Determination of Chromium in Tannery Effluent and Study of Adsorption of Cr(VI) on Sawdust and Charcoal from Sugarcane Bagasses

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Abstract

Spectrophotometric method using diphenylcarbazide as a colour developing reagent has been used to analyze the chromium content in tannery effluent located in Bara and Parsa districts of Nepal and Sirsiya River which is an ultimate drainage of these waste water streams. The adsorption of hexavalent chromium from aqueous solution onto formaldehyde treated sawdust and charcoal of sugarcane begasses has been investigated at various Cr(VI) concentrations of 5-40 mg/L and pH values. From the experimental observations, it has been found that chromium can be removed quantitatively at the equilibrium pH range of around 1 and the adsorption behavior revealed to follow Langmuir and Freundlich adsorption isotherms.

 Keywords: chromium, diphenylcarbazide, adsorption.

Introduction

In developing countries, many industries are operated in a small and medium scales; this small unit can generate a considerable pollution load which in many cases discharges directly into environment without any pretreatment.[1] Electroplating and leather industries are the major cause for the high influx of chromium to the biosphere.[2] The huge quantity of chromium salts discharge into tannery waste has raised several ecological concerns. The slug generated by chromium based industries is usually damped on the ground which pollutes in surface and subsoil

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[*] ***Corresponding author*** *and dedicated to the memory of Prof. Dr. D. M. S. Amatya.*

water in the vicinity of industrial units. Hexavalent chromium is formed due to oxidation of Cr(III) compounds which   percolates down into the soil during rainy season and polluting underground water.[3]

In general, industrial waste contains both hexavalent and trivalent forms of chromium which are most stable and exist in aqueous system.[4] The hexavalent chromium is of particular concern due to its great toxicity. It is known to be carcinogenic and mutagenic to living organisms.[5] Thus it is necessary to remove or recover the chromium before disposal of industrial waste.

Different methods have been developed for the removal of heavy metal ions from water and waste water, some of which are precipitation, ion exchange, electrolysis, reverse osmosis, solvent extraction, adsorption and filtration. Conventional process to remove the Cr(VI) by precipitation or ion exchange are not completely satisfactory and have several disadvantages.[5] Among all these techniques, adsorption is the most promising technique and feasible alternatives.[6]

Over last few years, many natural adsorbents have been tested for removing heavy metals. A review of more than 70 natural adsorbents and their potential uses was given by Baile et. al.[7] Thus there is a need for the development of low cost, easily available material that can remove and recover hexavalent chromium economically. A variety of material have been reported as adsorbent like granular activated carbon, soya cake, rubber tyres, saw dust, activated sludge, lingo cellular substance, fly ash, rice husk based activated carbon, rice barn etc.[8-10] Activated carbon is very effective in removing heavy metals but it is readily soluble under extreme pH.

In the present work, chemically treated saw dust and charcoal of sugar-cane bagasses are used to study the adsorption of chromium (VI). The effect of pH on adsorption of Cr(VI) at several concentrations have been studied.

Experimental Methods

The samples were collected from the different leather industries located in the Bara and Parsa districts of Nepal. Samples of effluent from six different leather industries and water samples of Sirsiya River from four different places were collected. Almost all the drainages of industrial waste were found drained directly into the Sirsiya River.

Effluents of industrial waste were collected into plastic bottles. Those plastic bottles were thoroughly cleaned by 8 M nitric acid solution followed by repeated washing with distilled water and dried over night. After collection, physical appearance and temperature of the samples were recorded and 1.5 ml of concentrated nitric acid per litre of sample was added as preservative. The pH of the samples was maintained below 2 by adding dilute nitric acid and stored at room temperature in the laboratory.

Saw dust used in this experiment was collected from a local sawmill (Kathmandu) and dried in sunlight until almost all the moisture evaporated. It was grinded to fine powder and sieved to pass 218 micron size. Saw dust contains water soluble compounds like lignin, lignocelluloses and cellulose together with tannin, which gave brown color to the effluents during the treatment. Chemical treatment with formaldehyde led to polymerization of the compounds responsible for colorization. Saw dust (25 g) was washed repeatedly with distilled water and subsequently dried for 24 hours at 50 °C to remove coloring materials. To improve the physical characteristics, it was treated with 1 % formaldehyde in the ratio of 1:4 (sawdust: formaldehyde) and 50 mL 0.2 N H_2SO_4. It was heated with cover over the hotplate at 50 °C for 6 hours with occasional stirring. The product was cooled and washed several times with distilled water and finally dried at 60 °C to eliminate all toxicity due to presence of formaldehyde.[11]

Sugar-cane waste was collected from the local juice shop (Kathmandu), internal white part was separated and perfectly dried in sunlight. It was crushed to small pieces and heated at 250 °C in hot air oven for about two and half hours. All the sugar-cane bagasses charred into black coal and it was grinded to fine powder in a mortar with pestle.

