Sorption of Toxic Cr(VI) From Aqueous Solutions by Using Treated *Acacia nilotica* Leaf as Adsorbent: Single and Binary System

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The use of cheap and eco-friendly adsorbents prepared from freely and abundantly available *Acacia nilotica* leaves for the removal of highly toxic Cr(VI) from aqueous solutions in single and binary ion solutions as well as from a mixture of it with Co(II) & Cu(II) was investigated by batch methods. The effects of pH, contact time, and initial metal ion concentration of Cr(VI) onto H_2SO_4-treated *Acacia nilotica* leaves (HAN) was investigated. The linear form of the Freundlich model achieved high coefficients of determination $R^2 = 0.9808$ for Cr(VI) adsorption. The R^2 values for fitting the adsorption rate data were greater than 0.983 for Cr(VI) ion, which indicates the applicability of pseudo-second-order kinetic model. The desorption and recycling ability of Cr(VI) and HAN were found to be good. The studies showed that this low-cost adsorbent could be used as an efficient adsorbent material for the removal of Cr(VI) from aqueous solutions.

Keywords: Adsorption; Cr(VI); Acacia nilotica leaves; Isotherms; Kinetics; Desorption

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INTRODUCTION

The presence of heavy metals in the environment can be detrimental to a variety of living species including human. Heavy metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. Compared to other heavy metal ions, chromium (VI) is abundant in nature and also highly toxic and carcinogenic (Goyer and Mehlman1977; Carson *et al.* 1986). Chromium exists in +3 and +6 oxidation states, as all other oxidation states are not stable in aqueous solutions. Both valences of chromium are potentially harmful (Dakiky *et al.* 2002). Hexavalent chromium, which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions, poses significantly higher levels of toxicity than the other valency states (Ahalya *et al.* 2010).The permissible limit of chromium ion for drinking water is 0.1 mgL^{-1} (as total chromium). Electroplating and tannery industry effluents are the major sources for the Cr(VI) production in wastewater streams. Eye irritation has been reported by factory workers exposed to chromium dust. Hence it is essential to remove chromium from industrial wastewater before discharging to natural water sources, in order to meet National Regulatory Standards as well as to protect public health. The treatment method for metal-bearing effluents commonly includes chemical precipitation (hydroxides, sulphides, *etc*.), membrane filtration (reverse osmosis, nano filtration, *etc.*), electrolytic reduction, solvent extraction, ion exchange, and adsorption (Rousseau 1987). These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal or treatment. The adsorption process is the most useful method to remove Cr(VI); this approach takes advantage of the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency (Harland 1994; Cooney 1999). A large number of different adsorbent materials containing a variety of attached chemical functional groups have been reported for this purpose. For instance, activated carbon is the most popular material; however its high cost restricts its large-scale use (Bable and Kurniawan 2003; Bailey *et al.* 1999). This problem has led many researchers to search for cheaper adsorption substitutes including fly ash, lignin, peat, natural material, (chitosan, alginate, biomass, *etc.*), clays (clinoptilolite, montmorillonite, kaolinite, *etc.*) (El-Geundi 1997), and cellulose-based hydrogels (Zhou *et al*. 2012). The present study evaluates the possibility of using *Acacia nilotica* leaf carbon as a low-cost adsorbent for the removal of Cr(VI) ions from dilute solutions. *Acacia nilotica* is native to Africa and the Indian subcontinent. *Acacia nilotica* leaves are used as an agricultural waste for the depollution of water effluents contaminated by heavy metals from industrial effluents (Santhi *et al.* 2011).

EXPERIMENTAL

Materials

Preparation of chemically treated adsorbent (HAN)

The leaves of *Acacia nilotica* used in this work were collected locally (Palladam, India). Leaves were shade-dried and powdered in a grinder. Then the mixture was impregnated with conc. H_2SO_4 for 20 h and washed thoroughly with distilled water until it attained neutral pH. It was soaked in 2% $NaHCO_3$ overnight in order to remove any excess of acid and kept in a hot air oven at 300°C for carbonization. Then the material was named as HAN and preserved in an air-tight container for further use.

Adsorbate

All the chemicals used were of analytical grade. A stock solution of 1000 mgL^{-1}Cr(VI) was prepared by dissolving 2.8287g of 99.9% potassium dichromate ($K_2Cr_2O_7$) in 1000 mL of distilled water. This solution was diluted as required to obtain standard solutions containing 50 to 200 mgL^{-1} of Cr(VI). Adjustment of pH was carried out by using 0.5N HCl and 0.5N NaOH solutions.

Methods

Batch adsorption experiments were carried to evaluate the effects of pH, contact time, initial concentration, and adsorbent dosage on the adsorbed amounts. Tests were carried out to evaluate adsorption kinetics, adsorption isotherms, and desorption of Cr (VI) on HAN. In all sets of experiments a fixed volume of single metal ion solutions (SMS) (50 mL) of various concentrations (50,100,150, and 200 mgL^{-1}) and for Binary Metal System (BMS) 50 mL volume of BMS solution with 25 mL of 50 mgL^{-1} concentration of working metal and 25 mL of Co^{2+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mgL^{-1}) were taken in a conical flask. For TMS, 50 mL volume of TMS solution with 25 mL of 50 mgL^{-1} concentration of working metal and 12.5 mL of both Co^{2+} and Cu^{2+} of various concentrations (10, 20, 30, 40, and 50 mgL^{-1}) were taken in conical flasks, which were thoroughly mixed with 0.2 g of biosorbent dose at room temperature at 160 rpm (revolutions per minute) shaking speed for 2 h. Two hours of equilibrium period for sorption experiment was used to ensure equilibrium. The pH values were adjusted from 2 to 10 using 0.1 N HCl and 0.1 N NaOH solutions and were measured using a digital pH meter (ELICO L1120). The initial Cr (VI) concentration was measured spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as a complexing agent (APHA 1985), and the absorbance was measured at λ_{max} of 540nm. The flasks were kept on a rotating shaker with constant shaking. At the end of the experiment, the flasks were removed and the solution was separated from the adsorbent by filtration through filter paper. The filtrate was analyzed to find out the amount of metal left after sorption. The amount of equilibrium uptake of metal (q_e) and the percentage removal were calculated using the following equations,

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

$$\text{Removal percentage} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_o and C_e are the initial and final equilibrium concentration, V is the volume (L) of the solution, and w is the weight (g) of the adsorbent.

