BIOWASTE MATERIALS AS SORBENTS TO REMOVE CHROMIUM(VI) FROM AQUEOUS ENVIRONMENT- A COMPARATIVE STUDY

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ABSTRACT

The adsorption of chromium(VI) ions from aqueous solutions has been investigated on Neem sawdust (NS), Mango sawdust (MS), Wheat shell (WS), Sugarcane bagasse (SB) and Orange peel (OP). The adsorbent which showed highest chromium(VI) removal was Neem sawdust. The influence of pH, contact time, biomass dosage and initial metal concentration on biosorption was investigated. The biosorptive capacities of the biosorbents were dependent on the pH of the chromium solution, with pH 2 being optimal. The adsorption data fitted well with the Langmuir isotherm model. The adsorption capacities were found to be 58.82, 37.73, 28.08, 23.8 and 19.80 mg/g for NS, MS, WH, SB and OP, respectively.

Keywords: biowaste material, biosorption, water pollution, heavy metals, chromium(VI), isotherm model.

INTRODUCTION

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr (III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent (Kowalski, 1994). The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Juang and Shiau, 2000; Yan and Viraraghavan, 2001). These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. In this context, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous effluents (Volesky and Holan, 1995). Biosorption is a property of certain types of inactive, non-living microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution. Biomass exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria, which was found responsible for this phenomenon (Volesky, 1990). Natural materials that are available in large quantities or certain waste from agricultural operations could be potential low cost adsorbents, as they represent unused resources (Raji and Anirudhan, 1996). The present study aims at comparative evaluation of biowaste materials viz. Neem sawdust (NS), Mango sawdust (MS), Wheat shell (WS), Sugarcane bagasse (SB) and Orange peel (OP) for removal of Cr (VI) ions from aqueous solutions.

MATERIALS AND METHODS

Preparation of biosorbents

The biowaste materials used for the study were NS, MS, WH, SB and OP. All the materials were obtained from local market. Materials were washed thoroughly with deionized water, dried and then pulverized and oven dried at 60^{o}C for 24 h. After drying the materials were kept in air tight plastic bottles. The particle size was maintained in the range of 425 - 600 µm.

Preparation of Cr (VI) solution

Stock solution (1000 mg/l) of Cr (VI) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionised distilled water. For biosorption experiments, Cr (VI) solutions having 100 mg/l were prepared and used. The pH of the solution was adjusted with 0.1 N HNO_3 and NaOH solutions.

Screening of biosorbents

For the comparative evaluation of different sorbents for Cr (VI) removal capacity, the experiments were conducted in 250 ml Erlenmeyer flasks at 28±1ºC on a rotary shaker at 120 rpm. Experiments were conducted at pH 2 to 8 and initial Cr (VI) concentration of 100 mg/l was maintained. After 4 h of mixing, the samples were filtered through Whatman No. 1 filter paper. Cr (VI) concentration in the filtrate was estimated using UV spectrophotometer at 540 nm wavelength by 1, 5- diphenyl carbazide method (APHA, 1998).

The amount of metal ion adsorbed per gram of biomass and the sorption efficiency (%) were calculated according to the expressions:

$$Q = \frac{(C_o - C_e)}{M} \times V$$

$$\text{Sorption efficiency (\%)} = \frac{(C_o - C_e)}{C_o} \times 100$$

Where where, Q = amount of metal ion biosorbed per gram of biomass, mg/g, C_o and C_e are the initial and equilibrium concentrations (mg/l), V the volume of solution (l), m the weight of biosorbents (g) and C is the solution concentration at the end of the sorption process.

Batch sorption isotherm studies

Batch sorption isotherm studies were conducted on the basis of experiment with the samples containing metal concentration used for biosorption ranged between 10 and 150 mg/l and 2 g/l biosorbents contacted with Cr (VI) solution at pH 2 with contact time (3 h) at constant temperature (28 ±1°C). The flasks were kept on a rotary shaker at 120 rpm. After agitating the solutions were filtered through whatman no.1 filter paper and the Cr (VI) concentration in the filtrate was estimated using UV spectrophotometer at 540 nm wavelength by 1, 5- diphenyl carbazide method (APHA, 1998). From the experimental data, the applicability of Langmuir and Freundlich isotherm models were judged. R^2 (regression coefficient square value) and isotherm constants values were determined from the models.

RESULTS AND DISCUSSIONS

Performance of various adsorbents for Cr (VI) removal

The experiments were conducted with initial Cr (VI) concentration of 100 mg/l and biosorbents dose of 2 g/l at different pH. The results are presented in Figure-1. At pH 2, the Cr (VI) removal was 34%, 42%, 50%, 60% and 80% for OP, SB, WH, MS and NS respectively. It further decreased at increase in pH. These results indicated the higher Cr (VI) removal capacity of Neem sawdust at pH 2, as compared to other biosorbents. The sequence of Cr (VI) removal was NS > MS > WH > SB > OP. Though percentage removal of Cr (VI) decreased with increase in pH, but the sequence of percent removal remained the same.

