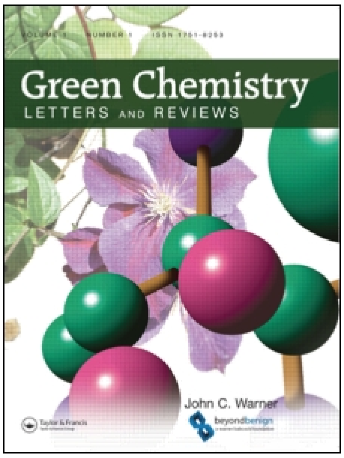

Green Chemistry Letters and Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t748292817

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To cite this Article Anwar, Jamil , Shafique, Umer , Waheed-uz-Zaman, Salman, Muhammad , Hussain, Zaib , Saleem, Maria , Shahid, Naeema , Mahboob, Saliha , Ghafoor, Samina , Akram, Mehwish , Rehman, Rabia and Jamil, Nadia(2010) 'Removal of chromium from water using pea waste - a green approach', Green Chemistry Letters and Reviews, 3: 3, 239 — 243

To link to this Article: DOI: 10.1080/17518251003730833

URL: http://dx.doi.org/10.1080/17518251003730833

Green Chemistry Letters and Reviews
Vol. 3, No. 3, September 2010, 239–243

RESEARCH LETTER

Removal of chromium from water using pea waste – a green approach

Jamil Anwar[a], Umer Shafique[a]*, Waheed-uz-Zaman[a], Muhammad Salman[a], Zaib Hussain[a], Maria Saleem[a], Naeema Shahid[a], Saliha Mahboob[a], Samina Ghafoor[a], Mehwish Akram[a], Rabia Rehman[a] and Nadia Jamil[b]

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(Received 6 January 2010; final version received 22 February 2010)

Agro-waste materials have carboxylic and phenolic groups that play the main role in metal adsorption. The advantages of these materials include easy availability, low cost, and reasonable metal removal capacity. One of the materials (usually considered as waste) is pea waste (pods). Present work comprises adsorption of chromium from aqueous solution using powder of pods of garden peas (*Pisum sativum*) in batch. Important parameters like adsorbent dose, pH, contact time, and agitation speed were studied. Adsorption equilibrium was explained by Langmuir, Freundlich, and Temkin isotherms. Maximum chromium uptake (q_m) was 3.56 mg/g of adsorbent. Heat of adsorption, as evaluated by Temkin isotherm was 1.96 kJ/mol. It is proposed that pea pods can be an effective and environmentally benign (green) adsorbents for removal of chromium from industrial effluents and waste waters.

Keywords: biosorption; chromium; pea pods; Langmuir isotherm; Freundlich isotherm; Temkin isotherm

Introduction

Water pollution caused by heavy metals is a serious problem for aquatic ecosystems, because some metals are toxic even at low levels and are not degradable naturally. Metals can enter our bodies through food, water, and air. Although some heavy metals, in traces, are essential to maintain the metabolism of the body, above certain levels they are toxic. Heavy metals are dangerous as they can bio-accumulate. Thus, metals with longer biological half-lives are dangerous because of the risk of chronic poisoning, even if the environmental levels are low (*1*). Tanneries, electroplating plants, and textiles produce large quantities of chromium-poisoned water. Trivalent chromium decreases immune system activity and causes structural perturbation in the erythrocyte membrane. This structural perturbation changes the biological membrane permeability affecting the functions of ion channels, receptors, and enzymes immersed in the erythrocyte membranes (*2,3*).

Chemical precipitation, lime coagulation, ion exchange, reverse osmosis, and solvent extraction are usually employed for removal of metals from water. However, disadvantages, like incomplete removal, high cost and energy needs, and generation of toxic sludge or other waste products that need careful disposal associated with these procedures, have made it necessary to replace them with a cost-effective and efficient treatment method like biosorption. Advantages of biosorption for removal of heavy and toxic metals are that it can be carried out *in situ* at the contaminated site and is environmentally benign with no secondary pollution. Factors that influence the performance of adsorbent in water are the nature and concentration of substance to be removed and the presence of interfering species, which may compete for the available adsorption sites and pH (*1*).

Agricultural waste has proven to be useful in providing low-cost adsorbents for heavy metal removal. Examples of few adsorbents used for removal of chromium are seaweed biosorbent (*4*), alfalfa biomass (*5*), wine processing waste sludge (*6*), and cow dung (*7*). The interaction between adsorbent and metal is due to the presence of polymeric groups like cellulose, hemi-cellulose, pectin, lignin, and proteins. The present study is concerned with the use of pods of *Pisum sativum* (garden peas) as adsorbent for the removal of Cr(III) from water.