RESULTS AND DISCUSSION

Characterization of HAN

Determination of Zero Point Charge (pH_{zpc}) was carried out to investigate the surface charge behavior of both adsorbents. For the determination of pH_{zpc}, 0.2 g of the sample suspension was prepared in 50 mL of $NaNO_3$ electrolyte of concentration approximately 10^{-2} M. Aliquots of suspensions were adjusted to various pH values with 0.5 N NaOH and 0.5 N HNO_3. After 60 min of equilibrium, initial pH was measured. Then 0.1 g of $NaNO_3$ was added to each aliquot to bring the final electrolytic concentration to about 0.45 M. After an additional 60 min of agitation, the final pH was measured. The results were plotted with initial pH (final pH - initial pH) against final pH.

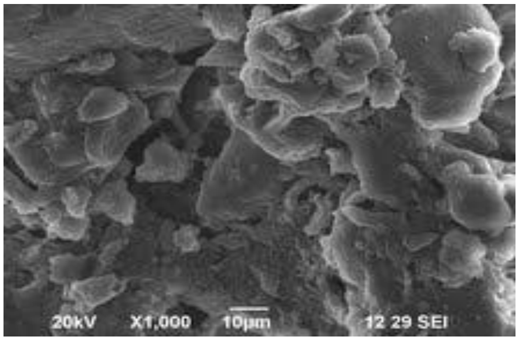

Fig. 1a. SEM image of HAN before Cr(VI) loading

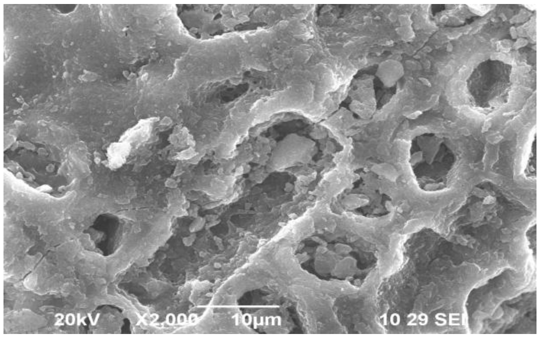

Fig. 1b. SEM image of HAN after Cr(VI) loading

The surface morphology was studied using scanning electron microscopy (SEM) (Fig. 1a.) An SEM image of HAN before Cr(VI) loading at a magnification of 1000X shows that the surface of material was porous, and Fig.1b shows the Cr(VI) loaded sites at magnification of 2000X. It is clear from the SEM image that the external surface of the sample was rough and contained abundant porous structures of different size and shapes. The inner cavities in porous structures provide new structures for the accommodation of Cr(VI) ions.

Effect of pH Cr(VI) Adsorption onto HAN

The pH of the solution is an important factor that controls the uptake of Cr(VI). The experimental results revealed that the percentage adsorption increased as the pH was decreased and reached 97% for 50 mgL^{-1} of Cr(VI) concentrations. When the pH increased above 3, the percent removal decreased (Fig. 2). Similar results have been reported (Donmez and Aksu 2002; Dakiky *et al*. 2002; Selvaraj *et al*. 2003; Yu *et al*. 2003; Ucun *et al*. 2002; Hu *et al*. 2003; Gupta *et al*. 2001). 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 reduction of Cr(VI) to Cr(III) has been found to proceed under highly acidic conditions (*i.e.* pH between 1 and 3). Researchers have observed that oxidation of surface groups of a cellulose-based sorbent material takes place when reductively adsorbing the Cr(VI) ion. Studies involving the blocking of specific sites have shown that both carboxyl groups and amino groups can participate in the reductive adsorption process of Cr(VI) and that the oxidation of the surface often increases the number of carboxylate groups, which are well suited to the bonding of the positively charged Cr(III) ions that result from the process (Hubbe *et al*. 2012). The effects of pH of Cr(VI) adsorption on various adsorbents are shown in Table 1.

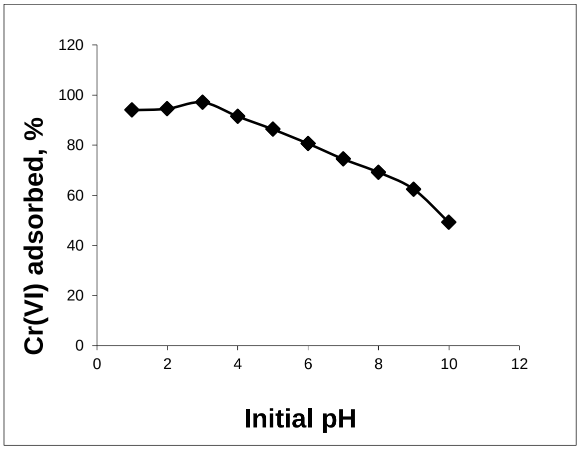

Fig. 2. Effect of pH onto HAN

Effect of Contact Time and Initial Concentration

The uptake of Cr(VI) onto HAN increased with increase in contact time. The adsorption equilibrium was achieved at 2 h. The nature of adsorbent and available adsorption sites affected the rate of adsorption of Cr(VI). The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle, and diffusion through the pores to the internal adsorption sites occurs at pH 3. In the initial stage of adsorption of Cr(VI), the concentration gradient between the film and the available pore sites are large, and hence the rate of adsorption of Cr(VI) is faster. The rate of adsorption decreases in later stage is probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent.

The uptake of Cr(VI) onto HAN as a function of contact time is shown in Fig. 3. It can be seen that with the increase in the Cr(VI) concentration from 50 to 200 mg g^{-1}, the percentage removal decreased from 97% to 58% and the adsorption capacity increased from 12.13 to 36.29 mg g^{-1}. The decrease in percentage can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. The increase in adsorption capacity with increase in Cr(VI) concentration may be due to the higher adsorption rate and utilization of all the available sites for the adsorption at higher concentration.

