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Agricultural Waste Adsorbents for Heavy Metals Removal from Wastewater

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ABSTRACT

With the onset of urbanization and industrialization mankind has witnessed various environmental issues in the society. One of the impacts is visible, in form of water pollution containing heavy metals. Removal of these metals from wastewater by adsorption demands low operating cost. Use of low cost adsorbent is one way of reducing the treatment cost. In the present research biosorption was carried out in a batch process to test the suitability of sugar cane bagasse and corn hob for removal of Cr (II) and Fe (II) ions from waste water effluent. The removal of heavy metals like chromium and iron by these adsorbents has been studied. Also, effect of parameters like contact time, pH and adsorbent dose on the metal removal is studied. The contact time was 100 min for both substrates. The results indicated that the amount of absorbed metal ions varied with substrates materials, and the maximum percentage removal was 91 percent for iron and 92.4 percent for chromium. The adsorption process was dependent on the parameters like contact time, pH and adsorbent dose. With adsorbent dose, the percent removal increases up to certain point and thereafter remains constant. The adsorption was more in acidic conditions. The percentage removal increases with time up to certain point and then remains constant because of saturation.

Keywords: *Adsorption, Waste water, Concentration, heavy metal, adsorbate*

INTRODUCTION

Urban and industrial revolution have led to the increasing pollution of the environment by heavy metals in the last few years by the excessive release of (Pb, Hg, Cd, As, Cu, Zn, Fe and Cr) into the environment (waterways, rivers and wells), causing environmental problems.

The heavy metal removal from effluent is very important. It is well established that heavy metals are highly toxic to living things and there is need to minimize their presence in the water system and food stuffs. Heavy metals can be absorbed by plants, wildlife and people through the food they eat. They can also be absorbed through water and breathing. Some heavy metals can become more concentrated when animals (predators) use other animals for food (prey) as part of the food chain.

Heavy metals can enter the environment by various sources like some mining industries, burning of fossil fuels, like coal, burning garbage or tobacco, and even forest fires, release heavy metals into the environment.

They are considered cumulative poisons due to the fact that they have high bio-magnification factor in living things and water. Whenever they are taken up and are stored faster than they are broken down or excreted [1]. This gives rise to the growing concern on the gradual build-up of toxic metals in the ecosystem.

Chromium and Iron are two such heavy metals. Chromium (III) and Iron (III) occur naturally in the environment, while chromium (VI), chromium (0) and iron (II) are generally produced by industrial processes. Chromium is important ingredient in the compounds used in the chemical industries such as chrome plating, the manufacture of pigments, leather tanning, wood treatment, and water treatment. Exposure may occur from natural or industrial sources of chromium. While iron is mainly from industries involved in pig iron and steel production, metal production, typically smelters, the manufacture of pigments, leather tanning, waste disposal, and mercury production, mainly for batteries.

Although, heavy metal removal methods are based on the conventional principle of ion exchange, chemical precipitation, coagulation, adsorption, membrane filtration technology, etc., has evolved in the past, the risk of generating secondary pollutants by these methods is of great concern [2]. Of all these methods above, adsorption method is simple, relatively cost-effective and reduces the possibilities of yielding unwanted chemicals. It has been reported that bio-sorption is a promising technique for the adsorption of heavy metals from aqueous environments, especially when adsorbents are derived from biological sources: lignocelluloses carbonaceous materials, natural resources, plant wastes, and agricultural wastes [3-7].

Banerjee *et al.* [8], reported that removal of Cr (VI) and Hg (II) from aqueous solutions using fly ash and impregnated fly ash is a very efficient treatment method. Dikshit [9], also carried out sorption on saw dust for chromium removal with success. Research by use of various biosorbents for chromium removal has been reported Gupta *et al*. and Huang *et al*. [10, 11]. Kumar *et al*. [12], also carried out a successful liquid−liquid extraction of chromium(VI) with tricapryl methyl ammonium chloride using isoamyl alcohol as the diluent.

