

Batch Adsorption Studies on Removal of Cr (VI) From Aqueous Solution by Using Pongamia Pinnata Seed Shell as Adsorbent

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ABSTRACT: Adsorption of hexavalent chromium by activated carbon prepared from pongamia pinnata seed shell using batch adsorption techniques. The study was carried out to examine the adsorption capacity of the low cost adsorbent pongamia pinnata seed shell for removal of Cr (VI) from synthetic solution. The influence of pH, adsorbent dose and initial concentration of metal ions on adsorption process was studied. Results revealed that adsorbent adsorb more metal when metal concentration in the solution was less. Chromium adsorption increased with increase in adsorbent dose up to 15mg. The pH value between 2 & 4 were optimum for adsorption. The Langmuir and Freundlich adsorption isotherm models were applied to analyse adsorption data, and were found to be applicable to this adsorption process. The R^2 value in the present analysis was less than one, representing that the adsorption of the metal ion onto adsorbent is favorable. Finally, it can be seen that pongamia pinnata seed shell was found to be more effective for the removal of Cr (VI) by experimental conditions. After treatment with adsorbent the levels of heavy metals were observed to decrease by 90 % (Cr). Results indicate that the freely abundant, locally available, low-cost adsorbent can be treated as economically viable for the removal of chromium ions.

KEYWORDS: Adsorption, chromium ion, Pongamia pinnata seed shell, isotherm models.

I. INTRODUCTION

Environmental pollution is presently one of the most important issues facing humanity. It was increased exponentially in the past few years and touched alarming levels in terms of its effects on living creatures. The presence of toxic metals in the environment precisely in various water resources is of major concern because of their toxicity, non-biodegradable nature and hazard to human, animal and plant life. Electroplating, painting, metallurgical, mining, textile, municipal incineration and chemical industrial all generate toxic metals of various levels. Strict regulations have been made by different countries for safe discharge standards of these effluents. Chromium ions and other toxic metal ions move into water and soil from various wastewater sources and thus pollute the water streams and soil. A number of crops and aquatic plants gross up these heavy metals and accumulate inside them. When humans consume food and water with chromium concentration greater than the permissible limits then problems like nausea, gastrointestinal disturbance, vomiting, liver and kidney damage etc. is likely to be caused. Researchers worldwide have developed a number of techniques such as chemical precipitation, oxidation or reduction, ion exchange, filtration, membrane separations, electrochemical treatment, reverse osmosis, evaporation, coagulation etc. for removing the toxic metals from industrial effluents afore discharging into aquatic streams. The conventional treatments produce toxic sludge and in turn disposal or treatment becomes expensive and not ecological. Adsorption is considered as one of the effective and cost-effective technology compared to others for removal of toxic metals from wastes. Activated carbon is widely used in numerous industries as an effective adsorbent for toxic metal removal. The charge of activated carbon is high. Usually industries try for low cost methods for waste water treatment and hence may go for low cost adsorbents. Though researches report shows varieties of low cost adsorbents, all adsorbents are not available effortlessly throughout the world. Hence, considering the availability of materials in precise region, the adsorbents may be suitably

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selected to satisfy the needs of that region. All parts of the Pongamia pinnata tree have many application in medicinal and other areas including the most important one the production of biofuel by Pongamia pinnata seeds. Hence, numbers of trees are grown at farms also availability of the seed shells is more. The present investigation shows the feasibility of using adsorbent prepared from Pongamia pinnata seed shell used for removal of chromium ions from simulated wastewater with parameters as pH, concentration of adsorbent and concentration of metal ion.

II. LITERATURE SURVEY

Addagalla et. al. [1] Billions of gallons of wastewaters containing oils and particulates are produced each year by metallurgical plants, ships, petroleum and gas operations, industrial washing operations and other processes. Unfortunately, water systems have long tended to be one of the ignored areas of the process plant. However, this situation is changing rapidly as environmental legislation tightens. A study has been undertaken to determine the removal of heavy metals (Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+}) of high environmental priority due to their toxicity, from dilute aqueous solutions studied in the present work by biosorption using low-cost biomaterials like activated sludge. Activated sludge is used widely in water treatment plants and is easily available. To know the action of bio metals uptake, the essential role played by extra cellular polymeric