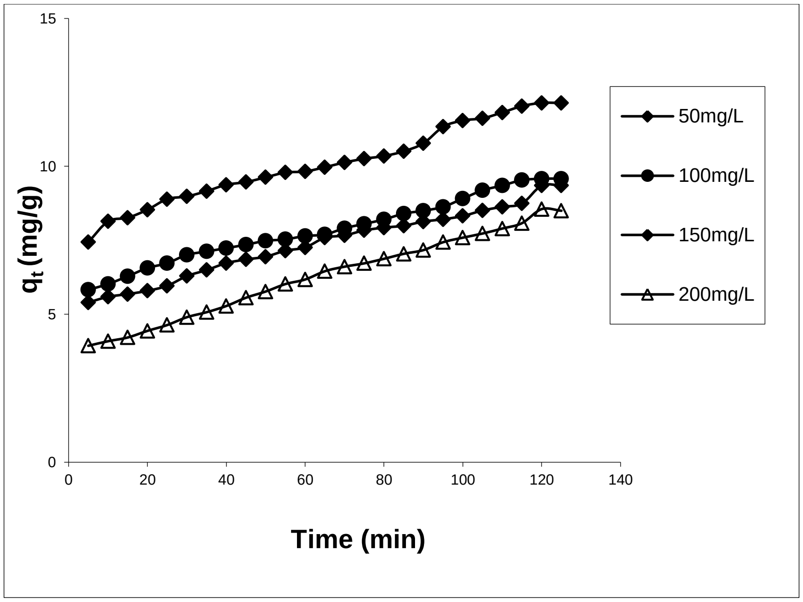

Fig. 3. Effect of contact time and initial concentration

Adsorption Isotherm

The Langmuir Isotherm

The Langmuir isotherm model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface (Langmuir 1918). There is an assumption that sorption takes place at specific homogeneous sites within the adsorbent. Once a metal molecule occupies a site, no further adsorption can take place at that site. It is commonly expressed as:

$$q_e = \frac{(\mathrm{Q_m K_a C_e})}{(1+\mathrm{K_a C_e})} \tag{3}$$

The equation (3) can be linearized into the following form (Kinniburgh 1986; Longhinotti *et al.* 1998),

$$\frac{c_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} c_e \tag{4}$$

where q_e (mg/g) and C_e(mg/L) are defined before in Eq(2). Q_m is a constant and reflects a complete monolayer (mg/g); K_a is the adsorption equilibrium constant (mg/L) that is related to the apparent energy of adsorption and is found to be 0.0846 mg/L. A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/(K_aQ_m)$, which is shown in the Fig. 4. The result obtained from the Langmuir model for the removal of Cr(VI) onto HAN is shown in Table 2.

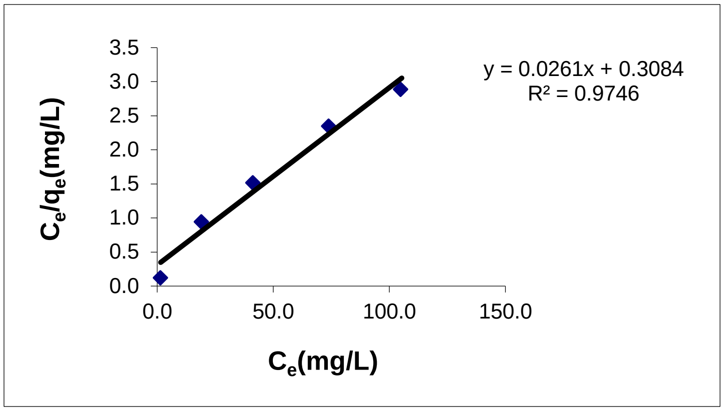

Fig. 4. Langmuir Isotherm for adsorption of Cr(VI) onto HAN

The Freundlich isotherm

The well-known Freundlich isotherm is often used to describe adsorption on heterogeneous surface energy systems (Schneider *et al*. 2007; Cooney 1999; Ozacar 2003; Agyei *et al*. 2000). The Freundlich isotherm can be derived by assuming a logarithmic decrease in enthalpy of adsorption with the increase in the fraction of occupied sites. The isotherm model is commonly expressed by the following non-linear equation:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

A linear form of this expression is,

$$\log q_e = logK_f + \frac{1}{n}\log c_e \tag{6}$$

where K_f is the Freundlich constant and n is the Freundlich exponent. K_f and n can be determined from the linear plot of log q_e versus log C_e, which is given in Fig. 5. The values of the Freundlich constants together with a high coefficient of determination R^2 value of 0.9808 are presented in Table 2, which represents the best fit of experimental data compared to Langmuir isotherm equations. This trend is due to the high surface area of the adsorbent and multilayer of adsorption on the HAN. Freundlich constants K_f and n were found to be 1.0278 mg/g and 3.9793, respectively. It has been shown by McKay *et al.* (1982) that n values between 1 and 10 indicate beneficial adsorption. This trend was investigated also by Schneider *et al.* (2007), who observed that the Freundlich isotherm gave the best fit.

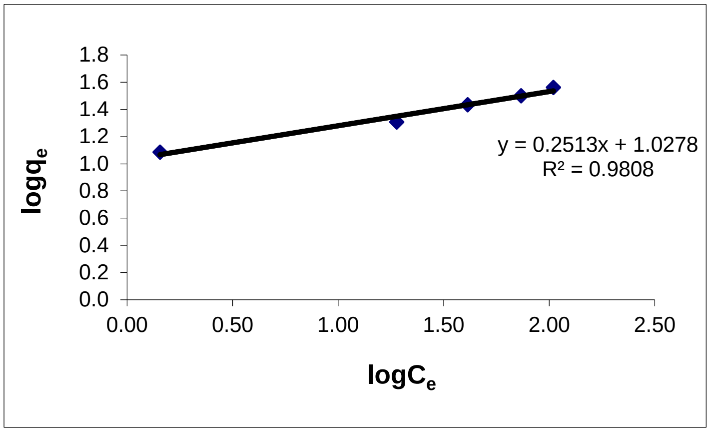

Fig. 5. Freundlich Isotherm for adsorption of Cr(VI) onto HAN

The Temkin Isotherm

Temkin and Pyzkey (1940) considered the effects of some indirect adsorbate or adsorbate interactions on adsorption isotherms and suggested that because of these interactions, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherms (Ozacar 2003; Choy *et al.* 1999) have been used in the following form:

$$q_e = \frac{RT}{b\ \ln(AC_e)} \tag{7}$$

A linear form of the Temkin isotherm can be expressed as,

$$\mathrm{q_e} = \ \beta\ln\alpha + \beta\ln\mathrm{c_e} \tag{8}$$

where

$$\beta = \frac{RT}{b} \tag{9}$$

The constant β is related to heat of adsorption (Akkaya and Ozer 2005; Pearce *et al.* 2003). The adsorption data can be analyzed according to Equation (8). Therefore, a plot of q_e versus $\ln C_e$ enables one to determine the constants A and b. A plot of this type is shown in Fig. 6, and the values of the Temkin constants *A*, *b*, and coefficient of determination are listed in Table 2.