Kumar *et al.* [13], applied a cellulose-clay composite bio-sorbent to remove chromium from industrial wastewater. Rad *et al*. [14], used the reverse osmosis membrane to remove chromium from aqueous solution, while Ahailya [15], used the hust of cicerarientinum to efficiently treat the removal of iron in water by biosorption process.

The current study aims at investigating low cost adsorbents prepared from sugar cane bagasse and corn hob for chromium and iron removal in waste water. It also involves comparative studies on removal of these metals by the two adsorbent. The parameters like adsorbent dose, time and pH were optimized.

MATERIALS AND METHOD

In the present study, all reagents used are of analytical grade and were used without further purification. Doubly distilled and de-ionzed water was used in preparation of all sample solutions. The adsorbent was prepared by initially sun drying the waste materials, crushed and then sieved to particle size of 0.626 mm. It was impregnated with strong hydrochloric acid and heated in an oven at about 400 ^{0}C. It was then washed with hot water, sun dried and then used as adsorbent.

Batch studies were carried out in a 500 ml conical flask. 100 ml of synthetic effluent was taken out and then transferred into a required amount of adsorbent. The flask was corked, uniformly agitated at about 250 rpm at room temperature and left for 24 hours. It was filtered into a clean dried empty conical flask and labeled accordingly. The filtrates were analyzed using already calibrated atomic absorption spectrophotometer (AAS). The equilibrium concentrations were determined by spectrophotometric (SL-159) methods.

50 ml solution was pipette from 100 mg/L into a conical flask followed by the dosage of different masses of the adsorbent between 1g to 5g and labeled accordingly. The resulting solutions were agitated and left till the next day. Solutions were filtered into clean dried empty conical flasks and labeled accordingly. The filtrates collected in sample bottles were analyzed by the use of AAS. The effect of time was studied using constant mass adsorbent and 100 ppm solution of adsorbate. Minimum of five sets were set up and each experiment terminated at a specific time between 0-100 minutes. The clear filtrate obtained in each case was analyzed by using AAS.

The amount of adsorbate adsorbed was calculated using the equation:

$$C_{ads} = \frac{(C_0 - C_s)}{M} mol/dm^3.g$$

(1)Where

C_0 = Initial concentration, *mol/dm*^{3}

C_s = Final concentration, *mol/dm*^{3}

M = Mass of adsorbent, grams (g)

C_{ads} = $mol/dm^3.g$

RESULTS AND DISCUSSION

It has already been established that agricultural wastes can be used as adsorbent for the removal of Cd (II), Cu (II), Pd (II) and Zn (II) ions from aqueous solutions [3, 5-9, 15].

Here, we present the results of the comparative effect of mass of adsorbent on the adsorption rate, comparative effect of pH of adsorbate on the adsorption efficiency and comparative effect of time variation on the adsorption rate of the metal ions.

Effect of contact time:

Figure 1 shows effect of contact time or agitation time for iron and chromium removal. The values of equilibrium time for iron and chromium were 60 and 50 minutes. The percentage removal for iron was slightly more, about 88 % than that for chromium, about 84 %.

From Figure 2, it can be seen that, by using corn hob adsorbent, equilibrium is reached within 70 minutes with percentage removal of 84 % for iron. In case of chromium, the equilibrium percentage removal of 83 % was achieved in 59 minutes. If we consider removal of iron by these two adsorbent, corn hob adsorbent needs less contact time of 59 minutes as compared to bagasse adsorbent, which needs 70 minutes for equilibrium. It is depicted in Figure 3. From Figure 4 it is evident that chromium needs more contact time i.e. 70 minute compared to 50 minutes for iron.