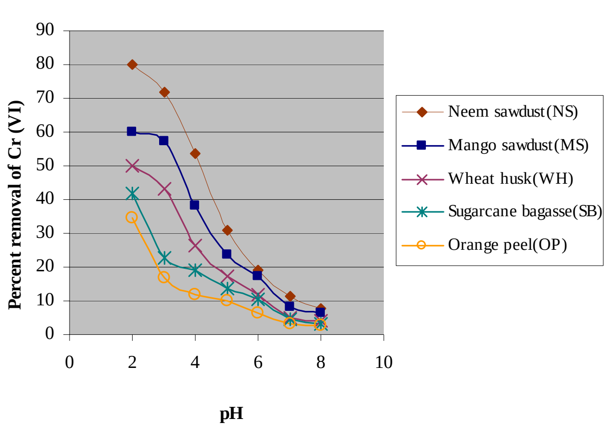

Figure-1. Effect of pH on biosorption of chromium (VI). Initial Cr (VI) conc. = 100 mg/l,
Biosorbent dosage = 2 g/L, Contact time = 24 hrs.

Effect of pH on sorption

In order to establish the effect of pH on the biosorption of Cr (VI) ions onto the six different biosorbents mentioned above, the batch sorption studies at different pH values were conducted in the range of 2.0 to 8.0. It was observed that the maximum adsorption of Cr (VI) ions was observed at pH 2.0 for all the biosorbents and significantly decreased by increasing the pH values up to 8.0 (Figure-1). At lower pH, the biosorbent is positively charged due to protonation and dichromate ion exists as anion leading to an electrostatic attraction between them (Boddu *et al*., 2003). A sharp decrease in adsorption above pH 4 may be due to occupation of the adsorption sites by anionic species like $HCrO_4^-$; $Cr_2O_7^{2-}$; CrO_4^{2}, etc., which retards the approach of such ions further toward the sorbent surface (Das *et al*., 2000; Donmez and Aksu, 2002).

Uptake of Cr (VI) increased markedly with decreasing pH. At pH 2 and 8 corresponding uptake yield values were found to be 80.1% and 4.3 % for NS, 60 and 12.6 % for MS, 50.2 and 9.6 % for WH, 42 and 8.1 % for SB and 34.5 and 4.11% for OP. So, the maximum uptake of Cr (VI) at pH 2.0 was recorded in Neem Sawdust (NS) and thereafter decreased with further increase in pH. The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent. (Popuri *et al*., 2007)

Effect of contact time

The equilibrium time required for the biosorption of Cr (VI) on NS, MS, WH, SB and OP with 2 g/l of the biosorbent at different time intervals were studied. Figure-2 showed that adsorption capacity sharply increased with increase in time and attains equilibrium in 60 min for (NS), 120 min for (MS), 180 min for (WH), 180 min for (SB), 180 min for (OP), respectively. The removal rate of Cr (VI) increases with the increase of the adsorption time. However, it remains constant after an equilibrium time of 150 min, which indicates that the adsorption tends toward saturation. Therefore, the adsorption time was set to 180 min in each experiment. The rate of adsorption is higher in the beginning due to large available surface area of the biosorbent. After the capacity of the adsorbent gets exhausted, i.e. at equilibrium, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the biosorbent particles (Verma *et al*., 2006).

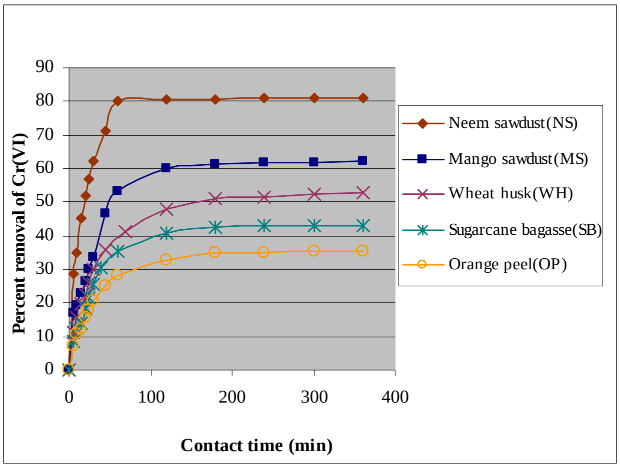

Figure-2. Effect of contact time on biosorption of chromium (VI).
Initial Cr (VI) conc. = 100 mg/l, pH 2,
Biosorbent dosage = 2 g/l.

