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Removal of Heavy Metals Cr (VI), Cd (II) and Ni (II) from Aqueous Solution by Bioabsorbtion of Elaeagnus Angustifolia

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ABSTRACT: The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. One of the most important environmental problems is water resources pollution by Heavy metals. Bioabsorbtion is affordable adsorbents for the removal of heavy metals from aqueous solutions. This study explores the adsorption potential of Cr (VI), Cd (II) and Ni (II) by Elaeagnus angustifolia fruit powder in aqueous solution. The influences of several main parameters such as pH value of solution, sorbent amount, initial metal ion concentration, and contact time in batch experiments have been studied. The adsorption was depended on pH, adsorbent dosage, and contact time. Maximum removal of Cr (VI), Cd (II) and Ni (II) were obtained 7.19mg/g, 2.42 mg/g and 1.97 mg/g respectively. Adsorption isotherms were compared with both Langmuir and Freundlich adsorption models. The experimental data best fit with the Langmuir isotherm model. Experimental results show natural biosorbent was effective for the removal of pollutants from aqueous solution.

Key word: Chromium (VI), Cadmium (II), Nickel (II), Adsorption, Elaeagnus angustifolia

INTRODUCTION

Water pollution by heavy metals has received wide spread attention for many decades and has been a major cause of concern due to generation of a high toxicological risk for human health, ecosystem, and agriculture. Most of heavy metals are toxic and due to their non- biodegradability and persistence, they tend to accumulate in living organisms causing various diseases and disorders. Ni, Cd, Hg, Zn, Pb and Cr are examples of metals that are harmful wastes produced by industries which pose a risk of contaminating groundwater and other water resources (Chuah *et al.*, 2005; Yupeng *et al.*, 2002). According to the World Health Organization (WHO), the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead. In particular, cadmium and cadmium compounds are especially dangerous and highly toxic. Cadmium toxicity contributes to a large number of health conditions, including the major killer diseases such as heart disease, cancer and diabetes. Cadmium concentrates in the kidney, liver and various other organs and is considered more toxic than either lead or mercury. It is toxic at levels one tenth that of lead, mercury, aluminum, or nickel (Linder, 1985). Cadmium is produced in different industrial activities such as galvanizing, pigments, stabilizers, thermoplastics, batteries and alloys (Ulmanu *et al.*, 2003).According to WHO's recommendation Cd (II) limit in drinking water is 0.005 mg/L. The health effects of nickel include higher chances of the development of lung, nose, larynx, respiratory failure and birth defects.Certain compounds of nickel have been listed as carcinogenic. The U.S. Environmental Protection Agency (EPA) requires nickel not to exceed 0.015 mg/L in drinking water (Carrasco-Martin *et al.*, 1985).The majority of nickel compounds that are released into

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the environment will adsorb onto sediment or soil particles and as result become immobile. However, in acidic soils, nickel is more mobile and often leaches out into the groundwater (Sajwan *et al.*, 1996). Nickel concentration in industrial wastewaters ranges from 3.40 to 900 mg/L (Petterson *et al.*, 1987). Environmental regulation related to the discharge of nickel and other heavy metals make it necessary to develop methods for their removal from wastewater. Waste streams from nickel electroplating industries and textile industries are the main sources of nickel environmental pollution. Cr (VI) is a toxic metal and on the list of priority pollutants due to its mutagenic and carcinogenic properties deûned by the US EPA (Environmental Protection Agency) (Kobya, 2004). Chromium exists in either +3 or +6 oxidation states, as all other oxidation states are not stable in aqueous systems. Chromium (VI) is 100-1000 times more toxic to organisms than Cr (III) and more readily transported in soils (Karthikeyan *et al.*, 2005).Cr (VI) is mainly from electroplating, leather tanning, textile dyeing and metal ûnishing industries. The US EPA requires Cr (VI) in drinking water and inland surface waters is 0.05 and 0.1 mg/L, respectively (Namila and Mungoor, 1993). The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities. Several methods have been proposed for the removal of heavy metals as ion exchange (Dizge *et al.*, 2009), filtration (Fatin rouge *et al.*, 2006), coagulation (El samrani *et al.*, 2008), adsorption (Aguado *et al.*, 2009) and electrochemical deposition (Chen and Lim., 2005). Most methods to remove metal ions from solution are expensive (Rocha *et al.*, 2009), so the use of cheap agricultural wastes such as rice straw (Farooq *et al.*, 2010), sawdust (Bulut *et al.*, 2007), carrot residues (Nasernejad *et al.*, 2005), tobacco dust (Qi and Aldrich., 2008), orange residue (Khormaei *et al.*, 2007), apple residue (Lee *et al.*, 1998), coconut shell powder (Pino *et al.*, 2006) and powdered leaves of castor tree (Al Rmalli *et al.*, 2008) as adsorbents have been highlighted for metal removal from wastewater. Adsorption is one of the more popular methods for the removal of metals ions from the aqueous solutions. Adsorption is a surface phenomenon, in which molecules of adsorbate are attracted and held to the surface of an adsorbent until equilibrium is reached between adsorbed molecules and those still freely distributed in the carrying gas or liquid.The adsorption phenomenon depends on the interaction between the surface of the adsorbent and the adsorbed species. The interaction may be due to: 1) chemical bonding; 2) hydrogen bonding; 3) hydrophobic and 4) Vander Waals forces (Bansal and Goyal, 2005).