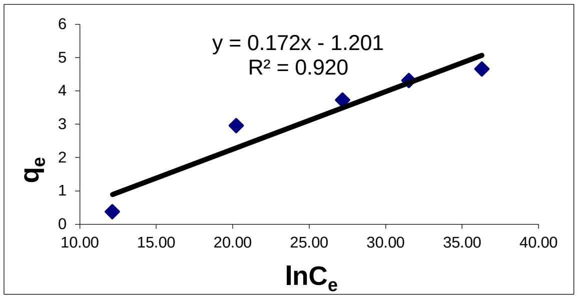

Fig. 6. Temkin Isotherm for adsorption of Cr(VI) onto HAN

The coefficient of determination obtained from the Temkin model was lower compared to those obtained for Langmuir, Freundlich, and D-R models, which indicates a poorer fit for adsorption of Cr(VI) onto HAN.

The Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich isotherm and the Langmuir isotherm equations have been used for the adsorption of metal ions on surfactant-modified montmorillonite and adsorption of acid dyes on activated carbon (Choy *et al.* 1999; Lin and Juang2002) or adsorption of phosphorus on calcined alunite (Ozer 2005). It can be used to describe adsorption on both homogeneous and heterogeneous surfaces (Shahwan and Erten 2004). The Dubinin-Radushkevich equation has the following form (Dubinin and Radushkevich 1947; Gregg and Sing 1982),

$$q_e = lnQ_m - K\varepsilon^2 \tag{10}$$

where Q_m is the theoretical saturation capacity (mg/g), K is a constant related to adsorption energy, and ε is the Polanyi potential calculated from (Eq.11),

$$\varepsilon = \mathrm{RT}\ln(1 + \frac{1}{\mathrm{c_e}}) \tag{11}$$

where R is the gas constant (8.314 J $mol^{-1}K^{-1}$), T is the absolute temperature, and C_e is the equilibrium constant. By plotting q_e versus ε^2, it is possible to determine slope K and the value of Q_m(mg g^{-1}), which is the intercept and plot and is shown in Fig 7. The mean free energy E (KJ mol^{-1}) of adsorption can be estimated by using the K value obtained from the following equation:

$$E = \frac{1}{\sqrt{2K}} \tag{12}$$

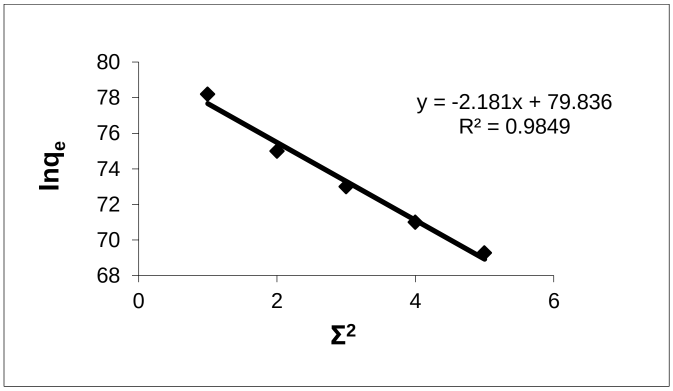

Fig. 7. D-R Isotherm for adsorption of Cr(VI) onto HAN

The calculated Dubinin-Radushkevich constants are given in Table 2. The saturation adsorption capacity Q_m obtained using D-R isotherm model for adsorption of Cr(VI) onto HAN was 18.386 mg g^{-1}. The value of mean total error was determined, and the value was higher than both Freundlich and Temkin values but lower than Langmuir value. Therefore, the Dubinin-Radushkevich equation represents a better fit of experimental data than the Langmuir, Freundlich, and Temkin models.

Table 1. Maximum Adsorption Capacity of Various Low Cost Adsorbents and Agricultural Waste (Gupta and Babu 2009)

S/NO	Adsorbent	Maximum adsorbent capacity Q_m (mg g-1)	Optimum pH
1.	Activated neem leaves	62.97	2
2.	Coconut husk fiber	29	2.05
3.	Leaf mould	25.9	2.5
4.	Pine needles	21.5	2
5.	Treated *Acacia nilotica* leaf	36.29	3
6.	Activated tamarind seeds	.08	7
7.	Polymer grafted sawdust	9.4	3
8.	Maple sawdust	8.2	4
9.	Cactus	7.08	2
10.	Activated alumina	7.44	2
11.	Maize cob	13.8	1.5

Table 2. Isotherm Constants for Cr(VI) Adsorption onto HAN

Isotherm model	Constants and Correlations	Values
Langmuir	Q_m(mg g^{-1})	38.3142
	K_a(L mg^{-1})	0.08463
	R^2	0.9746
Freundlich	1/n	0.2513
	K_f(mg g^{-1})	1.0278
	R^2	0.9808
Dubinin-Radushkevich	Q_m(mg g^{-1})	183.86
	K($\times 10^{-5}$ $mol^2 KJ^{-2}$)	2.181
	E(KJ mol^{-1})	0.4788
	R^2	0.9849
Temkin	α (L mg^{-1})	4.9658
	β (mg L^{-1})	0.1726
	b	14450.8
	R^2	0.920

Kinetic Studies

Figure 3 shows that the amount of Cr(VI) adsorption increased with time and that it remained constant after a contact time of about 2 h. (*i.e.* equilibrium time). The equilibrium time was independent of initial Cr(VI) concentration. The time profile of chromium uptake could be represented by a single, smooth, and continuous curve leading to saturation, suggesting the possible multilayer coverage of chromium on the surface of the adsorbent. In order to investigate the mechanism of adsorption and potential rate controlling steps such as chemical reaction, diffusion control, and mass transport process, kinetic data were analyzed using pseudo-first order (Lagergren 1898), pseudo-second order (Ho *et al.* 2000), Elovich, and intra-particle diffusion (Weber and Morris 1963) equations. Many models such as the homogeneous surface diffusion model and the heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbate inside the adsorbent particles (Fadali *et al.* 2005; Wu 2001; Raven *et al.* 1998). The conformity between experimental data and the model predicted values was expressed by the coefficient of determination (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.

Pseudo first-order model

The sorption kinetics may be described by a pseudo first-order equation (Hossain *et al.* 2005). The pseudo-first-order equation of Lagergren is,

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303t} \tag{13}$$

where q_e and q_t are the amounts of chromium that are adsorbed at equilibrium and at time t (mg g^{-1}), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}). A plot of linear form of pseudo first-order model at all concentrations studied. The slopes and intercepts of plots of log (q_e-q_t) versus t are used to determine the pseudo first-order constant k_1 and equilibrium adsorption density q_e, which is shown in the Fig. 8. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients for the pseudo first order kinetic model obtained at all the studies concentrations were low. This suggests that this adsorption system is not a pseudo-first-order reaction and hence not a diffusion-controlled phenomenon.