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ISSN 1751-8253 print/ISSN 1751-7192 online

DOI: 10.1080/17518251003730833
http://www.informaworld.com

Results and discussion

The release of toxic metals in water has disastrous effects on the aqueous ecosystem. Although various chemical and physical methods are being employed for removal of toxic heavy metals from effluents, these methods are either cost prohibited or not practicable on account of operational shortcomings. Agro-wastes have proven to be cost-effective adsorbents for the removal of heavy metals from aqueous streams (*8–11*). In the present study, powder of pods of *P. sativum* (garden peas) has been employed as adsorbent for the removal of Cr(III) from aqueous solutions.

Process parameters

The effect of adsorbent dose on adsorption of chromium is shown in Figure 1. Metal removal efficiency increases with an increase in the adsorbent dose. This is because of the greater availability of the exchangeable sites or surface area at the higher concentrations of the adsorbent (*12*). Beyond the optimal mass, little decrease in adsorption was observed by increasing the amount of adsorbent. At higher adsorbent doses, the adsorbent–adsorbent interaction may have increased in comparison to adsorbent–adsorbate interaction (*13*) that led to less adsorption (*14*) assemblage of adsorbent.

Equilibrium time is one of the most important parameters for an effective wastewater treatment system. The effect of contact time on adsorption is shown in Figure 2. The majority of metal ions were removed in the first 30 min. The behavior suggests that at the initial stage adsorption takes place rapidly on the external surface of the adsorbent (*15*). It has also been noticed that equilibrium is established in les time for higher adsorbent doses. Figure 3 summarizes the removal of chromium as a role of pH. Maximum removal has taken place at pH 4. Slightly acidic conditions are favorable, however, at very low pH as H^+ competes with metal cations for the available adsorption site.

Figure 4 reveals that agitation speed significantly affects the process of adsorption. Optimum agitation speed is 100 rpm. If shaking speed is too slow, powder

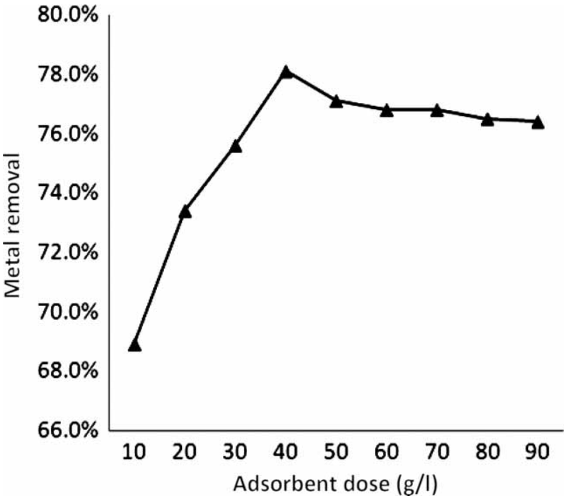

Figure 1. Effect of adsorbent dose (g/l) on adsorption of chromium. Metal concentration, 50 mg/l; agitation speed, 100 rpm; time, 40 min; pH, 6 and temperature, 25°C.

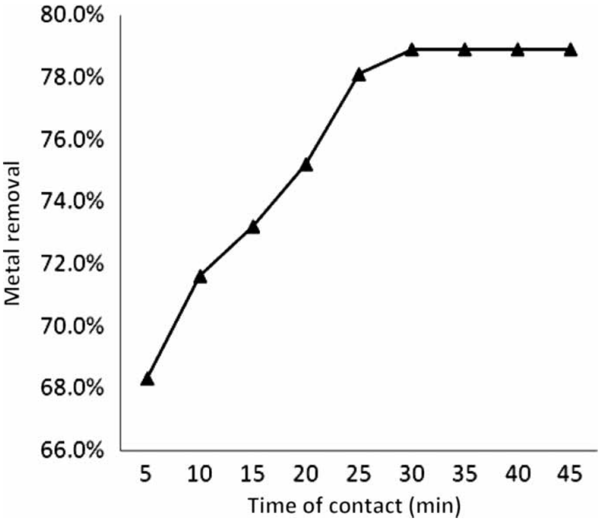

Figure 2. Effect of contact time (min) on adsorption of chromium. Adsorbent dose 2 g; metal concentration, 50 mg/l; volume, 50 ml; agitation speed, 100 rpm; pH, 6 and temperature, 25°C.

