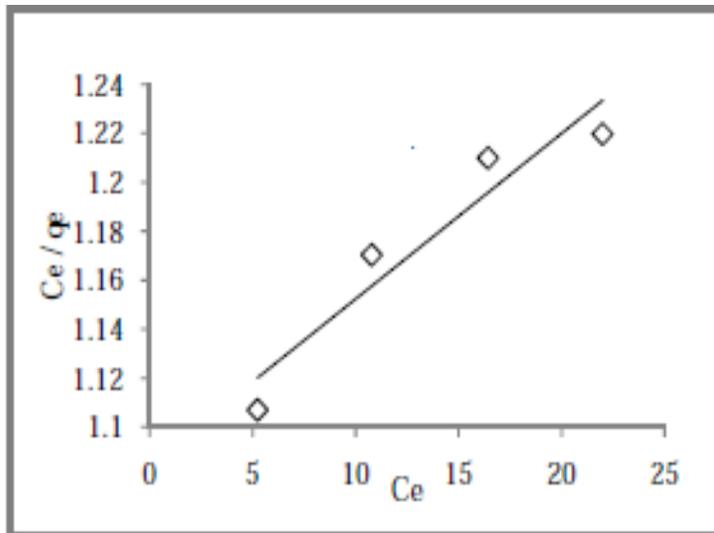


Figure 4. Langmuir adsorption isotherm

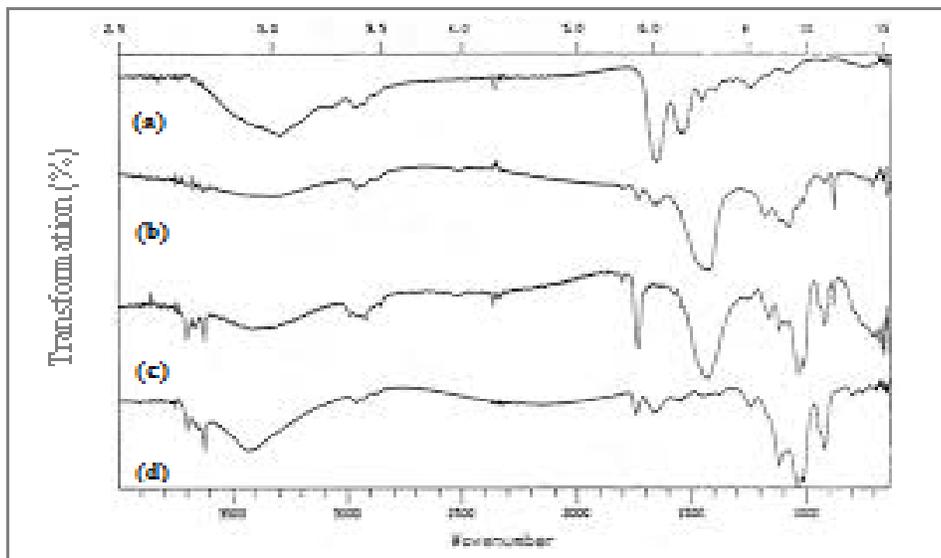


Figure 5. Fourier Transformation Infrared study of on heavy metal adsorption by (a)BGH, (b) TDH, (c)TH and (d) CH

adsorbate and adsorbents in the present study which is shown in Figure 4.

Fourier Infrared Transformation study (FITR)

Unreacted samples of the four adsorbents used in the present study namely Bengal gram husk (BGH), Tur dal husk (TDH), coffee husk (CH) and tamarind husk (TH) were subjected to Fourier transform infrared spectroscopy (FTIR). The spectra obtained are presented in Figure 5 (a) to (d) for BGH, TDH, TH and CH respectively. The spectra of BGH sample reveal the presence of several functional groups on the surface which facilitates the adsorption of metal ions. Wave

number of 3000 and 3750 cm⁻¹ for BGH indicates the presence of OH groups on the husk surface. The trough that is observed at 2918.18 cm⁻¹ and 893.25 cm⁻¹ indicates the presence of C-H groups. The 1634.34 cm⁻¹ band is a result of CO stretching mode, conjugated to a NH deformation mode and is indicative of amide 1 band. The trough at 1115.57 cm⁻¹ is due to CO or CN groups. The absorption spectra of TDH display a broad, intense --OH stretching absorption trough at 3431 cm⁻¹, although the bands are dominated by the -OH stretch due to bonded water. Weaker --CH stretch bands are superimposed onto the side of the broad -OH band at 3000–2800 cm⁻¹. The strong peak at 1733 cm⁻¹ is caused by the C=O stretching band of the carboxyl group. The peak at approximately 1100 cm⁻¹ is due to