Adhena Ayaliew et. al. [2] studied the removal of hexavalent chromium from tannery wastewater using activated carbon primed from sugarcane bagasse by adsorption process. The removal and recovery of chromium from tannery wastewaters is crucial for environmental protection and economic reasons. Thus, this work focuses on investigating low cost activated sugar cane bagasse for effective removal of hexavalent chrome from aqueous solutions. The maximum adsorption of Cr (VI) is observed at pH of 1. It was found that the Cr (VI) removal was increased with the increment of the adsorbent dosage and contact time. The result showed that the percentage of Cr (VI) recovered and adsorbent regenerated, increase with increasing pH and strength of regeneration solution, contact time and temperature.

Ahmed El Nemr et. al. [3] has conducted the batch experiment by using which is a red marine macro algae, was tested for its ability to remove toxic hexavalent chromium from aqueous solution. A new activated carbon obtained from Pterocladia capillacea via acid dehydration was also investigated as an adsorbent for toxic chromium the experiments were conducted to study the effect of important parameters such as pH, chromium concentration and adsorbent weight. The maximum sorption capacities for dried red alga and its activated carbon about 12 and 66mg /g respectively, as calculated by Langmuir model. The ability in activated red alga P. capillacea and developed activated carbon to remove chromium from synthetic sea water, natural sea water and waste water was investigated as well. Different isotherm models were used to analyze the experimental data and models parameters were evaluated. This study shows that the activated carbon developed from red alga p. capillacea is a promising activated carbon for removal of toxic chromium.

Hany Hussein et. al. [4] explored biosorption experiments for Cr(VI), Cu(II), Cd(II) and Ni(II). In this study nonliving biomass of different Pseudomonas species are used. The applicability of the Langmuir and Freundlich models for the different biosorbent was tested. The coefficient of determination (R^2) of both models were mostly greater than 0.9. In case of Ni(II) and Cu(II), their coefficients were found to be close to one. This indicates that both models adequately describe the experimental data of the biosorption of these metals. The maximum adsorption capacity was found to be the highest for Ni followed by Cd(II), Cu(II) and Cr(VI). Whereas the Freundlich constant k in case of Cd(II) was found to be greater than the other metals.

Karnib Mona et. al.[5] has conducted the batch experiment to test the ability of activated carbon for the removal of lead, cadmium, nickel, chromium and zinc from water. In his study nickel showed the highest removal percentage by activated carbon and the removal percentages decrease as the concentration of heavy metals increase. Silica / activated carbon (2:3) composite was more efficient in the removal of nickel ions than activated carbon and silica nanoparticles. In their study, activated carbon showed the greatest affinity towards nickel with 90% removal percentage.

III. EXPERIMENTAL METHODS

A. Chemicals: reagents used for heavy metal solutions; concentrated HCl and NaOH were used to adjust pH values of samples. In all experimental work, distilled demineralized water was used.

B. Adsorbent: Pongamia pinnata seed shells were collected from the campus of pravara rural engineering college Ioni.

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The shells were washed with distilled water. It was sundried for 2 days. Then the shells were dried out in hot air oven for 110°C for 24hours and pulverized into powder, than this powder was subjected to sieve analysis in sieve shaker, to get 425µm retained powder. This powder was physically activated to form activated carbon by heating the pongamia pinnata seed shell powder in furnace at 750°C. Then the prepared activated carbon powder was subjected to sieve analysis in sieve shaker, to get 300µm retained powder.

C. Stock solution: An 1000 mg/L of Cr (VI) was prepared by dissolving 2.8287 g of potassium dichromate in double distilled water. The stock solution was diluted with distilled water to obtain the required standard solutions.

D. Glass wares and Apparatus used: Glass wares: Conical flasks, Pipette, measuring jar, beakers. Instruments used : Atomic absorption spectrophotometer, Digital weighing balance, Whatman filter paper, Sieve shaker, orbital shaker apparatus, pH meter, Glass jars, conical flask.