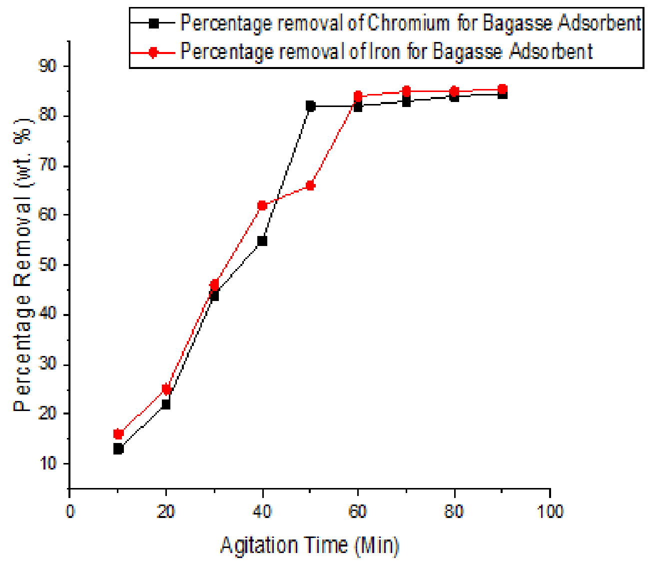

Figure 1: Effect of Contact Time for Bagasse Adsorbent for Iron and Chromium Removal

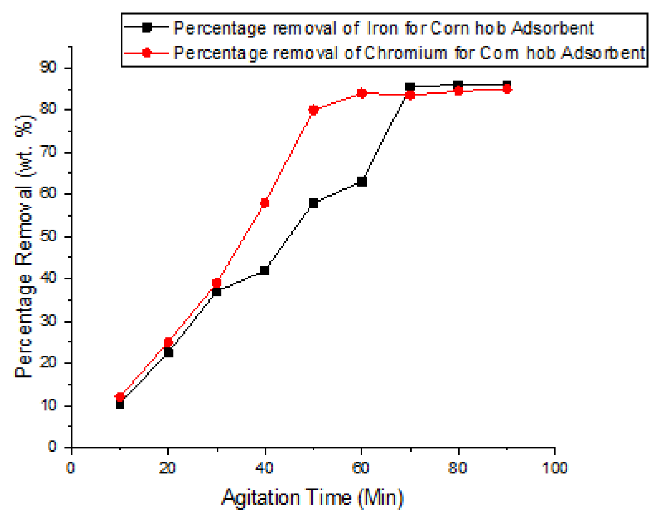

Figure 2: Effect of Contact Time for Corn hob Adsorbent for Iron and Chromium Removal

Effect of Adsorbent Dose

For chromium, 2 grams/100 ml of adsorbent was optimum and for iron the optimum dose was 2.5 grams/100 ml using bagasse adsorbent as shown in Figure 5. For corn hob adsorbent, adsorbent dose required was 2.5 grams for both iron and chromium removal as shown in Figure 6. For removal of iron both the adsorbent were needed in same amount of 2.5 grams/100 ml, as shown in Figure

7. From Figure 8 it is evident that for chromium removal, 2-3 grams of bagasse adsorbent was optimum, and the optimum value for corn hob adsorbent was 2.5 grams.