In the present work, we describe the use of Elaeagnus angustifolia fruit (Bioabsorbent) without activation has been used to remove Cr (VI), Cd (II) and Ni (II) from aqueous solution. The effects of adsorbent dose, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated. The equilibrium of adsorption was modeled with the Langmuir and Freundlich isotherms.

MATERIALS & METHODS

Elaeagnus angustifolia fruit was prepared from Birjand and washed and dried on oven with a temperature of 60 ^{c} and stored for more use. Special surface area for Elaeagnus angustifolia fruit powder using the BET method in Materials and Energy research was determinate 1847 m^2/g. The Elaeagnus angustifolia fruit was characterized by applying FTIR analysis (using Jasco FT/IR-300E spectrometer) to predict the functional groups on the surface of the biomass responsible for the adsorption process. The stock solution (100mg/L) of the nickel, cadmium and Chromium ions was prepared by dissolving a known quantity of appropriate weight of pure salt ($K_2Cr_2O_7$, $Cd(NO_3)_2$, $NiCl_2$) in distilled water. Fresh dilutions were used for each study. The pH of solution was adjusted by 0.1M HNO_3/0.1M NaOH solution. The concentration of the samples of Cr (VI) was analyzed in a spectrophotometer (PG Instrument/VIST80$^+$ is model) using 1,5diphenylcarbazide as the complexing agent at a wave length of 540 nm (Eaton, *et al.*, 1995) and atomic absorption spectrometer (AAS) (Model 929, Unicam) was used to analysis the concentrations of Ni and Cd. The metal loadings on sorbents were computed based on mass balance through loss of metal from aqueous solution. Effect of various pH (2, 3, 4, 5, 6, 7, 8); adsorbent dose (0.5, 1, 1.5, 2, 2.5 and 3 g/L of solution); contact time (10, 30, 60, 90, 120,150and 180 min); initial concentration (2, 4, 6, 8, 10, 20 and 40 mg/L) were studied. All experiments were performed in duplicate and the results average reported. The change in metal concentration in solution before and after sorption was determined with the following equation:

$$q_e = [V(C\ o - C)]\ /W \qquad (1)$$

Where q_e is adsorbed metal (mmol/g adsorbent), V is the volume of solution (L), W is the amount of sorbent (g), and C o and C (mg/L) are the initial and equilibrium Cr (VI) concentrations of the solution, respectively. The heavy metals removal percentages (%) were calculated using the following equation:

$$\text{Metals Removal}\ (\%) = [(Co - Ce)Coe]/100] \qquad (2)$$

The adsorption isotherms represent the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of solute remaining in the solution at equilibrium. Langmuir and Freundlich isotherms models are frequently used for describing adsorption of metal ions by different materials. Both the Langmuir and Freundlich isotherms can be applicable for the equilibrium data of adsorbents from many materials, suggesting that either monolayer or multilayer adsorption could occur on the surface, depending on the type of adsorbents. The Langmuir model assumes that sorption takes place on the homogeneous surface of the adsorbent and a saturation monolayer is formed, while the Freundlich expression is an empirical equation based on the adsorption on a heterogeneous surface. However, heavy metal adsorption on heterogeneous adsorbents has been interpreted by the aid of the Langmuir isotherm (Gopal and Elango, 2007).