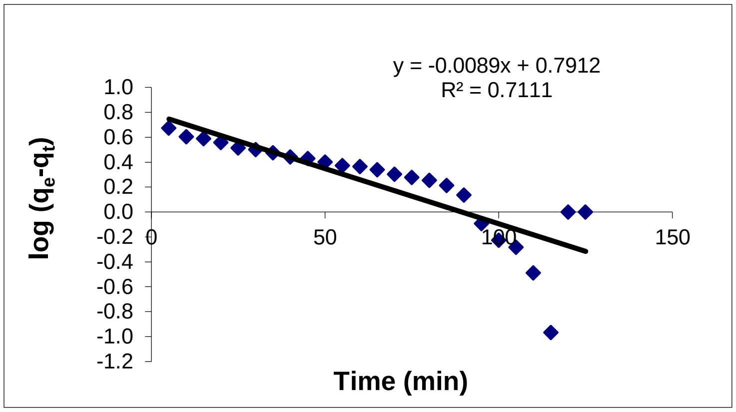

Fig. 8. Pseudo-First-order kinetics for adsorption of Cr(VI) onto HAN

Pseudo second-order model

The adsorption kinetics may also be described by a pseudo-second-order equation (Ho *et al.* 1999).

$$\frac{1}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}(t) \tag{14}$$

The pseudo second-order rate constants were used to calculate the initial adsorption rate, which is given by the following equation,

$$h = K_2 q_e \tag{15}$$

where K_2 and q_e values from the slopes and intercepts of plots t/q_t versus t were used to calculate the pseudo second-order rate constants k_2 and q_e, and the plot is shown in the Fig 9. Table 3 lists the computed results obtained from the pseudo-second-order kinetic model. The coefficients of determination for the pseudo-second-order kinetic model obtained were greater than 0.983 for all concentrations, indicating the applicability of the pseudo-second-order kinetic model. Similar phenomena also have been observed in adsorption of dye RR189 on cross-linked chitosan beads (Chiouand Li 2002), in adsorption of dye BB69 and DR227 on activated clay (Wu 2001), in adsorption of AB9 on mixed sorbents (activated clay and activated carbon) (Ho *et al.* 1999), and in adsorption of Chromium hexavalent on used black tea leaves (Hossain *et al.* 2002).

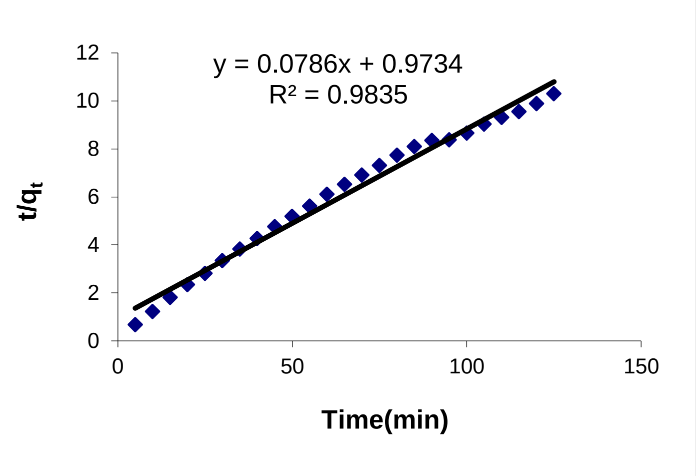

Fig. 9. Pseudo-second-order kinetics for adsorption of Cr(VI) onto HAN

Elovich equation

The Elovich model of the adsorption capacity generally is expressed as the following equation (Chienand Clayton 1980; Sparks 1986),

$$\frac{dqt}{dt} = B_E \exp(-A_E q_t) \tag{16}$$

where B_E is the initial adsorption rate (mg g^{-1}min^{-1}), and A_E is the desorption constant (g/mg) during any experiment. It is simplified by assuming A_E B_E >>*t*. By applying the boundary conditions q_t = 0 at *t* = 0 and q_t = q_t at *t* = *t*, equation (16) becomes:

$$q_t = \frac{1}{A_E}\ln(B_E A_E) + \frac{1}{A_E} ln(t) \tag{17}$$

If Cr(VI) adsorption fits the Elovich model, a plot of *qt* versus ln (*t*) should yield a linear relationship with a slope of 1/A_E and an intercept of (1/A_E) ln ($A_E B_E$). Figure 10 shows a plot of linearization form of Elovich model at all concentrations studied. The initial adsorption rate B_E increased from 15.8154. However, data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 3. The correlation coefficients for the Elovich kinetic model obtained at all the studied concentrations were low. This suggests that this adsorption system is not an acceptable one for this system.

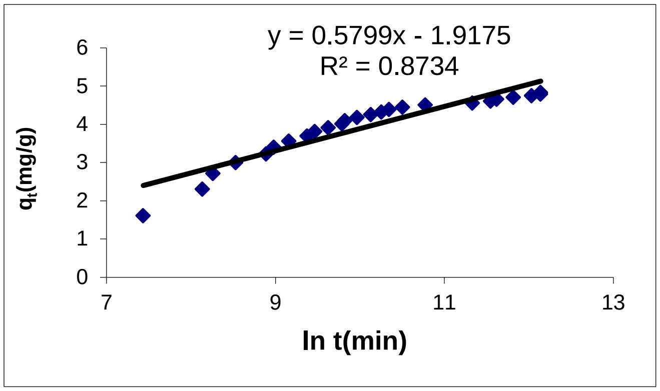

Fig. 10. Elovich equation for adsorption of Cr(VI) onto HAN

Intra-particle diffusion model

When diffusion (internal surface and pore diffusion) of metal ion inside the adsorbent is the rate-limiting step, then adsorption data can be expressed by the following equation (Srivastava *et al.* 1989),

$$q_t = K_{diff}\sqrt{t} + C \tag{18}$$

where, C (mg g^{-1}) is the intercept and K_{dif} is the intra-particle diffusion rate constant (in mg g^{-1} min$^{-1/2}$). The values of q_t were linearly correlated with values of $\sqrt{t}$, and the rate constant K_{dif} was directly evaluated from the slope of the regression line. Such plots may present a multi-linearity (Wu *et al.* 2001; Annadurai *et al.* 2002), indicating that two or more steps take place. The first, sharper portion represents the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intra-particle diffusion is rate-controlling. The third portion is the final equilibrium stage where intra-particle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. Figure 11 shows a plot of the linearized form of the intra-particle diffusion model at all concentrations studied. The values of intercept C provides information about the thickness of the boundary layer; the resistant to the external mass transfer increases as the intercept increases. The constant C was found to increase from with increase in initial concentration from 50 to 200 mg L^{-1} onto HAN, indicating the increase of the thickness of the boundary layer and decrease of the external mass transfer and hence increase in the chance of internal mass transfer. The R^2 values are close to unity indicating the applicability of this model. This may confirm that the intra-particle diffusion is the rate-limiting step.