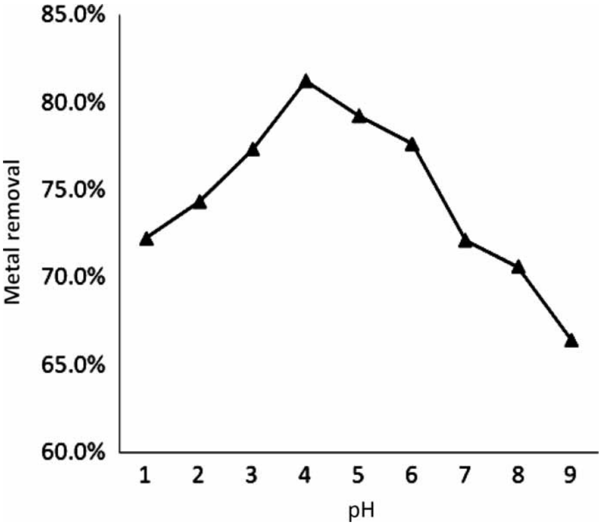

Figure 3. Effect of pH on adsorption of chromium. Adsorbent dose, 2 g; metal concentration, 50 mg/l; volume, 50 ml; agitation speed, 100 rpm; time, 30 min and temperature, 25°C.

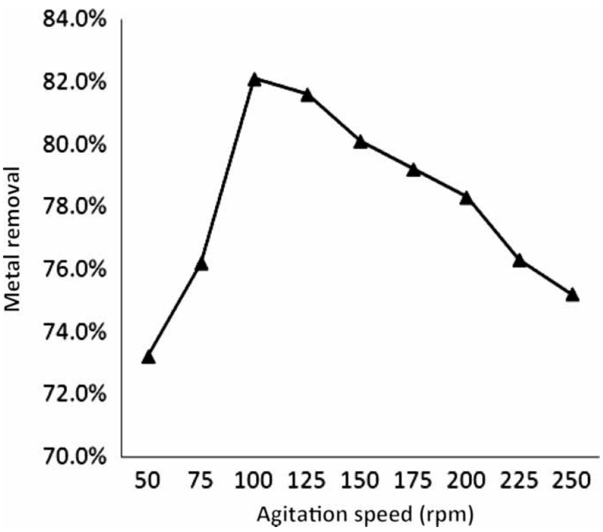

Figure 4. Effect of agitation speed on adsorption of chromium. Adsorbent dose, 2 g; metal concentration, 50 mg/l; volume, 50 ml; time, 30 min; pH, 4 and temperature, 25°C.

of pea pods instead of spreading in the solution gathers at bottom and various active sites got buried under the above layers of adsorbent. Since adsorption is surface phenomenon, under-buried layers do not take part in adsorption. Thus, the shaking rate should be enough to enssure that all the binding sites are readily available for metal uptake (*1*). However, high speed makes adsorption difficult as it does not allow enough time to metal ions to be taken up by adsorbent.

Adsorption isotherms

To describe the chromium adsorption behavior by pods of peas, isotherms data obtained were fitted to the Langmuir, Freundlich, and Temkin adsorption models. Maximum adsorption capacity, q_m, corresponding to complete monolayer coverage revealed that mass capacity of powder of pea pods is 3.56 mg/g for chromium (Table 1). The adsorption coefficient, b, is related to apparent energy of adsorption. The value of b is 0.043 dm^3/g. R^2 (correlation coefficient) values approaching to 1 clearly suggest that the Langmuir isotherm provides a good linear model for adsorption of Cr(III).

The values of $1/n$ and K_F, which roughly correspond to the adsorption intensity and maximum adsorption capacity, respectively, were evaluated with the help of slope and intercept of the linear Freundlich plot. $1/n$ can be used for the measurement of adsorption intensity of metal cations on pea pods. It was 0.739 for chromium (Table 1). Taking reciprocal of $1/n$, the n value obtained is in the range 1–10, showing favorable adsorptions (*16*). Eventual adsorption capacity, K_F, as calculated from Freundlich isotherm is 0.192. R^2 value approaching to 1 points out good linearity of the Freundlich model for adsorption of chromium on pea pods.

Temkin adsorption potential, K_T, for Cr(III) is 2.04 (Table 1). It marks the good potential of pea pods for Cr(III). B_T, related to heat of adsorption, is 1.96 kJ/mol for chromium. Values less than 8 suggested a weak interaction between metal and pea pods (*17*). The process, as indicated by B_T, can be termed physiosorption as for chemical bonding, since the value of B_T is above 8 kJ/mol (*17*). Linearity of Temkin model holds well as pointed out by R^2 value in Table 1, however, slightly less in comparison to Langmuir and Freundlich models.