The Freundlich equation is:

$$Q= (qm.k1.c)/(1+k1.c) \quad (3)$$

$$C/Q=1/(K1*Qm)+(C/Qm) \quad (4)$$

The Langmuir equation is:

$$Q= Kf.C^{1/n} \quad (5)$$

$$\text{Log } Q= \log Kf + (1/n) . \log C \quad (6)$$

Where qm is the amount of adsorbed material at equilibrium (mg/g), C is the equilibrium metal Concentration of the adsorbate (mg/L), qmax e (mg/g) and b (L/mg) are the Langmuir constants, and K and n are Freundlich constants (Langmuir., 1918; Freundlich., 1926).

RESULTS & DISCUSSION

FTIR spectroscopy was applied to identify the functional groups of Elaeagnus angustifolia fruit powder responsible for metal adsorption. By comparing the FTIR spectra of Elaeagnus angustifolia fruit powder before and after adsorption, was shifted in some bands (Table 1). These bands are the function groups of Elaeagnus angustifolia fruit powder participate in Cr (VI), Ni (II) and Cd (II) biosorption.

Fig. 1 shows the adsorption of Cr (VI), Ni (II) and Cd (II) by Elaeagnus angustifolia fruit powder as a function of time. Effect of contact time on the removal efficiency in systems was studied in range of 10 to 180 min, pH = 3, amount of adsorbent 1.5gr/l and initial concentration of heavy metals (4 mg/L). The optimum time for removal of Cd (II), Ni (II) and Cr (VI) was 120, 70 and 150 min respectively. Fig.1 shows rapid adsorption in the initial min for all absorbent.

Table 1. FTIR spectra characteristic of Elaeagnus angustifolia fruit powder before and after biosorption of Ni (II), Cd (II) and Cr (VI)

FTIR peak	Transmission band (per cm)				Assignment
	Before adsorption	After adsorption of Ni(II)	After adsorption of Cd (II)	After adsorption of Cr(VI)	
1	3340	3321	3429	3341	Stretching vibration of - OH
2	2921	2924	2922	2928	Aliphatic C-H group
3	1650	1656	1634	1624	Double bands of the carboxyl ate ions

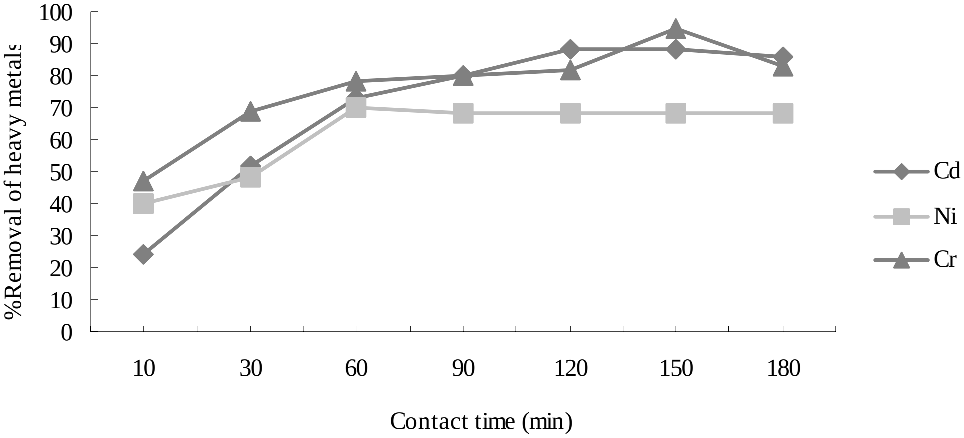

Fig.1. Effect of contact time on the removal of Cd (II), Ni (II) and Cr (VI) (initial metal concentration=4 mg/L, adsorbent dose =1/5g/L, pH = 3)