E. Batch mode adsorption studies: Effect of several parameters such as pH, concentration of metal ion and concentration of adsorbent on adsorption of chromium on prepared activated carbon was studied by batch technique. All the experiments were carried out at room temperature so as to avoid the heating of effluent. Batch experiments were carried out at an agitation of 120 rpm, samples at predetermined time intervals were collected, than filtered by whatman filter paper and remaining chromium was analyzed by Atomic absorption Spectrophotometer as per standard methods. All the experiments were carried out at pH values 2 and the initial concentration of metal ion for 100 mg/L, 150 mg/L and 200mg/L. Adsorbent dose of 2.5 gm/l to 15 gm/l and particle size of 300µm and for the contact time of 60min. The percentage removal of toxic metal from the solution was calculated using the equation,

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100$$

Where C_i is initial concentration of toxic metal, C_f is final concentration of toxic metal.

IV. RESULTS AND DISCUSSIONS

1. Adsorbent Characterization: Characteristics of activated carbon prepared from pongamia pinnata seeds are presented in Table no.1 The determined surface area of pongamia pinnata seeds activated carbon was 228 m²/g and is comparable greater than various low cost adsorbents namely, peanut hull carbon - 208 m²/g (Periasamy and Namasivayam, 1996), eichhornia - 200 m²/g (Shekinah et al. 2002), cassava - 200 m²/g (Rajeshwari et al. 2001) and coconut tree saw dust carbon - 325 m²/g (Selvi et al. 2001).The moisture content of the carbon was found to be 5.32% determined by Karl fisher apparatus , decolorizing power were 22.5 mg/g. which indicates that the carbon prepared by physical activation method has good adsorption capacity. The surface area of pongamia pinnata seed shell activated carbon was visualized by surface area determination equipment.

Table 1.1. Adsorbent Characterization

pH (1% Solution)	10
Moisture content (%)	5.32
Ash content (%)	1.987
Decolorizing power (mg/l)	22.5
Apparent density (g/mL)	0.42
Water soluble matter (%)	2.0
Acid soluble matter (%)	7.0
Surface area (m ² /g)	228m ² /g

2. Batch mode adsorption studies:

A. Effect of pH: pH variation is one of the most important parameters controlling the uptake of toxic metals from wastewater and aqueous solutions. The studies were conducted at room temperature with an initial metal ion concentration of 100mg/l, 150mg/l, and 200mg/l with constant adsorbent dose of 10gm/l solution, at an agitation period of 60min. Effect of pH on adsorption was conducted at ranges of 2, 4, 6, 8, and 10 in each solution. The maximum

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percentage of adsorption was found in range of pH between up 2 to 4, and there after it decreases with further decrease in pH between up 6 to 8 as shown in figure 2.1.

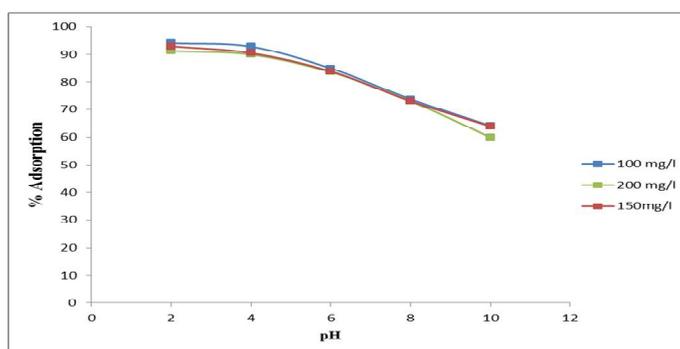


Figure 2.1 Effect of pH on percentage removal of chromium

B. Effect of amount of adsorbent: As the quantity of adsorbent was increased used for chromium ion removal, the available number of vacant sites for adsorption also increased. Thus adsorption of metal ion significantly increased with an increase in amount of adsorbent. The studies were conducted at room temperature with an initial metal ion concentration of 100mg/l, 150mg/l and 200mg/l with pH of 2 at an agitation period of 60min. Effect of amount of adsorbent was conducted at adsorbent doses of 2.5g, 5g, 7.5g, 10g, 12.5g and 15g respectively for 100ml of stock solution. Removal is highly effective at the dose of 15g, and the removal efficiency increases gradually with increase in adsorbent dosage as shown in figure 2.2.

