Adsorption 10: 327–338, 2004

Adsorption of Chromium (VI) on *Azadirachta Indica* (Neem) Leaf Powder

ARUNIMA SHARMA AND KRISHNA G. BHATTACHARYYA*
Department of Chemistry, Gauhati University, Guwahati 781 014, Assam, India
krishna111@sancharnet.in

Received June 17, 2003; Revised August 20, 2004; Accepted September 23, 2004

Abstract. A novel adsorbent was developed from mature leaves of the Neem tree (*Azadirachta Indica*) for removing metal ions from water. The adsorbent, in the form of fine powder, was found to be very effective in removing chromium (VI) from aqueous solution. The adsorption was carried out in a batch process taking different concentrations of the metal ion in aqueous solution with variation in adsorbent amount, pH, agitation time and temperature. The suitability of the adsorbent was tested with Langmuir and Freundlich isotherms and with various equilibrium kinetic data. A small amount of the Neem Leaf Powder (NLP) (1.6 g dm^{-3}) could remove as much as 87% of Cr (VI) in 300 min from a solution of concentration 14.1 mg dm^{-3} at 300 K. The optimum range of pH for the adsorption process was 4.5–7.5 and since the natural pH of the Cr (VI) solution was 5.5, no addition of acid or alkali was necessary for achieving maximum adsorption. The adsorption coefficients indicated a high potentiality for the NLP to be used as an adsorbent for removing Cr (VI) from water.

Keywords: Neem Leaf Powder, Chromium (VI), Metal removal by adsorption

1. Introduction

Adsorption onto solid adsorbents can effectively remove pollutants from both aqueous and gaseous streams and therefore has considerable environmental significance. Activated carbon, the most popular adsorbent, has been traditionally used for the removal of odor, taste, and colors, which are designated as trace pollutants. Its high adsorptive capacity and versatility have expanded its application to the treatment of numerous industrial waste streams. Other commercial adsorbents, having increased reversibility, have been recently reviewed (Thomas and Crittenden, 1998) and although their versatility and adsorption capacity are generally less than those of activated carbon, they are advantageous for certain applications. Such low cost adsorbents (Ho and McKay, 1999; Bailey et al., 1999) have found use in laboratory scale for treatment of various pollutants from water and wastewater.

The present work aims to develop a non-conventional adsorbent from the leaves of the *Azadirachta Indica* (Neem) tree to be used for toxic pollutants, such as Cr (VI) in aqueous medium. Chromium is a naturally occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. The most common forms of chromium present in the environment are chromium (0), chromium (III), and chromium (VI). Chromium (III) occurs naturally in the environment and is an essential nutrient that helps the use of sugar, protein, and fat by the body (ATSDR, 2001). Chromium (VI) and chromium (0) are generally produced by industrial processes. The metallic chromium [Cr (0)] is used for making steel. Chromium (VI) and chromium (III) are used in chrome plating, dyes and pigments, leather tanning, and wood preserving. Chromium enters air, water, and soil mostly in the forms of Cr (III) and Cr (VI). In air, chromium compounds are present mostly in the form of fine dust particles, which eventually settle over land and water. Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper

---

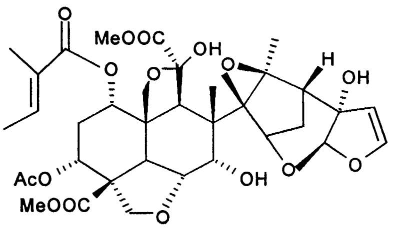
*To whom correspondence should be addressed.

in the soil to underground water. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. Several studies have shown that chromium (VI) compounds can increase the risk of lung cancer (Norseth, 1986; U.S Department of Health and Human Services, 1991; Cieslak-Golonka, 1995). The World Health Organization (WHO) has categorized chromium (VI) as a human carcinogen (WHO, 1974).

Adsorption at a surface or interface is largely the results of binding forces between the individual atoms, ions or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions. The net dispersion, electrostatic, chemisorptive and functional group interactions broadly define the affinity of an adsorbent for a specific adsorbate. A number of parameters, specific to a given system, affect adsorption. For the adsorbate, concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration and the nature of background or competitive adsorption are important. The important characteristics of the adsorbent that determine equilibrium capacity and rate, are surface area, the physicochemical nature of the surface, the availability of that surface to adsorptive molecules or ions, the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also markedly influence adsorption to the extent that they effect changes in any one or more of the above parameters. The accumulation of concentration of a solute at the surface of a solid is essentially based on adsorbate-adsorbent interaction involving van der Waals forces due to permanent dipoles, induced dipoles and quadruples. An adsorbate molecule interacts with a large assemblage of atoms in the solid surface simultaneously.

