Journal of Scientific Research
Vol. XXXVIII No. 2, December, 2008

ISSN 0555-7674

REMOVAL OF CHROMIUM(III) AND ZINC(II) BY USING PODS OF PISUM SATIVUM (GARDEN PEAS)

Jamil Anwar, Muhammad Umer Shafique, Muhammad Salman, Waheed-uz-Zaman, Iram Asif
Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan

Abstract: The adsorption of Chromium(III) and Zinc(II) on ground pods of Pisum sativum (Garden peas) have been studied. The effects of adsorbent dose, pH, contact time and agitation speed on adsorption were studied. The study has revealed that pea pods have high metal removal efficiency. Cr(III) has been removed up to 80.92% and Zn(II) up to 75.11%. Adsorption equilibriums for both metals were developed, which were well described by the Langmuir and Freundlich isotherms. The maximum amounts of Cr(III) and Zn(II) adsorbed (Qmax), as evaluated by Langmuir isotherms were 1.88 mg and 1.45 mg per gram of pea pod's powder, respectively. It is anticipated that waste materials like pea pods can be used for removal of toxic metals like Cr(III) and Zn(II) from industrial effluents/waste waters.

Key Words: Pea pods, Chromium(III), Zinc(II), Adsorption and Isotherms

Introduction

Rapid industrialization is the major cause of the inclusion of heavy metals into the environment especially in water bodies, all over the world. The heavy metal contamination of aqueous streams is becoming a serious threat to aquatic ecosystems because of their high toxicity even at a very low concentrations. Heavy metals are not susceptible to biological degradation and usually accumulated in living tissues after entering through food chain.

Chromium is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans.[1] The permissible limit of chromium for drinking water is 0.1 mg/L (as total chromium) according to EPA standard.[2] Chromium is released into the environment by both natural and anthropogenic sources. The Cr(III) compounds are sparingly soluble in water and can be found in water bodies as soluble Cr(III) complexes.[3] The use of chromate and dichromate in electroplating industries and as corrosion control agents in cooling towers is quite extensive. Textile industries, dyes and pigment industries and tanneries also contribute a fair amount of trivalent chromium into the environment. Human exposure to chromium can result in both acute and chronic forms of toxicity.

Zinc is also found in the drain containing the agricultural and sewage wastewater. Zinc is used extensively by metal alloy, metal plating, cosmetic, pharmaceutical, electrical storage batteries and the industries manufacturing shampoos, toothpastes and deodorants. Acute zinc toxicity after oral ingestion causes nausea, vomiting, and fever. Chronic large doses of zinc may cause zinc chills, hypochromic anemia, arteriosclerosis, gastroenteritis[4] and depression of immune system[5].

Heavy metal remediation of aqueous streams is of special concern. Methods traditionally employed for removing metal ions from aqueous streams include chemical precipitation, ion exchange, reverse osmosis, electro dialysis, ultra filtration and phytoremediation. But these methods entail high cost,

1-For Proof and Correspondence: **Jamil Anwar**

incomplete metal removal, high reagent cost, energy requirement or generation of large amount of toxic sludge that requires disposal or expensive treatment.

The search for new technologies involving the removal of toxic metals from wastewaters has attracted attention to adsorption. The noticeable advantages of this method are high metal removal efficiency, low investment and operational cost, minimization of chemical sludge and regeneration of the adsorbent. The mechanism of adsorption is complex. It mainly involves ion exchange, chelation and surface binding by physical and chemical linkages. There are several chemical groups that would attract and sequester the metals on the adsorbent, for example, —OH, —COOH, —NH_2, —C=O and —NH—C=O etc.

Agricultural wastes have proved to be very useful and low cost adsorbents for the removal of metals[6-9]. The interaction between adsorbent and metal occurs due to the presence of polymeric groups like cellulose, hemicellulose, pectin, lignin and proteins.[10] The high binding capacities of the cationic species on the adsorbents are mainly the result of columbic interactions.[11] The present study is concerned with the use of pods of Pisum sativum (garden peas) as adsorbent for the removal of Cr(III) and Zn(II) from wastewater.