Figure reveals that the rate of the percentage of heavy metal ions removal is higher at the beginning. That is probably due to the larger surface area of the Elaeagnus angustifolia fruit powder being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The removal of Cr (VI) and Cd (II) is rapid, but it gradually decreases with time until it reaches equilibrium. Further increase in contact time did not show an increase in biosorption (Bishnoi *et al.*, 2004; Ajmal *et al.*, 2001).The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the adsorbent surface at the beginning (Jain *et al.*, 2013; Gueu *et al.*, 2007). This result is interesting because equilibrium time is one of the important considerations for economical wastewater treatment applications. Maximum Ni (II) and Cd (II) removal was achieved within 70 min and 120 min respectively after which Ni (II) and Cd (II) concentration in the test solution became constant. It may be explained by the fact that initially for adsorption large number of vacant sites was available, which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase (Zhou and Kiff, 1991). Earlier studies have shown that solution pH is an important parameter influencing the biosorption of metal ions (Gupta *et al.*, 2001; Donmez and Aksu, 2002; Dakiky *et al.*, 2002). Chromium (VI), Cd (II) and Ni (II) removal was investigated as a function of solution pH and the result is indicated in Fig. 2. As seen from this figure, the biosorption of chromium (VI), Cd (II) and Ni (II) on to Elaeagnus angustifolia fruit powder is strongly pH-dependent. The optimum uptake occurred when the initial pH was 2.0, 97% for Cr (VI), when 6.0, 89% for Cd (II) and when 6.0, 61% for Ni (II) was removed from the solution. Similar results were reported by researchers for a variety of pH systems. (Kobya 2004; Jain *et al.*, 2013; Khazaei *et al.*, 2011; Qaiser *et al.*, 2009; Gupta *et al.*, 2001; Hasan *et al.*, 2008; Hu *et al.*, 2003; Sayad *et al.*, 2010; Bansal *et al.*, 2009; Kannan *et al.*, 2008; Radjenovie *et al.*, 2010; Hannachi *et al.*, 2010; Hamidi *et al.*, 2005; Mostaedei *et al.*, 2010; Ajmal *et al.*, 2003; AnnadurrI *et al.*, 2002)The high adsorption of Cr (VI) can be explained by the species of chromium and the adsorbent surface. At acidic pH, the predominant species of Cr (VI) are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}. Under acidic conditions, the surface of the adsorbent becomes protonated and attracts anionic species of Cr (VI). The decrease in the adsorption with the increase in solution pH may be ascribed to the decrease in electrostatic force of attraction between the sorbent and the sorbate ions (Ahalya *et al.*, 2005). As the pH is increased above the zeta potential of the adsorbent, there is a reduction in the electrostatic attraction between the Cr (VI) species and the adsorbent surface, with a consequent decrease in percentage adsorption (Khazaei *et al.*, 2001). Nickel (II) removal was maximum in the pH 6.0. The influence of pH on the Ni (II) removal may be in the lower pH, higher concentration hydrogen ions resent in the mixture; this competes with the positively charged metal ion for the adsorption sites resulting in the reduced uptake of metal ions (Goyal *et al.*, 2003). As the pH increase the concentration nickel(II) ion remains constant and therefore uptake of metal ions on the surface of carbon can be explained as H^+ - Ni^{+2} exchange reaction. As shown in fig. 2 at low pH values, the adsorption percentage of Cd (II) is low due to the increase in positive charge density (protons) on the surface sites, resulting in electrostatic repulsion between the metal ions (cd^{+2}) and edge groups with positive charge (OH^{+2}) on the surface. Electrostatic repulsion decreases with increasing pH because of the reduction of positive charge density on the sorption edges, thus resulting in an increase in metal ion adsorption on the surface, according to fig. 2. The maximum adsorption of Cd (II) occurred at pH 6.0. At pH values higher than 6 metal precipitation occurred and adsorbent capacity was decreased with accumulation of metal ions (Torab mostaedi *et al.*, 2010). This shows that the pH of the solution is a very important parameter for the removal of heavy metal ions, which is the toxic form of the chromium, cadmium and nickel metals.

The effect of sorbent variation on the removal of Cr (VI), Cd (II) and Ni (II) ions by Elaeagnus angustifolia fruit powder is shown in Fig.3. The effect of adsorbent dose on Cr (VI), Cd (II) and Ni (II) ions uptake was investigated by varying the adsorbent dose (0.5, 1, 1.5, 2, 2.5 and 3 g/L) for an optimum time for any metal ions. Experimental results showed that the percentage removal Cr (VI), Cd (II) and Ni (II) ions increases with the increasing amount of adsorbent up to 3g/L for Cr (VI) and Ni (II) and 2gr/l for Cd (II). Experimental results showed that the percentage removal Cr (VI), Cd (II) and Ni (II) increases with the increasing amount of adsorbent. After this dose of adsorbent no significant change was observed. The increase in percentage adsorption with increase in adsorbent dosage is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent (Asubiojo and Ajelabi 2009). However very slow increase in removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions (Khazaei *et al.*, 2011). Similar results are also reported by researchers for a variety