As can be seen from Table 3, the pseudo second-order kinetic model provided the best correlation for all of the adsorption process, whereas the intra-particle diffusion model fit the experimental data well for an initial period of the adsorption process only. Hence, it was concluded that the pseudo second-order kinetic model represented the rate-limiting step in adsorption, followed by the intra-particle diffusion model. Similar phenomena have also been observed in adsorption of chrome dye (OCRME) on mixed adsorbents-fly ash and coal (Gupta *et al.* 1990), in adsorption of phenols on fly ash (Singh and Rawat1994), in adsorption of lead (II) on cypress leaves (Salim *et al.* 1994), and in adsorption of chromium (VI) on the activated carbon prepared from agricultural wastes (Demirbas *et al.* 2002).

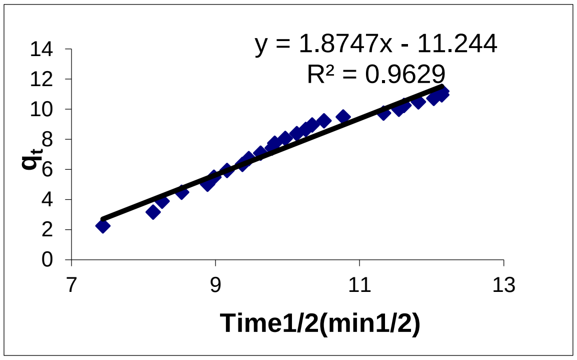

Fig. 11. Intraparticle diffusion for adsorption of Cr(VI) onto HAN

Table 3. Kinetic Parameter for the Adsorption of Cr(VI) onto HAN

Kinetic models	Constants and Correlations	Values
Pseudo- first-order	K_1 (min)	0.0205
	q_e(mg g^{-1})	6.1801
	R^2	0.7111
Pseudo-second-order	K_2(g mg^{-1}min^{-1})	0.006
	q_e(mg g^{-1})	12.7226
	R^2	0.983
Elovich equation	A_E	1.7244
	B_E	15.8154
	R^2	0.873
Intra-particle Diffusion Model	K_{diff}	1.8747
	C	11.244
	R^2	0.9629

Batch Studies of Binary and Ternary Metal System (BMS & TMS)

In the BMS system, one metal ion (Cr(VI) was used as the main metal, the initial concentration of which was made to remain unaltered while the other two metal ion (Co^{2+} and Cu^{2+}) concentrations were varied from 10 to 50 mg L^{-1} to determine the maximum adsorption. The proposed binary mixtures were in the following combinations: Cr-Co and Cr-Cu, whereas a grouping of Cr-Co-Cu was taken as a ternary aqueous phase. The adsorption experiment was carried out in the similar fashion as was performed for SMS. Figure 12 shows that there was a considerable reduction in metal sequestering ability of the adsorbents in binary and tertiary metal systems in comparison with single metal systems. Thus, in the case of binary metal system, the HAN exhibits the highest decline of 47% in adsorption efficiency for Cr-Cu than Cr-Co – 60% compared to 97% percentage removal of Cr(VI) in SMS which is shown in Fig. 12. It was observed that there was a reduction of 68% in Cr(VI) uptake efficiency of HAN in TMS in contrast to metal confiscating potential in SMS (97%). In other words, the percentage adsorption of Cr(VI) in TMS was only 29%.

The results for binary and ternary systems showed clearly that the combined action of multiple ions was antagonistic. Thus, the metal removal efficiency was greater in the single component system in comparison with multiple component one. This is probably due to the absence of competitive processes between metal and adsorbent in a single component system (Kovacevic *et al.* 2000). The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and /or the screening effect by the competing metal ions (Sheng *et al.* 2007). Results of the present research shows that Cr(VI) adsorption is affected by Cu followed by Co. A similar phenomenon had been observed in the binary adsorption of Pb(II), Cu(II), Cd(II), and Ni(II) with the heterogeneous adsorbents (Papini *et al.* 2004; AmnaShoaib *et al.* 2011).

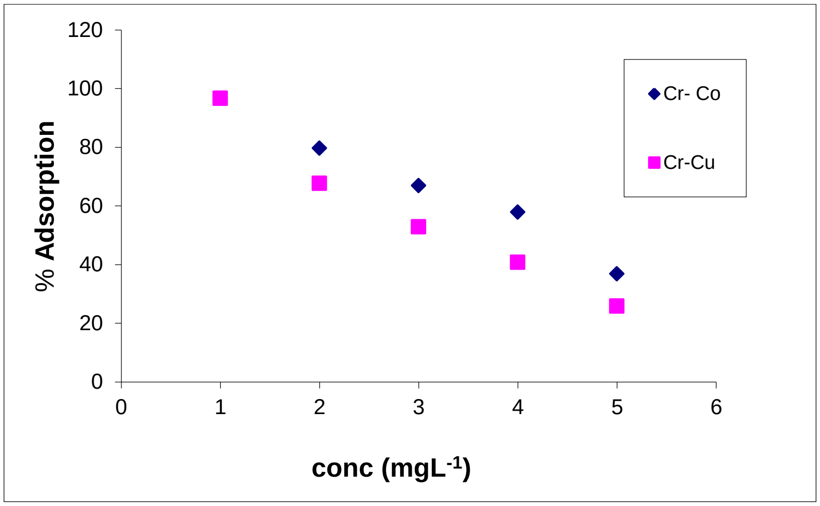

Fig. 12. Adsorption of Cr(VI) onto HAN in binary system

Desorption

The regeneration of the adsorbent and/or disposal of the adsorbate-loaded adsorbent (or spent adsorbent) is very important. It has potential to make the treatment more economical and feasible. Desorption helps to elucidate the mechanism of metal adsorption and recycling of the spent adsorbent and the metal. In the present study, HAN was regenerated and is used for the removal of Cr(VI) at different pH range (1 to10). Cr(VI) adsorption is an example of physical adsorption, and it is possible to regenerate the HAN, which can be considered for reuse.