EXPERIMENTAL WORK

Preparation of Adsorbent (Pea pod powder)

After the separation of pea seeds, the pods were washed with distilled water and dried in an oven at 105°C overnight. Dried pods were ground to fine powder in a ball mill and sieved through 60 mesh steel sieves.

Preparation of Solutions

Stock solutions of Cr(III) and Zn(II) were prepared by dissolving 5.12g of $CrCl_3.6H_2O$ (Riedel-de Haen) and 4.39g of $ZnSO_4.7H_2O$ (Riedel-de Haen) in distilled water (1000ml). Successive dilution of stock solutions were carried out to set up standard solutions ranging 5-50 ppm for both metals. Solution of 50ppm was used as a sample for both metals.

Effect of Amount of Adsorbent:

Sample solution of chromium (50ppm, 50ml) was taken in nine different clean and dry conical flasks. The effect of adsorbent dosage was studied by adding finely powdered pea pods in different amounts ranging from 0.5g to 4.5g. All flasks were agitated on orbital shaker (top loaded) at 150 rpm for 30 minutes. The solutions were filtered to remove the adsorbent and the filtrates were subjected to atomic absorption spectrophotometer (AAnalyst 100) to measure the absorbance of Cr(III) at 357.9nm.

The same procedure was repeated for Zn(II) (50ppm, 50ml) and absorbance was measured at 213.9nm. Concentrations of metals were noted determined from calibration graphs.

Effect of Contact Time on Adsorption

Sample solution of chromium (50ppm, 50ml) was added to nine conical flasks. 2.0g dry sieved pea pod powder was added to each solution. The flasks were agitated with orbital shaker at 150rpm. Time of contact was varied from 5mins to 45mins with an interval of 5mins each time. The adsorbent is separated by filtration through whatman filter paper and the filtrates were subjected to atomic absorption spectrophotometer. The same step is repeated for Zn(II) (50ppm, 50ml) with adsorbent dose of 3.0g and absorbance was measured at 213.9nm using air-acetylene flame.

Effect of pH on Adsorption

Sample solution of chromium (50ppm, 50ml) was taken in nine flasks. Pea pod powder (2g) was added to each flask. pH of solutions were adjusted from 1, 2, 3 up to 9 by adding dilute hydrochloric acid and sodium hydroxide solution with the help of pH meter (HANNA instrument - 8417). The flasks were agitated on orbital shaker at 150 rpm for 30minutes. The contents of flasks were filtered and the filtrates were subjected to atomic absorption.

The same procedure was repeated for Zn (II), however, the adsorbent dose was 3.0g and the flasks were agitated for 35 minutes.

Effect of Agitation Speed On Adsorption

Nine flasks were taken and Cr(III) (50ppm, 50mL) were added to each. 2.0g pea pod powder was added to each solution. pH of solutions were adjusted to 4 by using HCl (0.1M) with the help of pH meter (HANNA instrument − 8417) and the solutions were agitated for 30 minutes on orbital shaker at variable speeds ranging from 50rpm, 75rpm, 100rpm, 125rpm up to 250rpm. The solutions were filtered and filtrates were subjected to atomic absorption spectrophotometer.

The same procedure was repeated for Zn(II) but the amount of pea pod powder added was 3.0g and pH of each sample solution was adjusted to 3 and flasks were agitated for 35 minutes.

Adsorption Isotherm Study

Solutions of concentration of 30ppm, 40ppm, 50ppm, 60ppm, 70ppm and 80ppm were prepared by proper dilutions of 1000ppm stock solution of Cr(III). Solutions (50ml) were added in six clean and dry conical flasks and 2.0g pea pod powder was added in each flask. The pH was adjusted to 4 by using HCl (0.1M) with the help of pH meter (HANNA instrument − 8417). The flasks were agitated on orbital shaker at 100rpm for 30minutes. The solutions were filtered and the filtrates were subjected to atomic absorption spectrophotometer.