Effect of biomass dosage

The effect of biosorbent dosage on the removal of chromium (VI) is shown in Figure-3. Amount of sorbent was varied from 1 to 9 g/l and equilibrated for 180 min at an initial Cr (VI) ion concentration of 100 mg/l. The results indicated that the percent removal of chromium (VI) increased with the increase in the amount of adsorbent and removal efficiency for NS, MS, WH, SB and OP were 92%, 70%, 61%, 53% and 44% of Cr (VI) respectively. The highest uptake yield was obtained at biosorbent concentration of 4 g/l for Neem sawdust and 5 g/l for all other biosorbents (MS, WH, SB and OP). The removal of metal ions increased with the increase in biosorbent concentration and attained equilibrium after 5 g/l of adsorbent dosage for the chromium (VI) ions. This is due to availability of more biosorbent as well as greater availability of surface area (Aoyama, 2003). More quantity of biosorbent results in increasing of surface area and biosorption regions which causes removal of more chromium. The decrease in Cr (VI) uptake at higher adsorbent dose may be due to competition of the Cr (VI) ion for the sites available (Baral, 2006).

Adsorption isotherms

The effect of Initial metal ion concentration is shown in Figure-4. In case of low Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The amount of Cr (VI) ions absorbed per unit mass of all the biosorbents increased with the initial metal concentrations as expected. Uptake of chromium (mg/g) increased with increase in chromium concentration and remained nearly constant after equilibrium time. The amount of chromium adsorbed (q_e) increased as the concentration was increased from 10 to 150 mg/l. It also showed that the adsorption was rapid in the initial stages and gradually decreased with progress of adsorption. Similar results were obtained in the case of Coconut coir pith. (Namasivayam and Suresh Kumar, 2008).

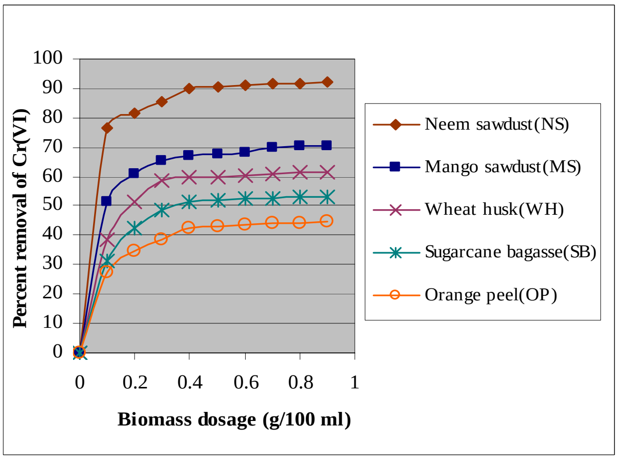

Figure-3. Effect of biomass dosage on biosorption of chromium (VI).
Initial Cr (VI) concentration = 100 mg/l, pH 2,
Contact time = 6 hrs.

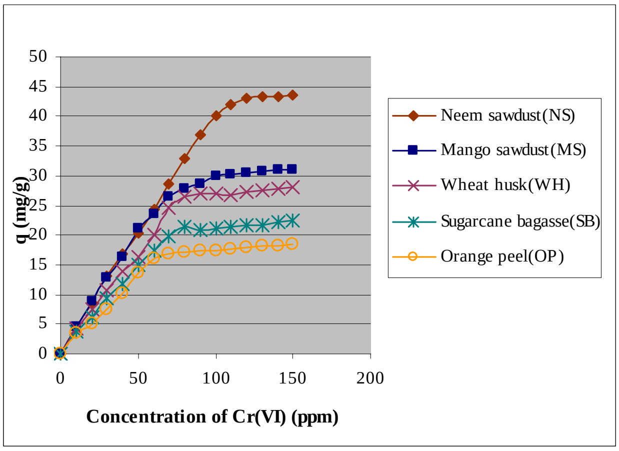

Figure-4. Effect of Initial metal concentration on biosorption of chromium (VI)
pH 2, Biosorbent dosage = 2 g/l Contact time = 6 hrs.

The equilibrium of biosorption of heavy metals is modeled using adsorption- type isotherms. The Langmiur and Freundlich isotherm model were used to describe the biosorption equilibrium of biomass. The Freundlich isotherm is a nonlinear sorption model. This model proposes a monolayer sorption with a heterogenous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The general form of this model is

$$q_e = K_f C_e^{1/n} \quad (1)$$

Where K_f (mg/g) stands for adsorption capacity and n for adsorption intensity.

The logarithmic form of Eq. (1) is:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (2)$$

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is represented in the following equation:

$$q_e = \frac{q_{max}\, bC_e}{1 + bC_e} \qquad (3)$$

Where q_{max} (mg/g) and b are Langmuir constants related to adsorption capacity and the energy of biosorption, respectively.