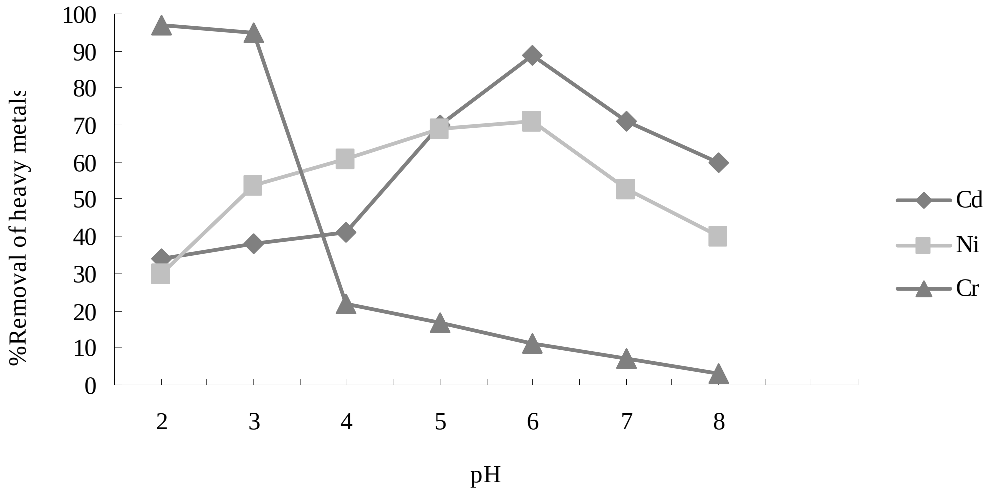

Fig. 2. Effect of pH on the removal of Cr (VI), Cd (II) and Ni (II) (initial metal concentration=4 mg/L, adsorbent dose=1/5 g/L contact time= optimum contact time for any metal ions)

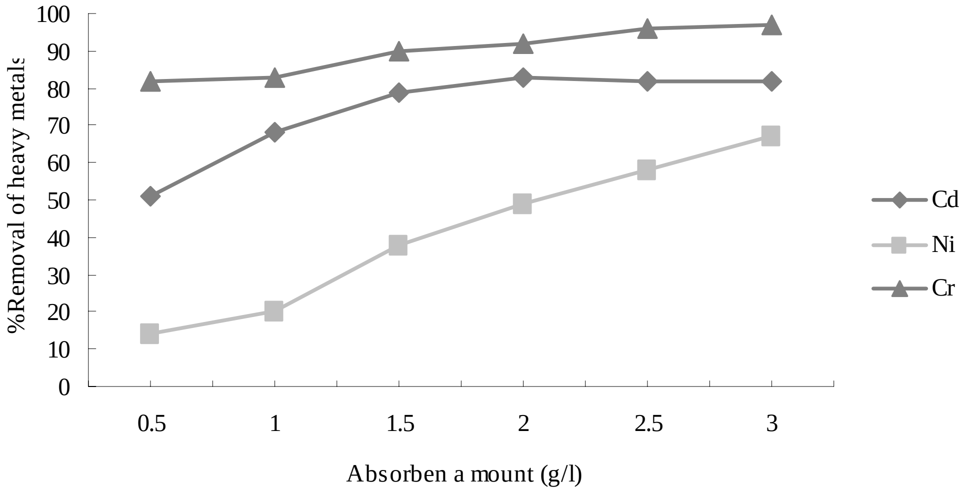

Fig. 3. Effect of amount of adsorbent on the removal of Cr (VI), Cd (II) and Ni (II) (initial metal concentration=4mg/L, contact time and pH= optimum quantity for any metal ions)

of adsorbate–adsorbent systems (Jain *et al.*, 2013; Jain *et al.*, 2010, Chundhury *et al.*, 2012; Qaiser *et al.*, 2009; Sayad *et al.*, 2010; Bansal *et al.*, 2009; Torab Mostaeei *et al.*, 2010).