Similarly, the Zn(II) solutions (50ml) were taken and 3.0g pea pod powder was added. The pH was adjusted to 3 by using HCl (0.1M) with the help of pH meter. The flasks were agitated on orbital shaker at 100 rpm for 35minutes. The solutions were filtered and the filtrates were subjected to atomic absorption spectrophotomete.

The factors 1/q, 1/Ce, Log Ce and Log q were calculated and Langmuir and Freundlich isotherms were plotted for both metals. The corresponding parameters for both metals were calculated from their respective graphs.

Results and Discussion

The release of toxic metals has disastrous effects on the ecosystem. Various chemical and physical methods are being used presently for the removal of toxic heavy metals from the effluents but these methods are either cost prohibited or not practicable on account of operational shortcomings. Nowadays, various plants and several other biological materials are being investigated for the removal of heavy metals by adsorption process. Agro wastes have proved to be cost effective adsorbents for the removal of heavy metals from aqueous streams. Being an agricultural country, a vast amount and wide variety of crops are cultivated in Pakistan. In the present study, powder of pods of Pisum sativum (garden peas) has been used as adsorbent for the removal of Cr(III) and Zn(II) from aqueous solutions. By utilizing the adsorption properties of pods of garden peas, these metals have been successfully removed from their aqueous solutions.

The amount of adsorbent dose is clearly an important parameter that affects the adsorption process as shown in Fig-1. The effect of adsorbent dose in case of zinc is more significant as compared to chromium. As illustrated by the figure metal removal efficiency increases with increase in adsorbent dose, since contact surface of adsorbent particles is increased. Maximum removal was found to be 80.92% and 75.11% for optimum doses of 2.0g and 3.0g for Cr(III) and Zn(II), respectively. Beyond the optimum values, there is a decrease in the adsorption, as the desorption of metal ions starts.

Contact time is another important factor in batch adsorption process. Effect of contact time on adsorption was studied and the results are given in Fig-2. It revealed that the rate of metal uptake increases with the increase in the contact time. Particular time of contact is required to establish equilibrium between metal and adsorbent that usually depends upon the nature and concentration of metal. The optimum contact time was found to be 30 mins and 35 mins for Cr(III) and Zn(II), respectively.

pH is one of the most important parameter in the adsorption process. For Cr(III), maximum removal has taken place at pH 4 while for Zn(II), the optimum pH was found to be 3, as illustrated in Fig-3. Substances show different adsorption behaviors on different pH values. On increasing pH above optimum value, a decrease in percentage removal efficiency has been observed. This is probably due to the fact that because of weakening of forces of attraction between the adsorbate and adsorbent that ultimately lead to the reduction in sorption capacity.[12] While at pH lower than optimum value, functional groups of pea pod powder are protonated and thus active sites of adsorbent become less available, so the metal removal efficiency decreases.

From Fig-4, it can be observed that agitation speed significantly affects the adsorption. Optimum agitation speed is found to be 100 rpm for both the metals. On increasing the agitation speed, adsorption increases. If shaking speed is slow, pea pod powder instead of spreading in the sample accumulates in the bottom and various active sites are buried under the upper layers of adsorbent and the under buried layers can not take part in adsorption. Thus the shaking rate should be sufficient to assure that the entire binding sites are readily available for metal uptake.

The Langmuir adsorption isotherms for chromium and zinc are shown respectively in Fig-5 and Fig-6. The corresponding parameters are given in Table-1. Qmax (Langmuir monolayer adsorption capacity) value calculated for Cr(III) is 1.88mg/g of pea pod powder and for Zn(II), it is 1.45mg/g of pea pod powder. Qmax value for Cr(III) is higher than Zn(II), indicating that the process is more favorable for chromium as compared to Zinc.

