Asian Journal of Chemistry; *Vol. 23, No. 6 (2011), 2635-2638*

ASIAN JOURNAL OF CHEMISTRY

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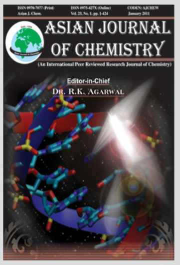

Removal of Hexavalent Chromium from Aqueous Solution using *Vigna Radiata* Husk (Green Gram)

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(*Received*: 13 August 2010; *Accepted*: 16 February 2011) AJC-9628

In this study, *Vigna radiata* Husk (VRH) activated carbon was prepared and used to remove Cr(VI) from aqueous solution. The influences of initial Cr(VI) ion concentration (250-1000 mg/L), pH (1-11), adsorbent dose (0.25-2.5 g), contact time (15-150 min) and particle size (0.15-0.85 mm) had been reported. A comparison of isotherm models applied to the adsorption of Cr(VI) ions on the adsorbent was evaluated for Langmuir, Freundlich and Redlich Peterson isotherms. Adsorption of Cr(VI) was highly pH dependent and the results indicate that the optimum pH for the removal was found to be 2. The obtained results showed that the adsorption of Cr(VI) by *Vigna radiata* Husk follows Redlich-Peterson isotherm equation with a correlation coefficient equal to 0.99. In addition, the kinetics of the adsorption process follows the pseudo second-order kinetic model. The results indicate that *Vigna radiata* Husk can be employed as a low cost alternative to commercial adsorbents in the removal of Cr(VI) from water and wastewater.

Key Words: *Vigna Radiata* husk, Adsorption, Heavy metal removal, Isotherms, Kinetics.

INTRODUCTION

Toxic metals are released into the environment in a number of ways. Coal combustion, sewage wastewaters, automobile emissions, battery industry, mining activities and the utilization of fossil fuels are just a few examples[1]. Excess heavy metals are introduced into aquatic ecosystems as by-products of industrial processes and acid-mine drainage residues. They are highly toxic as ions or in compound forms. They are soluble in water and may be rapidly absorbed into living organisms[2]. The release of heavy metals into the environment by industrial activities is a serious environmental problem because they tend to remain indefinitely, circulating and eventually accumulating throughout the food chain. Due to their extreme toxicity, metal ions are nowadays among the most important pollutants both in surface water and in ground water. Since levels of metals in the environment have increased because of industrial pollution[3,4], the elimination of such ions from water is essential to protect public health.

Heavy metals, such as lead, copper, zinc, chromium, cadmium and nickel are among the most toxic pollutants present in marine, ground and industrial wastewaters. In addition to their toxicity effects even at low concentrations, heavy metals can accumulate throughout the food chain, which leads to serious ecological and health hazards as a result of their solubility and mobility[5]. It can cause mental retardation and semi permanent brain damage in young children[6]. Chromium(VI) which has widespread use in leather tanning, paint and pigment manufacturing, chrome plating, wood preservation, fertilizers, textile dyeing, electroplating, cement, mining and photography industries[7], is a major metal pollutant of the environment. The permissible limit of chromium(VI) in drinking water is 0.05 mg/L[8].

Among them, paint and pigment, chrome plating, textile and match industries discharge Cr(VI), which is a powerful epithelial irritant and a human carcinogen[9]. Additionally, Cr(VI) is toxic to many plants, aquatic animals and bacteria[10]. The United Nations Food and Agriculture Organization recommended maximum level of chromium for irrigation waters is 0.1 mg/L[11]. Wastewaters generated by these industries usually contain significant quantities of salts such as sodium chloride, so the effects of these salts on the removal of chromium(VI) should be investigated[12,13].

The removal of toxic metal ions and recovery of valuable ions from mine wastewaters, soils and waters have been important in economic and environmental problems[14-17]. Different conventional processes (precipitation, ion exchange, electrochemical processes and/or membrane processes) are usually applied to the treatment of industrial effluents but the application of such processes is often limited because of technical or economic constraints[18]. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness[19].

Chromium is hazardous to health when its limit in potable water exceeds 0.05 mg/L of Cr(VI) (ICMR). Natural materials that are available in large quantities may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration.

The aims of this study are to investigate the chromium adsorption from aqueous solution, the effect of different parameters such as contact time, pH, adsorbent dose and initial chromium concentration on adsorption process and find optimum adsorption isotherm as well as the rate of adsorption kinetics.