Diphenylcarbazide (DiPC) method, a colorimetric method was used for determination of 0.005 % to 0.2 % chromium. This colorimetric method is useful for the minimum Cr(VI) in natural and industrial waste in the range of 100 to 1000 µg/L. In this method for the determination of total chromium content, all the chromium was converted to hexavalent state by oxidation with potassium permanganate. The reaction is very sensitive and the molar absorptivity based on the chromium being about 40,000 Lg^{-1} cm^{-1} at 540 nm with DiPC in acidic medium. If interferences such as Mo, V, Fe and Cu are present, they can be removed by extracting as cupferrates with chloroform.[12,13]

100 ml of the well preserved sample solution was taken in a conical flask and heated on a hotplate till the volume was reduced to nearly 10 ml. This reduced volume was transferred into a separating funnel, 40 ml distilled water was added and chilled in ice bath then 5 ml of ice cold cupferron solution was added and left in ice bath for one minute. Pure chloroform (5 ml) was added and shaken for 5 to 10 minutes then the solution was left undisturbed until separation of organic and aqueous phase. Organic phase was separated from the aqueous phase and discarded. This process was repeated three times and the solution was transferred into a conical flask. The solution collected in a conical flask was boiled for 5 minutes to evaporate chloroform. To the cool solution, concentrated HNO_3 (5 ml) and concentrated H_2SO_4 (3 ml) were added and boiled until the appearance of SO_3 fumes. The solution was allowed to cool and additional concentrated HNO_3 (5 ml) was added and boiled to fumes to decompose the organic matters present. The solution was boiled again to SO_3 fumes, cooled, transferred into a volumetric flask and diluted up to the mark.

Digested sample solution was pipette out and transferred into a conical flask then methyl red indicator and few drops of concentrated NH_4OH were added until the solution turned yellow in color. Few drops of 1:1 H_2SO_4 was added until the solution turned acidic followed by additional 1 ml of 1:1 H_2SO_4. The volume of the solution was maintained nearly 40 ml and heated up to boiling. Potassium permanganate (2 drops) was added into the boiling solution so that the solution would turn dark red. When the solution became clear, two drops of $KMnO_4$ was added and boiled for two minutes. Sodium azide was added to the above solution and continued to boil. When red color was not completely faded after boiling (approximately 30 seconds) another 1 ml of NaN_3 was added and continued to boil for 1 min after which colour faded completely.

The wavelength of 540 nm was selected for the quantitative determination of Cr(VI) in water and waste water samples. For the determination of chromium(VI) in water samples, a calibration curve of potassium dichromate was made where the plot was linear up to 1.2 mg/L concentration of potassium dichromate . The determination limit of this method in the laboratory was measured to be 0.1 mg/L.

Results and Discussion

Chromium content in tannery effluents

Effluents of six different leather industries of Bara and Parsa districts (Nepal) were analyzed. The amounts of chromium present in effluents of leather industries and water of Sirsiya River are shown in Tables 1 and 2, respectively. Among the tannery effluents, maximum concentration (345 mg/L) of chromium is found in sample Sw-4 and minimum in sample Sw-3 (0.12 mg/L). This variation of concentration of chromium by large amount in different tannery effluents may be due to the time of sampling. Where the sampling was done immediately after the tanning process, has shown maximum concentration of chromium.

Table 1: Physical appearance and chromium content in different tannery effluents.

S.N.	Name of sample	Appearance	Chromium content (mg/L)
1	Narayani Leather Industry Pvt. Ltd. (**Sw-1**)	Light green	10.30
2	Everest Leather Industry Pvt. Ltd. (**Sw-2**)	Light green	13.50
3	Standard Tanning Industry Pvt. Ltd. (**Sw-3**)	Colorless	00.12
4	Progressive Leather Industry Pvt. Ltd. (**Sw-4**)	Green	345.00
5	Maruim Leather Industry Pvt. Ltd. (**Sw-5**)	Green	57.00
6	National Leather Industry Pvt. Ltd. (**Sw-6**)	Colorless	00.70

Similarly, for water samples of Sirsiya River, concentration of chromium is found in the range of 0.064 mg/L to 0.012 mg/L. Amount of chromium in samples no Swr-3 and Swr-4 is below the Nepal Standard (NS) of 0.05 mg/L and level of

chromium in samples Swr-1 and Swr-2 are found above the permitted limit of WHO standard.

Table 2: Physical appearance and chromium content in water of Sirsiya River.