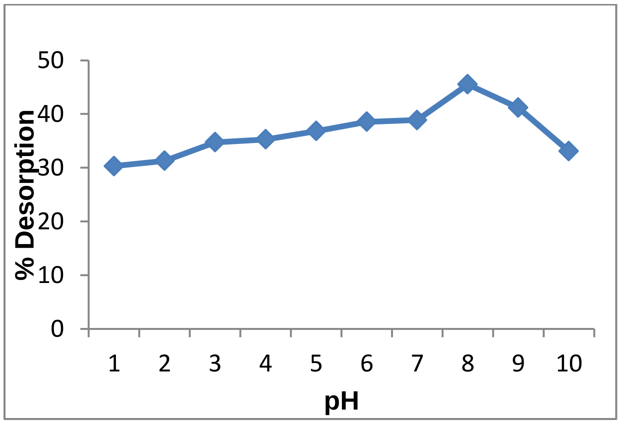

Fig. 13. Desorption of Cr(VI) onto HAN

The adsorption of Cr(VI) onto HAN was found to be dependent on pH, such that increased desorption of Cr(VI) was accomplished by increasing the solution pH. The maximum desorption of Cr(VI) onto HAN is obtained at pH 8 (Fig. 13), which is consistent with electrostatic repulsion between negatively charged Cr(VI) ions and the negatively charged cellulosic surface expected under such conditions. In addition, the fact that no more than 50% of the chromium could be desorbed throughout the pH range studied supports a hypothesis that at least some of the Cr(VI) had been converted to Cr(III) during the process of adsorption. Desorption of metal ions by aqueous solutions reveals that the metal ions were adsorbed onto the adsorbent through an ion-exchange mechanism.

CONCLUSIONS

1. It was shown that *Acacia nilotica* leaves (HAN) can serve as an effective adsorbent for the removal of Cr(VI) metal ion from aqueous solutions. The equilibrium adsorption was achieved in 120 min for adsorption of Cr(VI) onto HAN at pH 3.
2. The removal efficiency increased with an increase in agitation time and with initial concentrations.
3. Freundlich isotherm model fit well with the adsorption data, and the adsorption kinetics could be successfully fitted to the pseudo-second-order kinetic model with intra-particle diffusion as one of the rate-limiting steps.
4. Desorption and recycling ability of HAN was observed to be good. Therefore, the eco-friendly adsorbent HAN is expected to be environmentally and economically feasible for the removal of Cr(VI) from aqueous solutions.

REFERENCES CITED

Agyei, N. M., Strydom, C. A., and Potgieter, J. H. (2000). “An investigation of phosphate ion adsorption from aqueous solution by fly ash and slag,” *Concr. Res*. 30, 823-826.

Ahalya, N., Kanamadi, R. D., and Ramachandra, T.V. (2010). “Removal of hexavalent chromium using coffee husk,” *Int. J. Environ and Poll.* (Article in press) DOI:10.1504/IJEP.2010.035917.

Akkaya, G., and Ozer, A. (2005). “Adsorption of Acid Red 274 (AR 274) on *Dicranellavaria*: Determination of equilibrium and kinetic model parameter,” *Process. Biochem*. 40, 3559-3568.

Amna, S., Taskeen, B., and Nadila, A. (2011). “Removal of Pb(II), Cu(II) and Cd (II)from aqueous solution by some fungi and natural adsorbents in single and multiple metal systems,” *Pak. J. Bot*. 43, 2997-3000.

Annadurai, G., Juang, R. S., and Lee, D. J. (2002). “Use of cellulose-based wastes for adsorption of dyes from aqueous solutions,” *J. Hazard. Mate*. 92, 263-274.

APHA., AWWA., and WPCF., (1985). “Standard methods for the examination of water and wastewater,” 16thEd., Washington, D.C.

Bable, S., and Kurniawan, T.A. (2003). “Low-cost adsorbents for heavy metal uptake from contaminated water; A review,” *J. Hazard. Mater*. 97, 219-243.

Bailey, S. E., Olin, T. I., Bricka, M., and Adrian, D., (1999), “A review of potentially low-cost adsorbents for heavy metals,” *Water Res*. 33, 2469-2479.

Carson, B. L., Ellis, H. V., and McCann, J. L. (1986) *Toxicology and Biological Monitoring of Metals in Humans*, Lewis Publishers, Chelsea, MI.

Chien, S. H., and Clayton, W. R. (1980). "Application of Elovich equation to the kinetics of phosphate release and sorption on soils," *Soil Sci. Soc. Am. J.* 44, 265-268.

Chiou, M. S., and Li, H. Y. (2002). "Equilibrium and kinetic modeling of adsorption of reactive dyes on cross-linked chitosan beads," *J. Hazard. Mater.* 93(2), 233-248.

Choy, K. K. H., McKay, G., and Porter, J. F. (1999). "Sorption of acid dyes from effluents using activated carbon," *Resources, Conservation and Recycling* 27, 57-71.

Cooney, D. O. (1999). *Adsorption Design for Wastewater Treatment*, Lewis Publication, Boca Raton, FI, 189.

Dakiky, M., Khami, A., Manassra, A., and Mer'eb, M. (2002). "Selective adsorption of chromium (VI) in industrial wastewater using low cost abundantly available adsorbents," *Advances in Environmental Res.* 6(4), 533-540.

Demirbas, E., Kobya, M., Oncel, M. S., and Sencan, S. (2002). "Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies," *Bioresour. Technol.* 84, 291-293.

Donmez, G., and Aksu, Z. (2002). "Removal of chromium (VI) from wastewaters by *Dunaliella* species," *Process Biochem.* 38(5), 751-762.

Dubinin, M. M., and Radushkevich, L. V. (1947)."Equation of the characteristics curve of activated charcoal," *Proc. Acad. Sci. USSR* 55, 331-333.

El-Geundi, M. S. (1997)."Adsorption for industrial pollution control," *Adsorp.Sci. Technol.*15, 777-787.

Fadali, O. A., Ebrahiem, E. E., Magdy, Y. H., Daifullah, A. A. M., and Nassar, M. M. (2005). "Removal of chromium from tannery effluents by adsorption," *J. Environ. Sci. Health, Part A Environ. Sci. En.* 9, 465-472.

Goyer, R., and Mehlman, A. (1977).*Toxicology of Trace Elements*, John Wiley & Sons Inc., New York.

Gregg, S. J., and Sing, K. S. W. (1982).*Adsorption, Surface Area and Porosity,* Second Ed., Academic Press, London.

Gupta, G. S., Prasad, G., and Singh,V. N. (1990). "Removal of chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal," *Wat. Res.* 24, 45-50.