The Freundlich adsorption isotherms for chromium and zinc are shown respectively in Fig-7 and Fig-8. The corresponding parameters are given in Table-2. The value of 1/n calculated for Cr(III) is 0.48 while for Zn(II), it is 0.572. The smaller value of 1/n for Cr(III) indicates the formation of relatively stronger bond between Cr(III) and pea pod powder.

Conclusion

From the present study, it is concluded

that powder of pods of *Pisum sativum* (garden Peas) has successful application as an adsorbent and shows high efficiency for the removal of Cr(III) and Zn(II) from aqueous solutions. Pea pod powder is easily available as the pea crop is abundantly cultivated in Pakistan and thus easily available. The study showed that pea pod powder has relatively high adsorption efficiency for Cr(III) as compared to Zn(II). pH 4 was found to be optimum for maximum Cr(III) removal and for Zn(II), it is found to be 3. The suitable time of contact is almost 30 minutes for Cr(III) and 35 minutes for Zn(II). However, it decreases with increase in adsorbent dose. Moreover, the Langmuir and Freundlich isotherm models well described the adsorption of both Cr(III) and Zn(II) metals. The maximum Cr(III) removal i.e. (Q_{max}) was 1.88mg of Cr (III) per gram of pea pod powder whereas for Zn, the value is 1.45mg of Zn(II) per gram of pea pod powder as evaluated from Langmuir adsorption isotherm. Ultimately it can be suggested that pea pod powder can be a good choice for the removal of Cr(III) and Zn(II) from the effluents of tanneries, dyes, electroplating and textile industries.