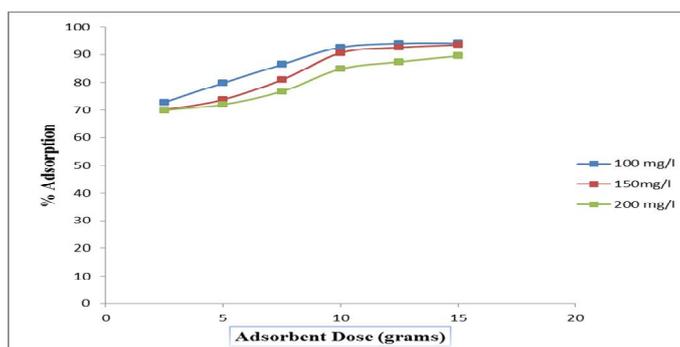


Figure 2.2 Effect of dose of adsorbent on percentage removal of chromium.

C. Effect of initial concentration of chromium ions: The adsorption of chromium ion by adsorbent depends on initial concentration and it can be seen that percentage removal decreases with increased initial metal ion concentration. At lower initial metal ion concentrations, adequate adsorption sites are available for adsorption of metal ions. However, at higher concentrations the number of metal ions relatively higher compared to availability of adsorption sites. The studies were conducted at room temperature at constant adsorbent dose of 10gm/l solution, with pH of 2 at an agitation period of 60 min. Effect of initial concentration of chromium ions was conducted at ranges of 10ppm, 20ppm, 30ppm, 40ppm, 50ppm,60ppm,70ppm,80ppm,90ppm and 100ppm. The percentage removal is highly effective at 10ppm initial ion concentration, after which percentage removal decreases gradually. Results obtained were as shown in figure 2.3.

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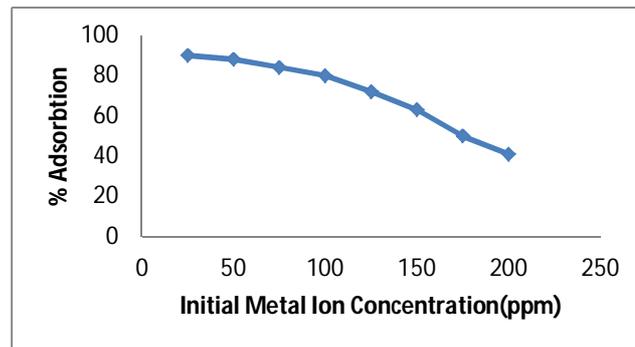


Figure 2.3 Effect of initial concentration of chromium ions on removal of chromium

IV. EQUILIBRIUM ISOTHERMS

Adsorption isotherms define how adsorbates interact with adsorbents and so are critical in optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. Isotherm studies have been performed for different experimental systems. Metal like Cr(VI) is removed from waste water at different adsorbent ranging from 2.5mg/L to 15mg/L using Pongamia pinnata seed shell. In order to optimize the design of a sorption system to remove Cr from effluents, it is important to establish the best appropriate correlation for the equilibrium curves. Two isotherm equations have been tested in the current study, namely, Langmuir and Freundlich.

3. Adsorption Isotherms:

Various isotherm models were used for examination of adsorption capacity in adsorption of hexavalent chromium from aqueous solution. The two models introduced in this study are Langmuir and Freundlich isotherms.

3.1 Langmuir isotherm model:

The Langmuir explains that the adsorption process occurs on the homogeneous surface of the adsorbent by monolayer of the adsorbate which has specific active sites. The linear equation is given by-

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

where K_L is Langmuir equilibrium constant (L/mg), and q_m (mg/g) is the monolayer adsorption capacity, which were calculated from a plot C_e/q_e versus C_e (adsorbed equilibrium concentration) Figure 2.4 . The characteristic parameter of Langmuir isotherm can be demonstrated in terms of dimensionless equilibrium parameter, RL is known as separation factor -

$$RL = \frac{1}{1 + K_L C_0}$$

where C_0 in this case is the highest initial solute concentration. The value of separation factor gives an suggestion for the type of the isotherm and the nature of the adsorption process. Regarding the RL value, adsorption can be unfavorable if ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$) or irreversible ($RL = 0$). The plots of C_e/q_e versus C_e show high linearity confirmed by the values of the correlation Coefficient R^2 , which indicated that the isotherm data fit this model.