S.N.	Name of sample	Appearance	Chromium content (mg/L)*
1	Back side of Agro Nepal (**Swr-1**)	Dirty	0.32
2	1.5 Km far below the first sample site (**Swr-2**)	Dirty	0.33
3	At Jyoti bridge (**Swr-3**)	Dirty	0.06
4	Kakarni Patel Village (**Swr-4**)	Clear	0.24

*measured by concentrating the original volume of the sample five times by evaporation.

Adsorption of Chromium content in tannery effluents

Figure 1 shows the effect of pH on the adsorption of DiPC-chromium complex. The maximum absorbance is found at pH around 1. The absorbance decreases above and below of this pH range. This is because when acidity of the solution is less than 0.05 N H_2SO_4 the reaction is slower and above about 0.2 N H_2SO_4 strength of acid the complex is unstable.[12]
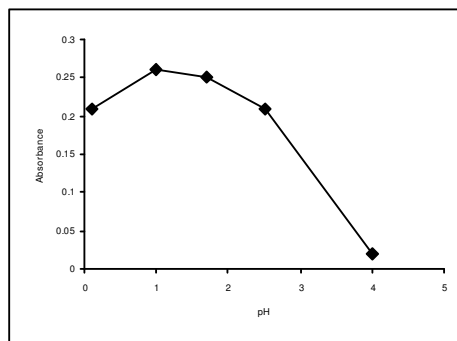

Figure 1: Effect of pH on the absorbance of DiPC-Chromium complex.

The adsorption experiment was carried out with the concentration of 10 mg/L of potassium dichromate (synthetic potassium dichromate) solution as a function of pH. Influence of pH on the adsorption of Cr(VI) on formaldehyde treaded Saw-dust and charcoal of sugar-cane bagasses is shown in Fig .2. It is evident that at lower pH, acid chromate ions ($HCrO_4^-$) are the dominant species with largest value of adsorption at pH around 1. When the pH is further increased a sharp decrease in the percentage of adsorption is observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent. When the pH was increases beyond 6, a gradual decrease in the percentage adsorption is observed which might be due to the competition between OH^- and chromate ions CrO_4^{--}, where the former being the dominant

species gets preferentially adsorbed. The net positive surface potential of the sorbent decreased with increasing pH resulting in weakening of electrostatic force between adsorbent and adsorbate which ultimately led to the lowering of sorption capacity.

Analysis of percentage adsorption and initial concentration of adsorbate were studied and it was found that the percentage adsorption decrease with increases in initial concentration of the adsorbate. From the Fig. 3, it is found that the uptake capacity of Cr(VI) increased with the increase in equilibrium concentration of chromium, which may be due to the ability of more number of Cr(VI) ion in solution for sorption.
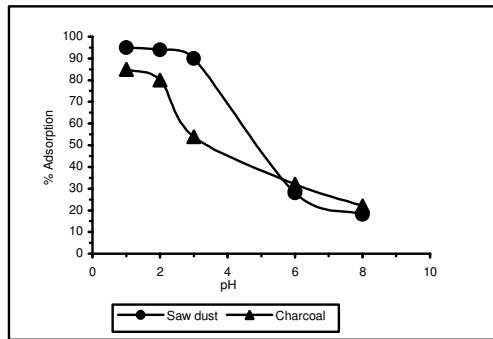

Figure 2: Effect of pH on adsorption of Cr(VI) onto the saw dust & charcoal of sugarcane.

Adsorption isotherm was carried out with a fixed initial adsorbent dose (0.1 g) and varying adsorbate concentration and applicability of the data to the Langmuir and Freundlich adsorption were tested at 24 °C.

The Langmuir model assumed that the sorption of metal ion occurs on homogenous surface by monolayer adsorption with no interaction between adsorbate ions. Langmuir adsorption isotherm is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_o\, b} + \frac{1}{Q_o}\, C_e \tag{1}$$

where, C_e is the equilibrium concentration and q_e is the amount of adsorbate per gram of adsorbent at equilibrium; Q_o and b are the Langmuir constant related to the adsorption capacity and energy of adsorption, respectively.

Figure 3 shows the adsorption of Cr(VI) by different adsorbents (formaldehyde treated Sawdust, Sugar-cane charcoal) as a function of C_e. It is found that the data agree with Langmuir model. The plot of C_e/q_e vs C_e is a straight line with slop 0.0673 and 0.065 for sawdust and charcoal of sugarcane bagasses, respectively. There is no deviation observed from linear behavior shown in Fig. 4, which may be attributed to the fact that there is no creation of additional sites during the adsorption, at initial concentration ranging between 0 to 40 mg/L. The value of Q_o and b of the monolayer could be calculated from the slop and intercept of straight line from Fig. 4 are given in Table 3. A comparison of Langmuir constants show that maximum adsorption capacity (Q_o) of the charcoal of sugar-cane bagasses and the

saw dust are nearly equal and the energy of binding (b) for sawdust is greater than the charcoal of sugar-cane bagasses.