The adsorption data obtained for chromium (VI) adsorption onto the biowaste materials used as biosorbents in the present investigation were modeled. The values of the Langmuir constants (q_m b) and Freundlich constants (K, n) are presented for the biosorption of Chromium (VI) by NS, MS, WH, SB and OP (Table-1). Neem sawdust had the maximum metal uptake capacity of 58.82 mg/g when compared to other bio waste materials. It shows that the R^2 value is more in Langmuir isotherm compared to Freundlich isotherm. Figure-5 and Figure-6 show that Langmuir and Freundlich isotherm model of Chromium (VI). In the Langmuir model, the linear plot of $1/q_e$ vs $1/c_e$ giving a straight line for Neem sawdust (R^2 = 0.9809) with greater R^2 value compared to other biosorbents with slope $1/q_m b$ and intercept $1/q_m$ and for Freundlich model, the linear plot of log q_e vs log c_e giving a straight line (R^2 = 0.739) with slope (1/n) and intercept log K_f confirmed that Langmuir isotherm model fits best to the sorption data of chromium (VI).

Table-1. Linear regression data for Langmuir and Freundlich isotherms for chromium (VI) biosorption.

S. No.	Biomass	Langmuir parameters			Freundlich parameters		
		q_{max} (mg/g)	B (L/mg)	R^2	N	K_f	R^2
1.	Neem sawdust	58.82	13.68	0.9809	2.1659	8.3926	0.739
2.	Mango sawdust	37.73	7.84	0.9784	2.5967	7.1779	0.8782
3.	Wheat husk	28.08	0.1213	0.9557	2.237	4.5708	0.9171
4.	Sugarcane bagasse	23.8	0.0738	0.9329	2.08	2.9471	0.8909
5.	Orange peel	19.80	0.0387	0.9004	1.9833	2.2449	0.6772

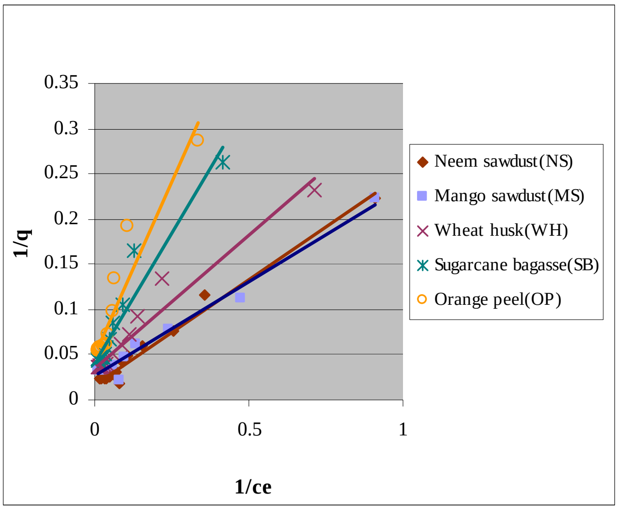

Figure-5. Langmuir isotherm models for Cr (VI) adsorption onto biosorbents.

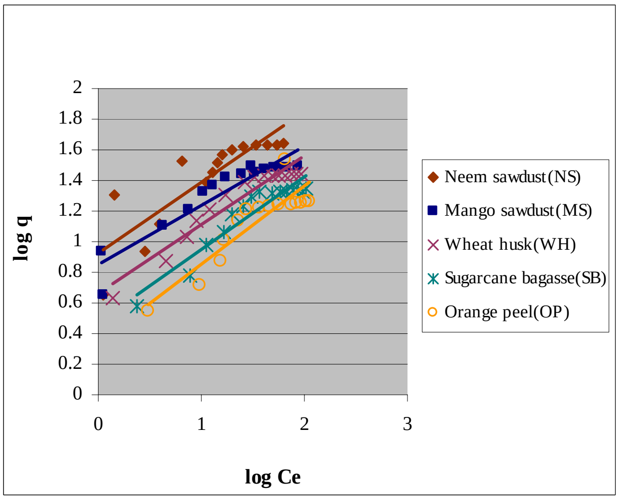

Figure-6. Freundlich isotherm models for Cr (VI) adsorption onto biosorbents.

CONCLUSIONS

The aim of this work was to find out the biosorption characteristics of biowaste materials for the removal of Cr (VI) ions. The maximum biosorption capacity was obtained at pH 2.0. The Freundlich and Langmuir biosorption models were used for the mathematical description of the biosorption equilibrium of Cr (VI) ions to biosorbents. The biosorption equilibrium data fitted well to the Langmuir isotherm. The sorption capacities were 58.82, 37.73, 28.08, 23.8 and 19.80 mg/g for NS, MS, WH, SB and OP, respectively. Neem sawdust (NS) presented the highest adsorption capacities for the Cr (VI) ion. Neem sawdust is easily available material and can, therefore, be used in batched reactors by small scale industries having Cr (VI) in wastewater.

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