Experimental

Preparation of adsorbent

Pea seeds were separated and the pods were washed with distilled water thoroughly. Pods were dried in sunlight for two days and then in an oven (Memmert, Model 100–800) at 80°C overnight. Dried pods were ground and sieved to 60 mesh (ASTM).

Table 1. Langmuir, Freundlich, and Temkin isotherm data.

Langmuir isotherm parameters ($y = 6.53x + 0.28$)				
Slope	Intercept	b (dm^3/g)	q_m (mg/g)	R^2
6.53	0.28	0.043	3.56	0.99
Freundlich isotherm parameters ($y = 0.739x – 0.716$)				
Slope	Intercept	1/n	K_F	R^2
0.739	–0.716	1.35	0.192	0.98
Temkin isotherm parameters ($y = 1.263x + 0.906$)				
Slope	Intercept	B_T (kJ/mol)	K_T	R^2
1.263	0.906	1.96	2.04	0.95

Notes: Adsorbent dose, 2 g; metal concentration, 30–80 mg/l; volume, 50 ml; time, 30 min; agitation speed, 100 rpm; pH, 4 and temperature, 25°C.

Stock solutions and standards

Stock solution of chromium (1000 mg/l) was prepared with appropriate weighed quantity of chromium chloride (Sigma–Aldrich). Standard solutions of the desired concentrations (5–100 mg/l) were prepared by successive dilutions of the stock solution.

Equipment and apparatus

Digital pH-meter (HANNA, Model-8417) was used for pH adjustments. HCl (0.1 M) and NaOH (0.1 M) were used for adjustment of pH, while standard buffers were used to keep the pH constant. Perkin Elmer atomic absorption spectrometer (Model-AAnalyst 100) was used for determination of chromium concentrations in the solutions at 357.9 nm.

Study of process parameters

A series of experiments was carried out to study the effects of four parameters (adsorbent dose, pH, contact time, and agitation speed) on adsorption of chromium by pea pods, for the solution of initial concentration 50 mg/l. To study the effect of a certain parameter, that parameter has been varied gradually keeping the other three constant. All the glassware used during the study were washed and dried in an oven at 105°C for 1 h. After adsorption under certain conditions, contents of the flasks were filtered and filtrates were subjected to atomic absorption for determination of chromium.

The effect of the adsorbent dose on adsorption of metal was studied, by varying the dose from 0.50 to 4.50 g for 50 ml solution. The effect of the pH was studied by varying the pH from 1 to 9. The effect of the contact time on adsorption was studied by varying the time of contact from 5 to 45 min and the effect of agitation speed was studied in the range 50–250 rpm.

Study of adsorption isotherms

A quantity of 30, 40, 50, 60, 70, and 80 mg/l solutions of chromium were prepared by proper dilution of stock solution of chromium. Adsorption was studied at pH 4 with time of contact 30 min and 100 rpm agitation speed (best conditions for chromium uptake). Langmuir (Equation 1), Freundlich (Equation 2), and Temkin (Equation 3) isotherms were plotted by using standard straight line equations and corresponding parameters were calculated from their respective graphs.

$$\frac{1}{q_e} = \frac{1}{b \cdot q_m \cdot C_e} + \frac{1}{q_m} \tag{1}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

$$q_e = \frac{RT}{B_T} \ln K_T + \frac{RT}{B_T} \ln C_e, \tag{3}$$

where q_e (mg/g of adsorbent) is the amount of metal adsorbed, whereas C_e (mg/l) is concentration at equilibrium. q_m (mg/g) and b (dm^3/g) are Langmuir isotherm parameters. K_F and n are Freundlich isotherm parameters. B_T (kJ/mol) is heat of sorption. B_T and K_T are Temkin isotherm parameters.

Conclusion

Detailed isotherm analysis of experimental data was carried out to explain the adsorption of Cr(III) on powder of pea pods. It has been found that pea pods possess a good tendency to adsorb chromium. Optimum conditions for removal of chromium are 2 g adsorbent for 50 ml solution (50 mg/l) with contact time 30 min and agitation speed 100 rpm. Four is the most suitable pH to work with. The present study evaluates the efficiency of pea pods, an agricultural waste material, to remove heavy metals from aqueous ecosystems, to overcome water pollution by economical means. The proposed method is no doubt green, economical, and capable to overcome metal pollution without using any hazardous chemicals.

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