Fig-1: Effect of adsorbent dose on the adsorption of Chromium and Zinc

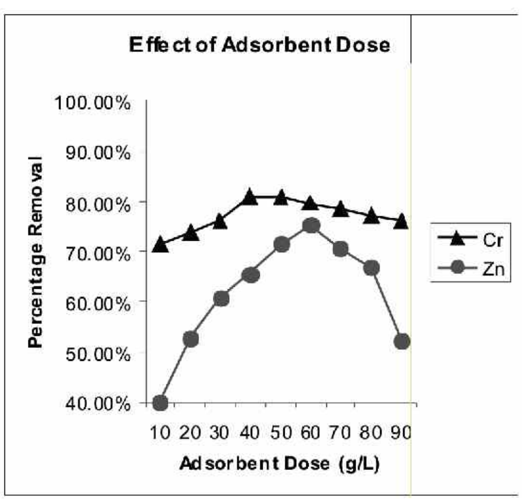

Fig-2: Effect of Contact Time on the adsorption of Chromium and Zinc

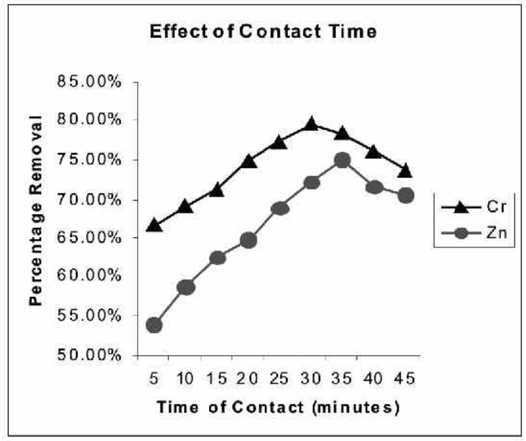

Fig-3: Effect of pH on the adsorption of Chromium and Zinc

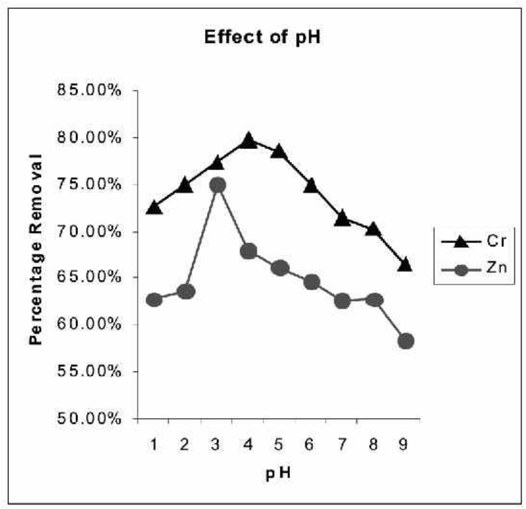

Fig-4: Effect of Agitation Speed on the adsorption of Chromium and Zinc

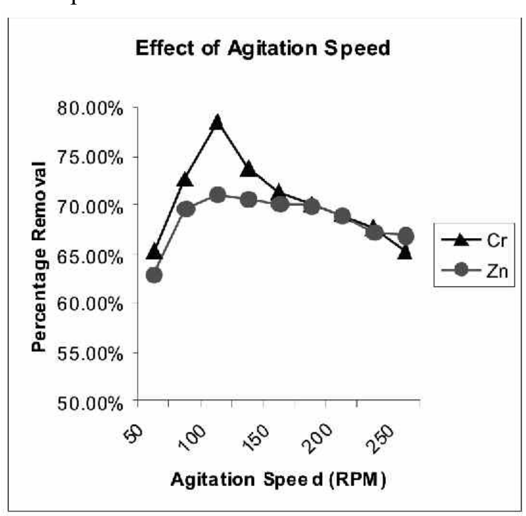

Fig-5: Langmuir Isotherm for Chromium

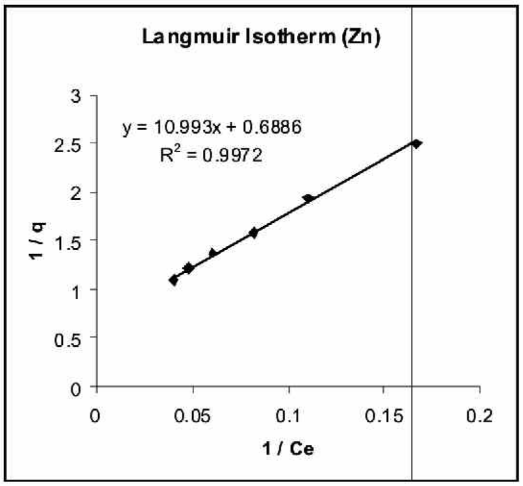

Fig-6: Langmuir Isotherm for Zinc

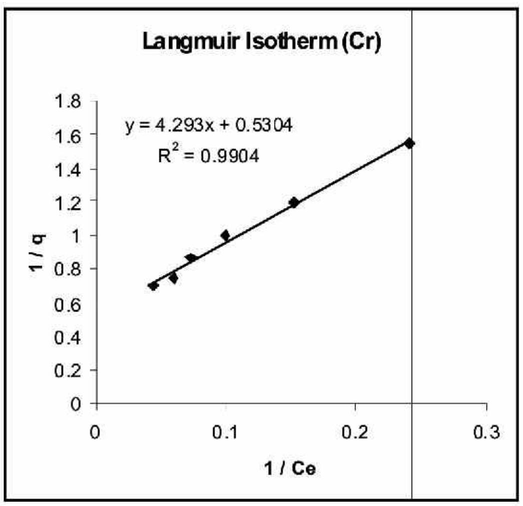

Fig-7: Freundlich Isotherm for Chromium

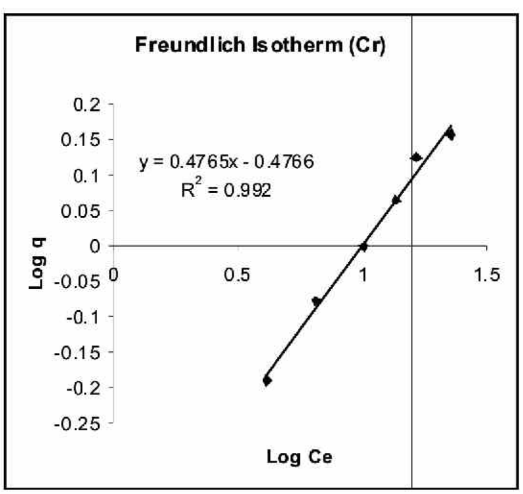

Fig-8: Freundlich Isotherm for Zinc

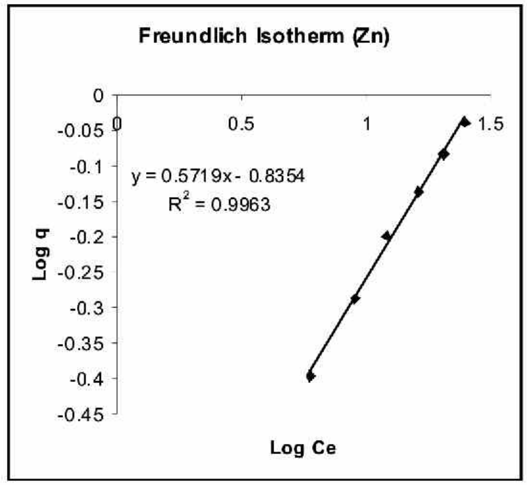

Table :1 Langmuir parameters

Metal	Qmax	b	R^2
Cr	1.88	0.12	0.99
Zn	1.45	0.062	0.99

Table : 2 Freundlich parameters

Metal	Kf	1/n	R^2
Cr	0.33	0.48	0.99
Zn	0.146	0.572	0.99

References

1) Torresdey, J. L. G.; Tiemann, K. J.; Armendariz, V., (2000) Characterization of Cr (VI) binding and reduction to Cr (III) by the agricultural byproducts of Avena monida (oat) biomass., J. Hazard. Mater., 80 (1-3), 175-188.

2) Drinking water standard, Environmental Protection Agency., Available from: http: //www.epa.gov/safewater/contaminants/index. html.

3) Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Chromium*. U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA. 1998.

4) Valko, M; Morris, H.; Cronin, MTD (2005). "Metals, Toxicity and Oxidative stress". *Current Medicinal Chemistry* 12 (12): 11611208.doi:10.2174/0929867053764635.

5) Aydemir, T, B.; Blanchard, R.K.; Cousins, R.J (2006). "Zinc Supplementation of Young Men Alters Metallothionein, Zinc Transporter, and Cytokine Gene Expression in Leucocyte Populations". *PNS* 103 (3): 1699-1704.

6) Krishnani, K. K.; Meng, X.; Christodoulatos, C.; Boddu, V. M. J. of Hazard. Mater. 2008, 153(3), 1222-1234.

7) Katsumata, H.; Kanceo, S.; Susuki, T.; Ohta, K.; Yobiko, Y. *photo/Electrochemistry & Photobiology in the Environment,* Energy fuel. 2004, 8, 165-172.

8) Meunier, N.; Laroulandie, J.; Blais, J. f.; Tyagi, R. D. Bioresource Technol. 2003, 90(3), 255-263

9) Acemioglu, B.; Alma, H. M.; Demirkiran, A. E. J. of Chemical Society of Pak. 2004, 26(1), 82-89.

10) Kou, Y.; Shang, H. S.; Yang, F.; Yan, Z. China patent 01115505, 2001.

11) Weixing, S.; Xiangjing, X.; Gang, S. (1998) Chemically modified sunflower stalks as adsorbent for colour removal from textile wastewater. *J. of Appl. Poly. Sci.* 71, 1841-1850.

12) Baral, S. S.; Dasa, S. N.; Rath, P., (2006). Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust., Biochem. Eng. J., 31 (3), 216-222.