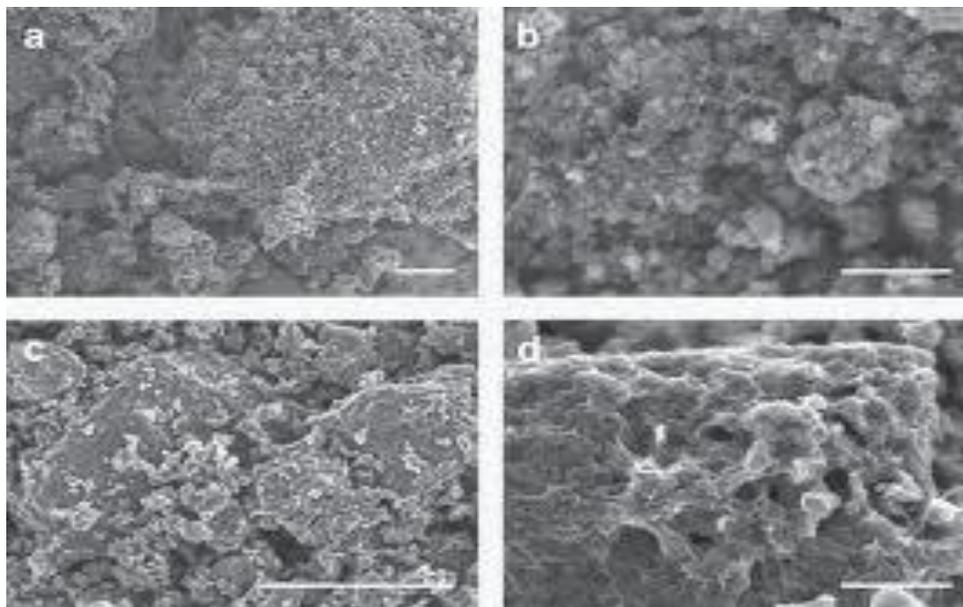


Figure 6. Scanning electron micrograph of on heavy metal adsorption by (a)BGH, (b) TDH, (c)TH and (d) CH

either the C-O stretch of the -OH bend. However, the N-H stretch (3300 cm^{-1}) and the C-N stretch (1000 cm^{-1}) are not seen in this spectra due to the dominance of the --OH stretch. The spectrum of the pristine TH is complex due to the numerous and multifarious functional groups on the surface of the adsorbent. The broad and strong band ranging from 3200 to 3600 cm^{-1} may be due to the overlapping of OH and NH stretching, which is consistent with the peak at 1115 and 1161 cm^{-1} assigned to C-O and C-N stretching vibration, thus showing the presence of hydroxyl and amine groups on the adsorbent surface. The strong peak at 1674 cm^{-1} can be assigned to a C=O stretching in carboxyl or amide groups. The bands at 2936 and 1558 cm^{-1} are attributed to CH stretching and N-H bending, respectively. The spectra of CH display a number of absorption peaks, indicating the complex nature of the material examined. The FTIR spectroscopic analysis indicated broad bands at 3412 cm^{-1} , representing bonded -OH groups. The bands observed at about 2921 – 2851 cm^{-1} could be assigned to the C-H stretch. The peaks around 1733 cm^{-1} correspond to the C=H group and at 1652 – 1512 cm^{-1} C=O. This C-O band absorption peak is observed to shift to 1035 cm^{-1} . Thus, it seems that this type of functional group is likely to participate in metal binding

Scanning Electron Micrograph (SEM)

To determine the active surface structure the scanning electron micrograph was carried out for BGH, TDH, TH and CH which is shown in Figure 6 (a) to (d). It was observed that CH has more porous and well arranged structure was formed. Which are responsible for maximum adsorptive of heavy metal ion. For BGH, TDH

and TH the structure are not in shape it looks like powder of organic salt.

CONCLUSION

Agriculture waste was found to be suitable for the Bioadsorption of heavy metal ion in the waste water. At any contact time, increase in initial adsorbate concentration decreased the percent adsorption and increased the amount of adsorbate uptake (q) per unit weight of the adsorbent. The effect of adsorbent dosage on the adsorption of metals showed that the percentage of metal removed increased with increase in adsorbent dosage due to increased adsorption surface area. For all the adsorbents studied adsorbent dosage of $1\text{ g} - 3\text{ g/L}$ was sufficient for adsorption of 99.5% of the initial metal concentration. Irrespective of the type of the adsorbent, the optimum pH for the removal of chromium (VI) was 1; for iron (III) 3; for mercury (II) 5 and nickel (II) was maximally absorbed at pH 3.0. The amount of the metal removed at optimum pH increased with increase in initial metal concentration but the percentage absorbed decreased with increase in initial metal concentration. Adsorption data for wide ranges of adsorbate concentrations and adsorbent doses were treated by Langmuir and Freundlich isotherms. All the adsorbents and adsorbates followed the Langmuir and Freundlich isotherms. Comparison of the adsorption capacity of the four adsorbents with that cited in literature reveals that bengal gram husk, tur dal husk, tamarind and coffee husk had a higher biosorption capacity than the adsorbents reported in literature. The infrared spectral analysis of the adsorbents showed that Carbon bonded with hydrogen and oxygen atoms played a major role in

the adsorption of metals. The absorption spectra revealed that –C-O, C-N and C=O bonds were predominant in the surface of the adsorbents and played a major role in the adsorption process. The analysis of the carbon, hydrogen and nitrogen content of the husk, showed relatively low percentage of nitrogen, revealing the low content of protein in the adsorbents. This is advantageous over the protein rich algal and fungal biomass projected as metal biosorbents, since proteinous materials are likely to putrefy under moist conditions. Further, most metal sorption reported in literature is based on alga and fungal biomass, which must be cultured, collected from their natural habitats and pre processed, if available as discards and transported under special conditions, thus introducing the factor of additional costs. In contrast, BGH, TDH, TH and CH as agro-industrial wastes have negligible cost and have also proved to be an efficient biosorbent for the removal of metals. Furthermore, these adsorbed metal can be easily desorbed and the biomass be incinerated for final disposal. These biosorbents are of low cost; its utility will be economical and can be viewed as a part of a feasible waste management strategy.

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