The initial metal ions concentration was one of the most important factors that determined the equilibrium concentration. The effect of Cr (VI), Cd (II) and Ni (II) concentration on the sorbent by varying the initial ions concentration (2, 4, 6, 8, 10, 20 and 40 mg/L) for optimum value of time, pH and absorbent a mount for any metal ions show in Fig.4. The percentage removal was decreased with increase in Cr (VI), Cd (II) and Ni (II) concentration. The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific active sites, while at higher concentrations; lower adsorption yield is due to the saturation of adsorption sites. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. This appears to be due to the increase in the number of ions competing for the available active sites on the surface (Sayed *et al.*, 2010).

Several models had been used in literatures to describe the experimental data of adsorption isotherms. The Langmuir (Langmuir, 1918) Freundlich and (Freundlich, 1926) models are the most frequently employed models, these two models were used in the present work. Equilibrium data obtained were fitted to the Langmuir and Freundlich isotherms. Langmuir

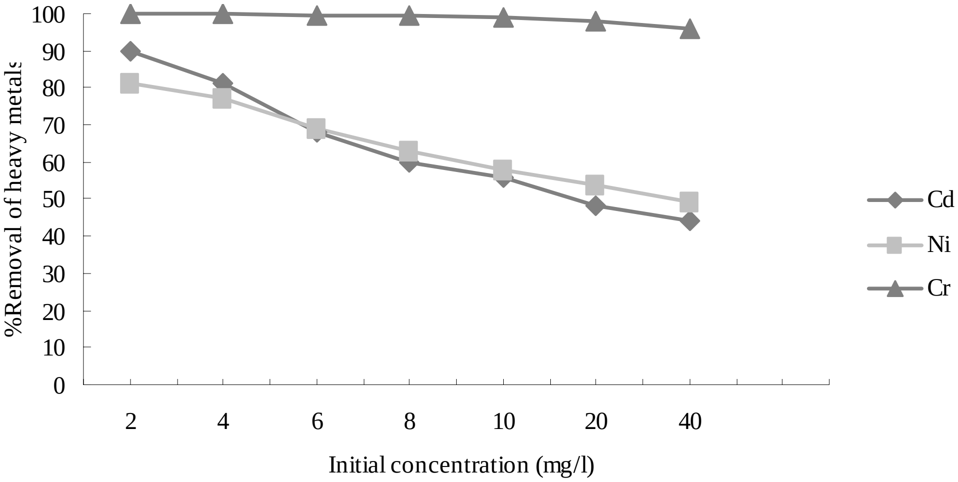

Fig. 4. Effect of initial Cr (VI), Cd (II) and Ni (II) concentration on the removal of metal ions (optimum contact time, pH and adsorbent dose for any metal ions)

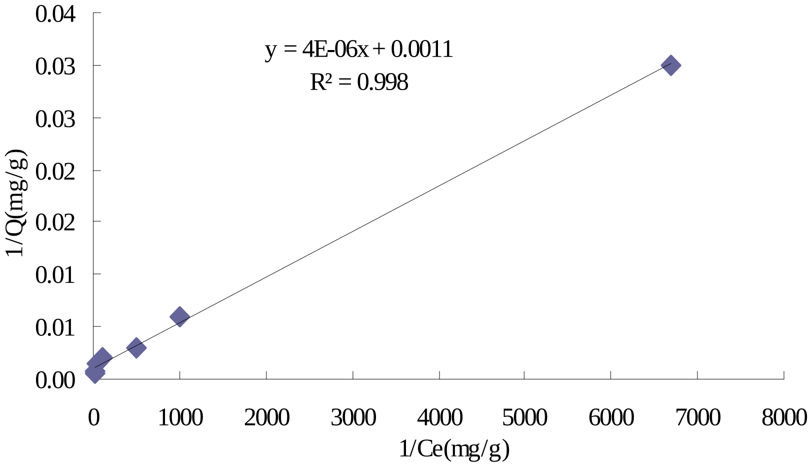

Fig. 5. Langmuir isotherm for AdsorptionCr (VI) by Elaeagnus angustifolia fruit powder