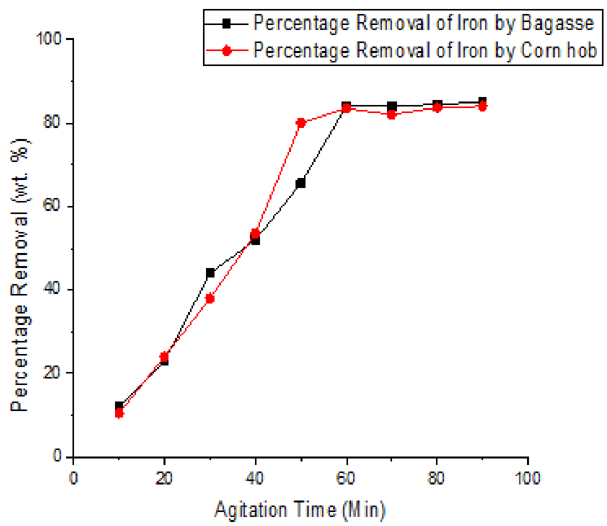

Figure 3: Effect of Contact Time for Iron Using Bagasse and Corn hob Adsorbent

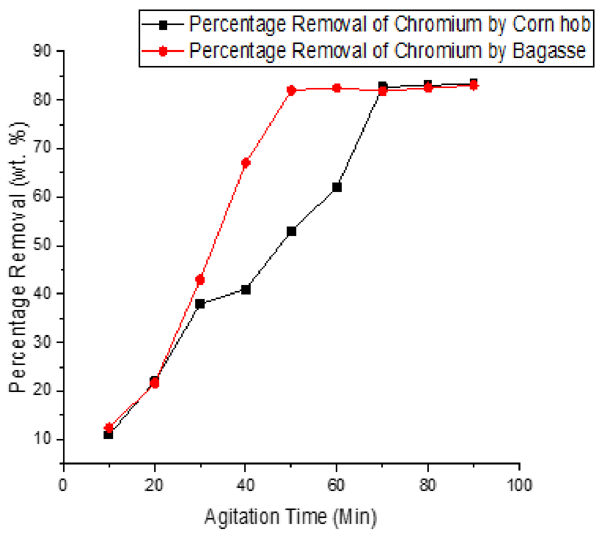

Figure 4: Effect of Contact Time for Chromium Using Bagasse and Corn hob Adsorbent

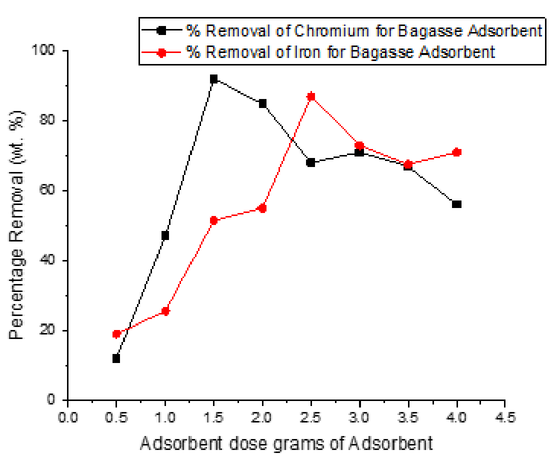

Figure 5: Effect of Adsorbent Dose for Bagasse Adsorbent for Iron and Chromium Removal

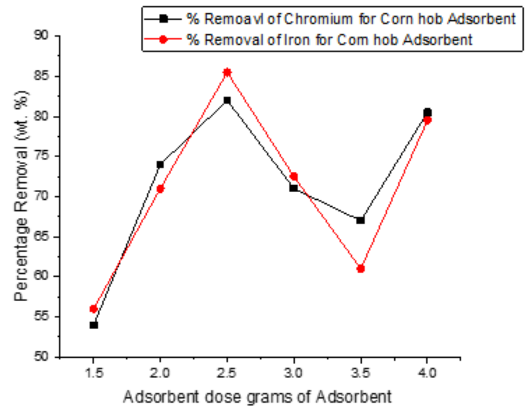

Figure 6: Effect of Adsorbent Dose for Corn hob Adsorbent for Iron and Chromium Removal