Gupta, S., and Babu, B.V. (2009). "Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: equilibrium, kinetics and regeneration studies," *Chem. Eng. J.*, 150, 352-365.

Gupta,V. K., Shrivastava, A. K., and Jain, N. (2001). "Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species," *Wat. Res.* 35(17), 4079-4085.

Harland, C. E. (1994). *Ion Exchange Theory and Practice*," 2nd Ed., Royal Society of Chemistry, Cambridge, United Kingdom, 258.

Ho, Y. S., and McKay, G. (1999). "Pseudo-second-order model for adsorption processes," *Process Biochem.* 34, 451-465.

Hossain, M. A., Kumita, M., Michigami, Y., and Mori, S. (2005). "Kinetics of Cr(VI) adsorption on used black tea leaves," *J. Chem. Eng. Japan,* 38(6), 402-406.

Hu, Z., Lei, L., Li, Y., and Ni, Y. (2003). "Chromium adsorption on high performance activated carbon from aqueous solution," *Sep. and Purifi. Technol.* 31(1), 13-18.

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2012), "Cellulosic substances for the removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287.

Kinniburgh, D. G. (1986). "General purpose of adsorption isotherms," *Environ. Sci. Technol*. 20, 895-904.

Kovacevic, Z. F., Sipos, L., and Briski, F. (2000). "Biosorption of chromium, copper nickel and zinc ion onto fungal pellet of *Aspergillus niger* 405 from aqueous solution," *Food Technol. Biotechnol.* 38, 211-216.

Langmuir, I. (1918). "The adsorption of gases on plane surface of glass, mica and platinum," *J. Am. Chem. Soc.* 40, 1361-1403.

Lin, S. H., and Juang, R. S. (2002). "Heavy metal removal from water by sorption using surfactant-modified montmorillonite," *J. Hazard. Mater*. 92, 315-326.

Longhinotti, E., Pozza, F., Furlan, L., Sanchez, M. D. N. D., Klung, M., and Laranjeira, M. C. M. (1998). "Adsorption of anionic dyes on the biopolymer chitin," *J. Braz. Chem. Soc*. 9, 435-440.

McKay, G., Blair, H.S., and Gardener, J.R. (1982) 'Adsorption of dyes on chitin I. Equilibrium studies', *Journal of Applied Polymer Science*, 27, 3043–3057.

Ozacar, M. (2003). "Equilibrium and kinetic modeling of adsorption of phosphorus on calcined alunite," *Adsorption* 9, 125-132.

Papini, M. P., Saurini, T., Bianchi, A., Majone, M., and Beccari, M. (2004). "Modelling the competitive adsorption of Pb, Cu, Cd, and Ni onto a natural heterogeneous sorbent material," *Industrial and Eng. Chem. Res.* 43, 5032-5041.

Pearce, C. I., Lioyd, J. R., and Guthrie, J. (2003)."The removal of dye from textile waste water using whole bacterial cells: A review," *Dyes and Pigments.*58, 179-196.

Raven, K. P., Jain, A., and Loeppert, R. H. (1998). "Arsenite and aresenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes," *Environ. Sci. Technol*. 32, 344-349.

Rousseau, R. W. (Ed.) (1987). *Handbook of Separation Process Technology*, Wiley, New York.

Salim, R., Al-Subu, M. M., and Qashoa, S., (1994). "Removal of lead from polluted water using decaying leaves," *J. Environ. Sci. Health, Part A Environ. Sci. Eng.* 29, 2087-2114.

Santhi, T., Prasad, A. L., and Manonmani, S. (2011). "A comparative study of microwave and chemically treated *Acacia nilotica* leaf as an eco-friendly adsorbent for the removal of rhodamine B dye from aqueous solution," *Arabian J. of Chemistry.* (Article in press) http://dx.doi.org/10.1016/j.arabjc.2010.11.008.

Schneider, R. M., Cavalin, C. F., Barros, M. A. S. D., and Tavares, C. R. G. (2007). "Adsorption of chromium ions in activated carbon," *Chem. Eng. J*. 132, 355-362.

Selvaraj, K., Manonmani, S., and Pattabhi, S. (2003). "Removal of hexavalent chromium using distillery sludge," *Bioresource Technol*. 89(2), 207-211.

Sheng, P. X., Ting, Y. P., and Chen, J. P. (2007), "Biosorption of heavy metal ions (Pb, Cu and Cd) from aqueous solution by the marine alga *Sargassum* sp. in single and multiple metal system," *Industrial and Eng. Chem. Res*. 46, 2438-2444.

Singh, B., and Rawat, N. S. (1994), "Comparative sorption kinetic studies of phenolic compounds on fly ash and impregnated fly ash," *J. Chem. Tech. Biotechnol*. 61, 57-65.

Sparks, D. L., *Kinetics of Reaction in Pure and Mixed Systems, in Soil Physical Chemistry,* CRC Press, Boca Raton (1986).

Srivastava, S.K., Tyagi, R., and Pant, N., (1989). "Adsorption of heavy metal ions on carbonaceous martial developed from the waste slurry generated in local fertilizer plants," *Wat. Res*. 23, 1161-1165.

Temkin, M. J., and Pyzhey, V. (1940).“Recent modifications to Langmuir isotherms,” *Acta Physiochem., USSR* 12, 217-222.

Ucun, H., Bayhan, Y. K., Kaya, Y., Cakici, A., and Algur, O. F. (2002). “Biosorption of chromium (VI) from aqueous solution by cone biomass of *Pinus sylvestris*,” *Bioresource Technol.* 85(2), 155-158.

Wu, F. C., Tseng, R. L., and Juang, R. S. (2001). “Adsorption of dyes and phenols from water on the activated carbons prepared from corncob wastes,” *Environ. Technol*. 22, 205-213.

Wu, F. C., Tseng, R. L., and Juang, R. S. (2001). “Kinetics of color removal by adsorption from water using activated clay,” *Environ. Technol*. 22, 721-729.

Yu, L. J., Shukla, S. S., Dorris, K. L., Shukla, A., and Margrave, J. L. (2003).“Adsorption of chromium from aqueous solutions by maple sawdust,” *J. Hazard.Mater,* 100(1-3), 53-63.

Zhou, Y., Zhang, L., Fu, S., Zheng, L., and Zhan, H. (2012). “Adsorption behavior of Cd^{2+}, Pb^{2+}, and Ni^{2+} from aqueous solutions on cellulose-based hydrogels,” *BioResources* 7(3), 2752-2765.

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