Adsorption of solute from solution onto a solid adsorbent is generally treated by Freundlich model,

$$y = k \, C^{1/n} \tag{2}$$

This Freundlich model assumed that the sorption of metal ion occur on the heterogeneous surface by monolayer adsorption and is described by the following equation.[14]

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{3}$$

where, y or q_e is the mass of substance adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration of the solute being adsorbed, while k_f and n are again empirical constants.
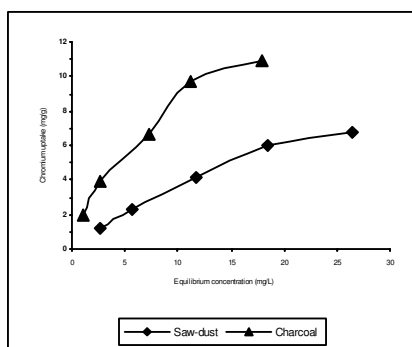

Figure 3: Adsorption isotherms of Cr(VI) onto sawdust and charcoal of sugar-cane.

The plots of log C_e vs log q_e are shown in Fig. 5, which shows straight line on both the adsorbents. This observation suggests that there is no change in rate and extent on adsorption. From the Table 3, the adsorption capacity (K_f) is less for charcoal of sugar-cane bagasses than that of sawdust. The slope (1/n), which reflects the intensity of adsorption, presents the same trend. The values of n for both adsorbents were obtained greater than one which indicates the good adsorption of chromium(VI) on both the adsorbents.[1]

Table 3: Langmuir and Freundlich constants for Cr(VI) on sawdust and charcoal of sugar-cane bagasses.

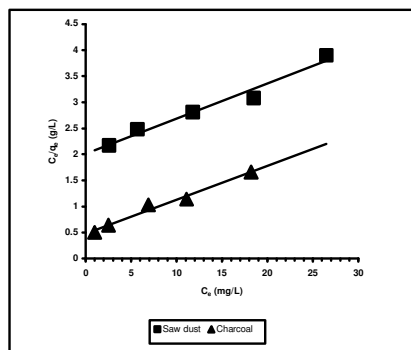| Adsorbents	Langmuir equation			Freundlich equation		
	Q_0(mg/g)	b (l/mg)	R^2	K_f(mg/g)	n	R^2
Saw dust	14.86	29.90	0.9716	2.11	1.67	0.9854
Charcoal of sugar-cane bagasses	15.38	7.35	0.9807	0.62	1.34	0.9890

Figure 4: Langmuir isotherm for chromium(VI) on formaldehyde treated saw-dust and charcoal of sugar-cane bagasses.
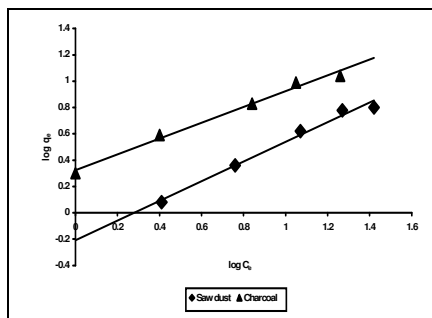

Figure 5: Freundlich isotherm of chromium(VI) on Saw-dust and charcoal of sugar-cane bagasses.

Conclusions

The method of chromium (VI)-DiPC complex is suitable for determination of chromium in water sample and effluent of tannery wastes. The Chromium (VI) develops red violet colored complex with diphenylcarbazide in the pH range of 1 to 2, which is suitable for spectrophotometer measurement.

The concentration of chromium in the tannery effluents is found in the range of 345 mg/L to 0.7 mg/L and that in Sirsiya River is in the range of 0.064 mg/L to 0.012 mg/L.

A relatively low cost adsorbents based on biomass waste has been explored for the effective adsorption of chromium which is considered to be one of the potential hazards in the waste water stream of tanning industries.

Since the adsorption of chromium (VI) is taken place at relatively low pH region, the effluents pH has to be maintained at neutral condition prior to its

disposal. Since feed material for the preparation of adsorbent was from wastes, such material is expected to be cheaper for the treatment of contaminant in waste water.

The adsorption of hexavalent chromium is found to be a maximum value at pH around 1 on both adsorbents (i.e., saw-dust and charcoal of sugar-cane bagasses). The percentage adsorption was found to be decreased with the increase in initial concentration of hexavalent chromium.

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