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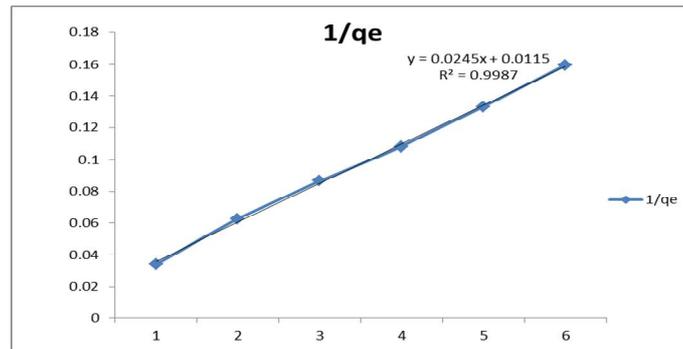


Figure 2.4 Plot of Langmuir Isotherm for the removal of Cr

3.2. Freundlich isotherm model

The Freundlich model is generally used to describe the adsorption by a heterogeneous surface of an adsorbent. The renowned logarithmic form of Freundlich is defined by the following equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where K_f (L/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The slope and intercept of the straight portion of the linear plot were attained by plotting $\ln(q_e)$ versus $\ln(C_e)$ figure 2.5. The correlation coefficient is used as a tool to determine the best suited parameters for each model, and to determine the adsorption process that is observed. It is detected that the linearity coefficient was high, and this gives better indication that adsorption process is followed by the Freundlich isotherm. The correlation coefficient (R^2) of 0.94 indicated that the adsorption process can be best described by Freundlich isotherm.

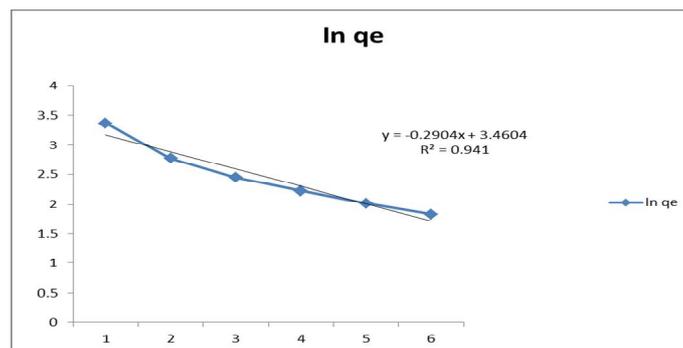


Figure 2.5 Plot of Freundlich Isotherm for the removal of Cr

V. CONCLUSION

As public awareness of the environmental impact of industrial activities increases, consequently placing greater pressure on governments and businesses to reduce the pollution, more stringent environmental regulations are being enacted and forced around the world. The increasing demand for more effective remedial technologies results in a huge window of opportunity for adsorption whose competitive advantage warrants its future success. A wide range of low cost adsorbents have been studied universally for heavy metal removal and it is evident from this work, that inexpensive and locally available material could be used. Adsorbent- pongamia pinnata seed powder was selected for this study due to its originality, availability as well as to access its ability to be used as low cost adsorbent. The adsorbent has been demonstrated to be a useful sorbent for chromium removal under batch condition. Obtained result

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showed that adsorbent-pongamia pinnata seed activated carbon was able to remove 94% chromium from its solution and the sorption capacity was strongly dependent on initial concentration, pH, and dose for batch study. Based on experimental results carried out in this work the following conclusions can be drawn.

1. The maximum removal of chromium ion by Pongamia Pinnata seed shell at optimum parameters were pH 2 with adsorbent dose of 10g/100ml, for contact time of 60 and 10ppm, 20ppm and 30ppm initial metal ion concentration.
2. The effect of adsorbent dosage on the adsorption of heavy metal showed that the percentage of metal removed increases with increase in adsorbent dosage due to increased adsorption surface area.
3. The effect of concentration of chromium solution on the adsorption of heavy metal showed that the percentage of metal removal decreases with increase in concentration of chromium solution.
4. It is also found by Langmuir and Freundlich equilibrium isotherms that the percent removal matches with the theoretical values.

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