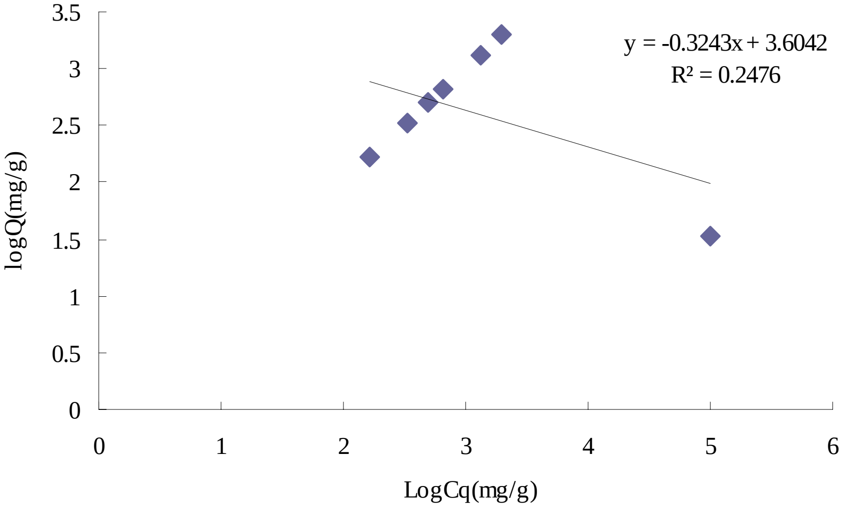

Fig. 6. Freundlich isotherm for AdsorptionCr (VI) by Elaeagnus angustifolia fruit powder

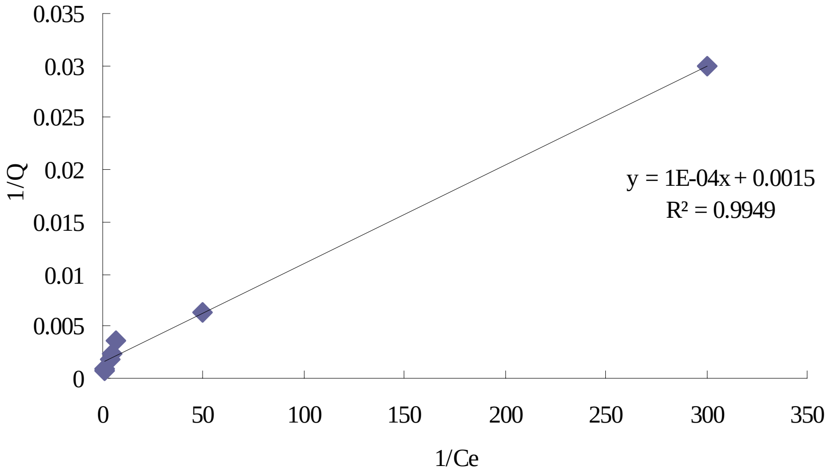

Fig.7. Langmuir isotherm for Adsorption Cd (II) by Elaeagnus angustifolia fruit powder

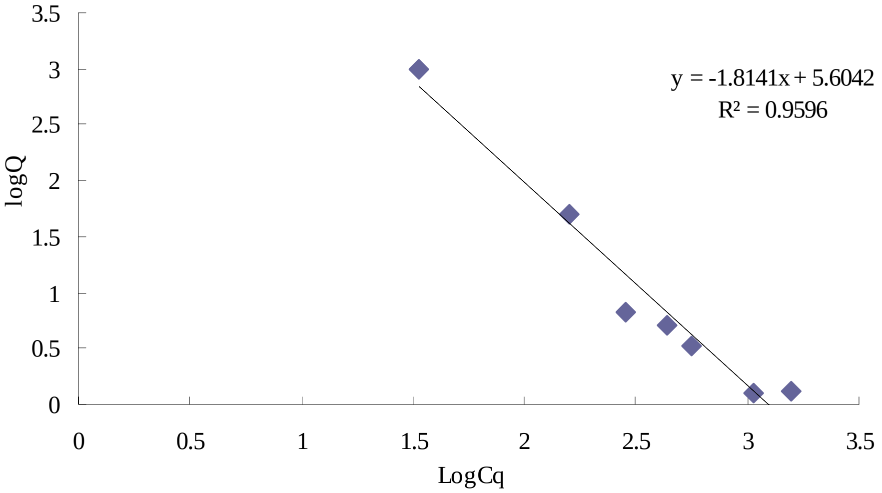

Fig. 8. Freundlich isotherm for Adsorption Cd(II) by Elaeagnus angustifolia fruit powder