EXPERIMENTAL

Preparation of adsorbent: The *Vigna radiata* Husk (VRH) was collected from processing unit and washed with clean water to remove colour and impurities. The biomass was then sun dried for 48 h, sieved (75-212 µm) and activated by 0.1 N H_2SO_4 for 24 h. The activated adsorbent was then filtered out, washed with distilled water to remove free sulfuric acid (pH is equal to distilled water) and sun dried for 24 h. These were subsequently used for the adsorption experiment.

Preparation of hexavalent chromium solution: The stock hexavalent chromium [Cr(VI)] solution was prepared by dissolving 2.8289 g of Analytical Reagent (AR) of potassium dichromate in 100 mL of double distilled water and then different concentrations of 250, 500, 750 and 1000 ppm, solutions were prepared by diluting the stock solution. These are the concentrations of hexavalent chromium solution, based upon which the whole experiment was conducted.

Batch adsorption study: Batch equilibrium experiments were conducted by adding a known quantity of the activated adsorbent to 50 mL of the heavy metal solution. The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter (AMIL Photo instrument).

pH: 0.5g of VRH was added to 50 mL of the heavy metal solution at different pH in an Erlenmeyer flask. The pH of the initial heavy metal solution was adjusted using 0.1 N HCl or 0.1 N NaOH accordingly. The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter.

Contact time: The time required to attain equilibrium for 250, 500, 750 and 1000 mg/L Cr(VI) concentration was determined. By 0.5 g of the activated adsorbent materials were added to 50 mL of the heavy metal solution in a flask, shaken and allowed to stand for 15, 30, 60, 90, 105 and 120 min. The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter.

Adsorbent dosage: Adsorption of Cr(VI) was studied by increasing adsorbent dose from 0.25-2.5 g for 50 mL of Cr(VI) concentration of 250, 500, 750 and 1000 mg/L. Keeping the pH of the heavy metal solution constant (pH of 2) following the results obtained earlier and allowed to stand for 2 h. The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter.

Particle size: The batch adsorption experiments were carried out by using various particle sizes of the adsorbent (0.21-0.85 mm) at pH 2, 30 ºC, 150 rpm and various initial concentration of chromium (250-1000 mg/L). The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter.

Initial chromium concentration: The experiments were done with variable initial chromium concentration (250, 500, 750 and 1000 mg/L) and constant temperature (30 ºC), pH (2), agitation speed (150 rpm), contact time (2 h) and 0.5 g of adsorbent dose (0.5 g/50 mL). The resultant solution with the adsorbent in the flasks was shaken and filtered. The filtrate was then analyzed for chromium using photoelectric colorimeter.

RESULTS AND DISCUSSION

Effect of pH: Metal sorption is critically linked with pH[20]. It can be observed from the Fig. 1 that the uptake of Cr(VI) decreases with increase in pH. The highest sorption capacity of adsorbent for Cr(VI) was at pH 2 and the decrease in sorption capacity with increase in pH may be attributed to the changes in metal speciation and the dissociation of functional groups on the sorbent. Similar observation was recorded by Elliot and Weng for Cr(VI) onto fly ashes[21]. Optimum biosorptive removal of chromium(VI) at low pH 2 has been reported for *Rhizopus nigricans*[22], *Bacillus* sp.[23] and *Dunaliella* sp.[24]. Electrostatic interactions have also been demonstrated to be responsible for Cr biosorption by fungi *Gonaderma lucidum* and *Aspergillus niger*[25,26].

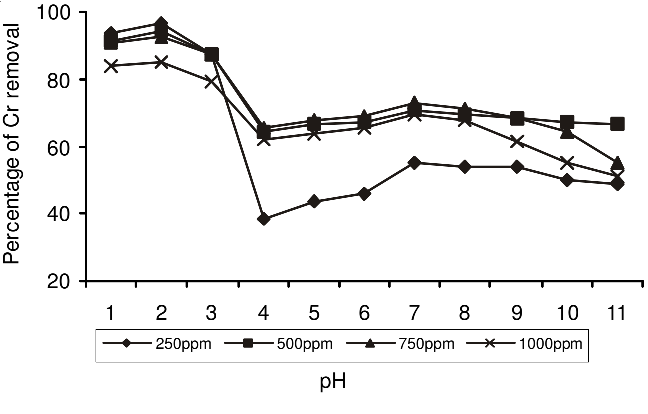

Fig. 1. Effect of pH on Cr adsorption

The decrease in the adsorption with increase of pH may be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is high. The surface charge of adsorbent is positive at low pH and this may promote the binding of the negatively charged $HCrO_4^-$ ions. The $HCrO_4^-$ species are most easily exchanged with OH^- ions at active surfaces of adsorbent under acidic conditions.