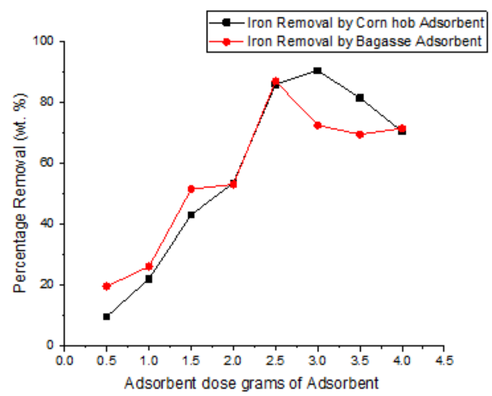

Figure 7: Effect of Adsorbent Dose for Iron Using Bagasse and Corn hob Adsorbent

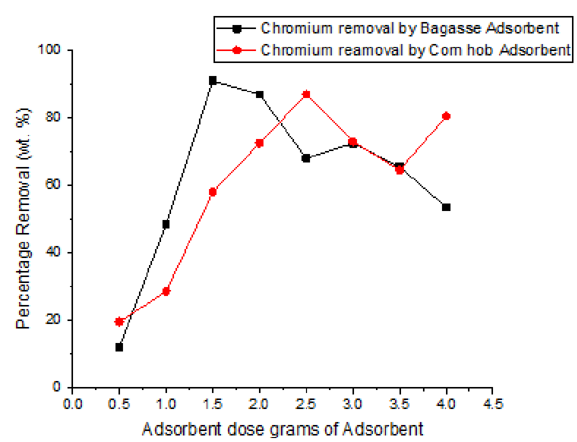

Figure 8: Effect of Adsorbent Dose for Chromium Using Bagasse and Corn hob Adsorbent

Effect of pH

From Figure 9, pH value of 5 was optimum for iron for bagasse adsorbent. For chromium, the optimum pH was 3. These pH values, had corresponding percentage removal of 81 and 87 % respectively. For corn hob adsorbent, the optimum pH values were 4 and 3 with removal percentage of 88 and 92 for iron and chromium as shown in Figure 10. The removal of iron for two different adsorbents is plotted in Figure 11 and removal of chromium by these two adsorbents is plotted in Figure 12. For bagasse and corn hob, pH of 3 is the optimum pH for chromium removal. For iron, the optimum values of pH values for these two adsorbents were 5.5 and 4 respectively with removal percentage of 81 and 88 % respectively.