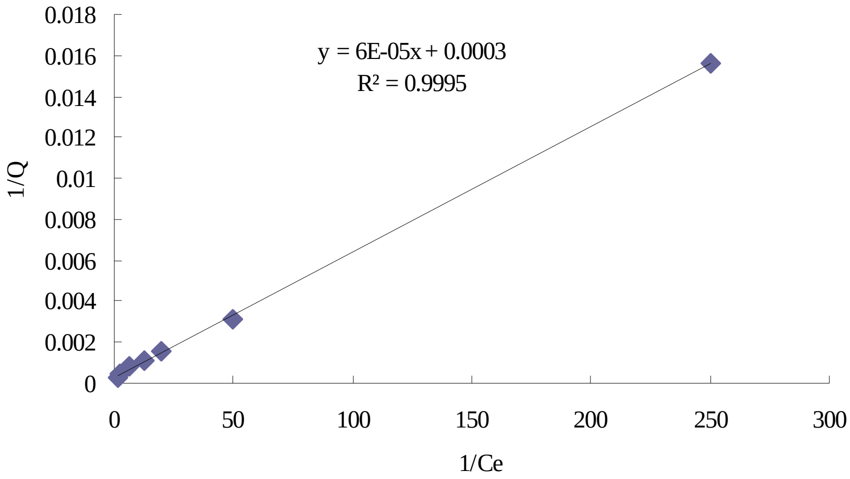

Fig. 9. Langmuir isotherm for Adsorption Ni (II) by Elaeagnus angustifolia fruit powder

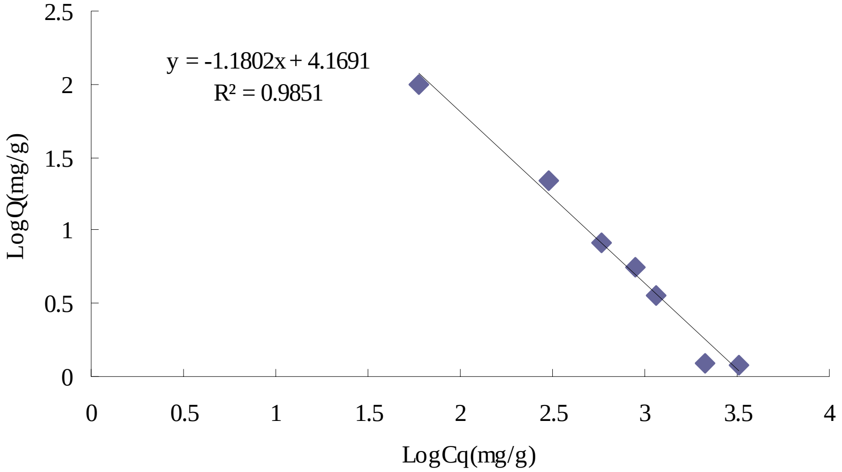

Fig.10. Freundlich isotherm for Adsorption Ni(II) by Elaeagnus angustifolia fruit powder

isotherm is based on the monolayer adsorption of chromium ions on the surface of absorbent sites (Kobya, 2004). Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption sites. Equilibrium data obtained were fitted to the Langmuir and Freundlich isotherms. The following expressions of straight line were found by means of mathematical transformation of isotherms equation. The estimated model parameters with correlation coefficient (R^2) for the two models are shown in fig. 5 to fig 10 it was observed that results fitted better in the Langmuir model in terms of R^2 value, recording 0.9984 for Cr (VI), 0.9949 for Cd (II) and 0.9995 for Ni (II).

CONCLUSION

The adsorption behavior of Cr (VI), Cd (II) and Ni (II) on expanded Elaeagnus angustifolia fruit powder was investigated in batch experiments. The adsorption was found to be drastically dependent on pH, adsorbent dosage, and contact time. The optimum pH for adsorption of metal ions was found to be 6.0 for Cd (II) and Ni (II) and 2.0 for Cr (VI). The rate of Cr (VI), Cd (II) and Ni (II) adsorption was rapid. The chromium, cadmium and nickel ions attained equilibrium in 150 min, 120 min and 70min, respectively. Isotherm analysis of the data showed that the adsorption pattern of three metal ions followed the Langmuir model. The maximum capacity of Elaeagnus angustifolia fruit powder was found to be 7.19 (mg/g) for Cr (VI), 1.97 (mg/g) for Ni (II) ions and2.42 (mg/g) for Cd (II) ions.

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