Effect of contact time: The results of percentage Cr(VI) adsorption at pH 2, with increasing contact time are presented in Fig. 2. It was found that the Cr(VI) adsorption percentage increased with increasing contact time. The initial rapid adsorption is due to the availability of the positively charged surface of the present adsorbent for adsorption of anionic Cr(VI) species present in the solution at pH 2.0. The later slow adsorption is probably due to the electrostatic hindrance between adsorbed negatively charged sorbate species onto the surface of adsorbent and the available anionic sorbate species in solution and the slow pore diffusion of the solute ion into the bulk of the adsorbent. However, the contact time required for maximum Cr(VI) adsorption onto VRH was found to be nearly 2 h, which is independent of the sorbate concentration.

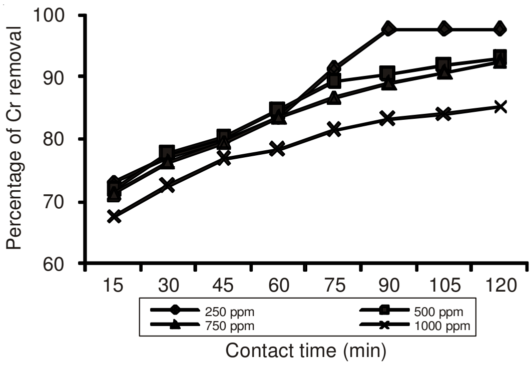

Fig. 2. Effect of contact time on Cr adsorption

Effect of adsorbent dose: The results indicated that the percentage of Cr(VI) adsorbed increased with an increase in adsorbent dosage for all Cr(VI) concentrations. The increase in percentage adsorption with increase in adsorbent dosage is due to the increase in the number of adsorption sites Fig. 3. The amount of ions bound to the adsorbent and amount of free ions remains almost constant even with further addition of dose of adsorbent. It is evident from the result obtained that the removal capacity was high at high dose rate.

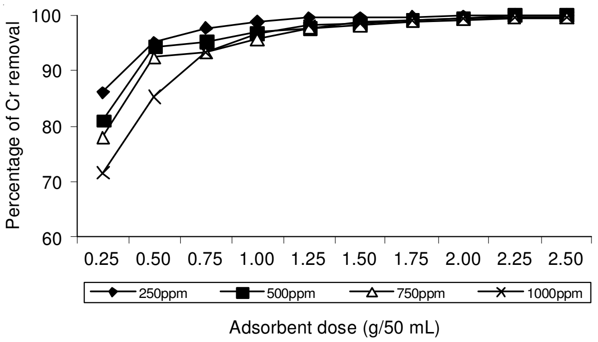

Fig. 3. Effect of adsorbent dose on Cr adsorption

Effect of particle size: Effect of particle size on Cr(VI) sorption capacity of VRH shown in Fig. 4. It is evident from the table that particle size of sorbents has a significant effect on Cr(VI) sorption. The larger sorbent size showed lesser Cr(VI) removal as compared to the smaller sorbent size. The reason may be that surface area available for adsorption decreases with the increase of particle size for the same dose of sorbent, providing less active surface sites for adsorption of sorbate. The reduction in Cr(VI) removal capacity with increase in sorbent size gives an idea about the porosity of sorbent *i.e.*, if the sorbent is highly porous then it would not have significant effect on Cr(VI) removal at equilibrium. The results obtained are in accordance with adsorption processes, where smaller particles of sorbents enhance the rate of metal uptake. The removal of Cr(VI) ions at different particle sizes showed that the removal rate increased better with a decrease in particle diameter.