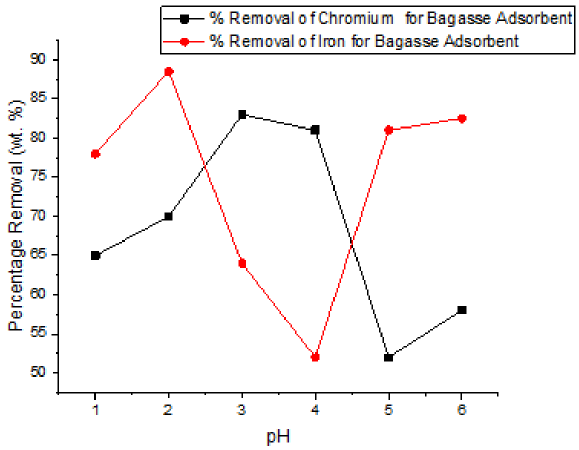

Figure 9: Effect of pH for Bagasse Adsorbent for Iron and Chromium removal

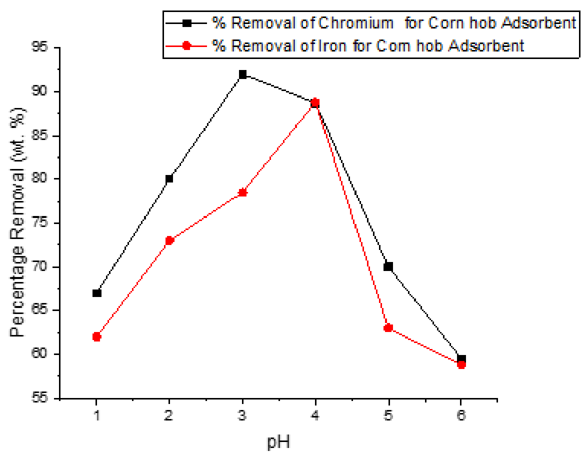

Figure 10: Effect of pH for Corn hob Adsorbent for Iron and Chromium Removal

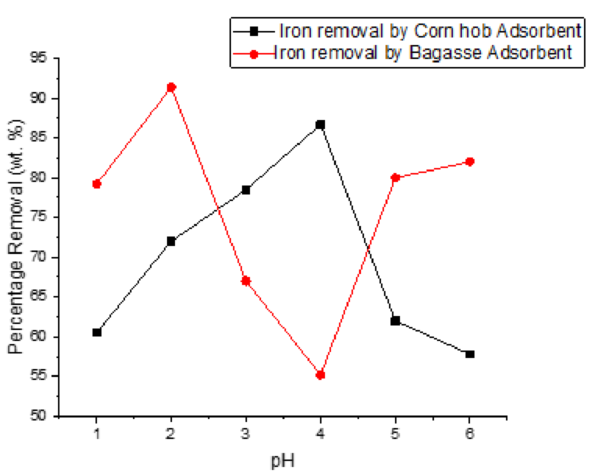

Figure 11: Effect of pH for Iron Using Bagasse and Corn hob Adsorbent

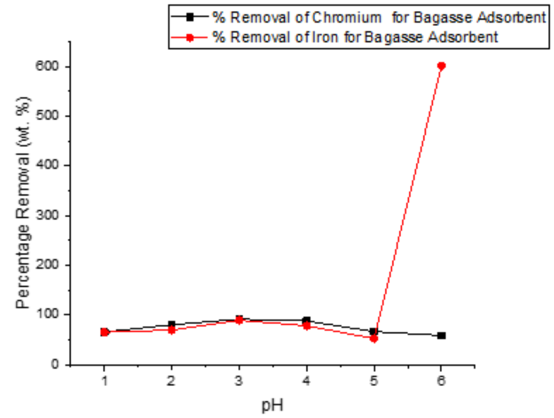

Figure 12: Effect of pH for Chromium Using Bagasse and Corn hob Adsorbent

Mathematical Modeling of Adsorptive Capacity of Agricultural Waste on the Metals

The data obtained for the experiments were fitted to the linearized form of Langmuir and Freundlich mathematical isotherms models [16, 17].

Linearized Freundlich Isotherm equation:

$$\ell n\ V_{ads} = \ell \text{n}\ K_F + \text{n}\ \ell \text{n} C_A \qquad (2)$$

Linearized Langmuir Isotherm equation:

$$\frac{C_A}{V_{ads}} = \frac{1}{K_A} + \frac{V_{max}}{K_A} C_A \qquad (3)$$

Where V_{ads} is the amount metallic ion adsorbed onto the clays (mol/dm^3.g), C_A is the concentration of adsorbate (ppm), V_{max} is the maximum adsorption capacity (mol/dm^3.g), K_F is the adsorption coefficient, n is the Freundlich constant and K_A is the adsorption equilibrium constant.

CONCLUSION

The study carried out to study the adsorption of iron and chromium shows that the waste materials like bagasse and corn hobs can be used effectively for heavy metal removal. The percentage removal of 90-92 % has been obtained by using the adsorbent prepared from these materials. The optimum time, adsorbent dose for iron and chromium varies with the adsorbents used. Optimum contact time values were 59 and 70 minutes for iron by using bagasse adsorbent and corn hob adsorbent respectively. For chromium these values were 50 and 70 minutes respectively. Optimum adsorbent dose for iron by bagasse adsorbent and corn hob adsorbent was equal and was 2.5 grams each. For chromium, these values were 1.5 grams and 2.5 grams respectively. The optimum pH values for iron were 5 and 4 respectively for bagasse and corn hob adsorbent. The optimum pH for chromium was 3 for both the adsorbents. It can be concluded that the adsorption by using low cost adsorbents is very economical and efficient method for iron and chromium removal.

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