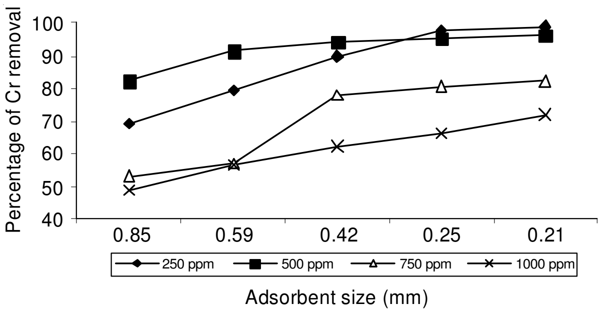

Fig. 4. Effect of adsorbent size on Cr removal

Effect of initial concentrations: Effect of ionic strength, besides pH is also one of the important factors that influence the equilibrium uptake. Experimental results of the effect of initial chromium concentration on removal efficiency were presented in Fig. 5. It is clear from the figure that chromium removal efficiency decreased with the increase in initial chromium concentration. In case of low chromium concentrations, the ration of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available site of adsorption becomes fewer and hence the percentage removal of metal ions depends upon the initial concentration. In general, adsorption decreases with increasing ionic strength of the aqueous solution. This behaviour may be due to the competition between anions of salt with chromate anions sorbed on the active centre of VRH. The results indicate the possibility that adsorption of Cr(VI) on VRH is mainly by chemisorption rather than physical sorption as effect of ionic strength is not so significant on the Cr(VI) removal capacity.

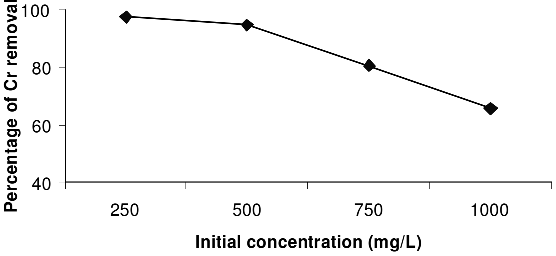

Fig. 5. Effect of initial concentration on Cr adsorption

Adsorption isotherms: To test the fit of data, the Langmuir[27], Freundlich[28] and Redlich-Peterson[29] models were applied to this study. The Langmuir and Freundlich isotherm models were chosen to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface, to estimate the adsorption intensity of the sorbate on the sorbent surface and to evaluate the adsorption potentials of the adsorbent for adsorbates. It has been reported that the typical range of bonding energy for ion-exchange mechanism is 252.24 kJ/mol. The high value indicates a strong interaction between sorbate and sorbent, supporting an ion-exchange mechanism for the present study. The Redlich-Peterson isotherm combines both the Langmuir and Freundlich isotherm equations and the mechanism of adsorption is hybrid and does not follow ideal monolayer adsorption. Present experimental data was found to fit well in the three-parameter model in terms of correlation coefficients R^2 value. The obtained correlation coefficients (R^2) are Redlich-Peterson (0.999) > Langmuir (0.997) > Freundlich (0.893). In the Langmuir equation, q_m (mg/g) was the measure of adsorption capacity under the experimental condition and the value was 66.67 mg/g.

Adsorption kinetics: The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption on the activated VRH was analyzed using first-order[30], pseudo first-order[31] and pseudo second-order[32]. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of Cr(VI) adsorption (first order = 0.0942, pseudo first-order = 0.951 and pseudo second-order = 0.997). Here the applicability of the kinetic models for the present data approximately follows the order: pseudo second-order > pseudo first-order > first-order.

Comparison with other adsorbents: The comparison of adsorption capacity of *Vigna radiata* husk with other materials reported in literature is given in Table-1. The sorption capacity of *Vigna radiata* husk is higher than adsorbents from various industrial and low-cost adsorbents.

TABLE-1
COMPARISON OF ADSORPTION CAPACITY OF Cr(VI) WITH OTHER ADSORBENTS

Adsorbent	Adsorption capacity (mg/g)	pH	Contact time (min)	Reference
Coffee husk	44.95	2	180	33
Hydrous stannic oxide	03.48	2	090	34
Neem leaf powder	07.43	7	300	35
Tamarind indica pod shells	27.73	2	120	36
Cornelian cherry	59.40	1	300	37
Wheat Brna	00.94	3	060	38
Solanum Elaeagnifolium	02.16	2	120	39
Vigna radiata Husk	66.67	2	120	Present study

Conclusion

The present study is about the adsorption of Cr(VI) on *Vigna radiata* Husk as an efficient, low cost adsorbent for the removal of toxic Cr(VI) from aqueous solution. Optimum pH for highest Cr(VI) sorption is 2. The contact time for the maximum adsorption required is nearly 90 min and equilibrium attained is nearly 3 h. The adsorption kinetics for Cr(VI) at pH 2.0 has been well described by the pseudo 2nd order equation in the concentration range studied. The equilibrium sorption data are satisfactorily fitted in the order: Redlich-Peterson > Langmuir > Freundlich.

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