No reference to work involving the use of Neem leaf powder for the removal of heavy metals from aqueous solutions has been found in the literature. The potentiality of Neem has been widely explored for solving various problems related to agriculture, public health, population control and environmental pollution. Awareness about the Neem-based technology, whether for pest management, public health, family welfare programmes, reforestation, etc. (National Research Council, 1992), has grown several fold, and production and commercialization of various neem products for domestic use and exports have been taken up aggressively by various agencies. No other plant perhaps yields as large a range of useful products as the Neem. The products, extracted from the Neem (Chopra et al., 1956; Chattopadhyay et al., 1993; Rawat, 1994; Venugopal and Venugopal, 1994; Majumdar et al., 1998) include antimalarials, spermicidals, antituberculosis agents, antipyrrhetics, anti viral drugs, antiseborrhoeics, antiallergic medicines, antienzemic and antifungal agents, antiscabic, antifurancular, and antidermatic compounds, bactericides, antigingivitis, insecticidal, and antiinflammatory medicines, larvicidal, antiperiodontitic, piscidal, ameobicidal, anticardiac arrest and diuretic compounds, nematicidal agents, etc. The Neem tree has been recognized as a natural air purifier and it has been suggested that the planting of Neem trees on roadside is an effective way to regulate traffic-related pollution.

The *Azadirachta Indica* tree grows almost all over the world and is very common in India. It is a fast growing, usually evergreen plant, which reaches a height of 15–20 m and a trunk girth of 1.5–3.5 m (Schmutterer, 1995). The unpaired, pinnate leaves are 20–40 cm long containing about 30 leaflets on both sides. The leaflets are 5–8 cm long with dark green colour and are asymmetrical in nature. Although several groups of natural products have been isolated from Neem, little work seems to have been done to evaluate structure-activity relationships (Kraus, 1995). The active principles belong to the group of tetranortriterpenoids, diterpenoids, triterpenoids, pentanortriterpenoids, and a small number of nonterpenoidal ingredients. The best-known active ingredients in Neem are *azadirachtin, salannin, meliantriol* and *nimbin*, which have been demonstrated to have ability to block insect growth covering a large range of species including the most deadly pests of agriculture and human health. These ingredients, commonly known as limonoids, are structurally related to one another. The structure of *azadirachtin*, which was the first active ingredient isolated from Neem and



Azadirachtin

Figure 1. Structure of the active ingredient a*zadirachtin* of the Neem leaves.

which has been projected as the main agent in Neem for fighting insects, is shown in Fig. 1 (Kraus, 1995).

The physicochemical characteristics of fresh Neem leaves have been reported as follows (Neem Foundation, 1997):

Moisture	59.4%	Proteins	7.1%
Fat	1.0%	Fiber	6.2%
Carbohydrates	22.9%	Minerals	3.4%
Calcium	510 mg/100 g	Phosphorous	80 mg/100 g
Iron	17 mg/100 g	Thiamine	0.04 mg/100 g
Niacin	1.40 mg/100 g	Vitamin C	218 mg/100 g
Carotene	1998 microgram /100 g	Calorific value	1290 Kcal/Kg
Glutamic acid	73.30 mg/100 g	Tyrosine	31.50 mg/100 g acid
Aspartic acid	15.50 mg/100 g	Alanine	6.40 mg/100 g
Proline	4.00 mg/100 g	Glutamine	1.00 mg/100 g

2. Experimental

All the chemicals used in the experiments were of analytical grade and they were used without further purification. Chromium (VI) (up to 0.5%) was determined spectrophotometrically (Perkin-Elmer Lambda EZ-201) in alkaline solution as chromate following the standard procedure (Vogel, 1969). The absorbance of the Cr (VI) solutions was measured at 365–370 nm. The standard solutions used for the preparation of the calibration curve had the same alkalinity as the sample solution.

2.1. Preparation of Adsorbent

Mature Neem leaves, collected from a number of tall Neem trees (District Morigaon, Assam, India) were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry first at room temperature in a shade and then in an air oven at 333–343 K for 30 h till the leaves became crisp (the active principles decompose if high temperature is used (Kraus, 1995), and therefore, the drying of the leaves was done only 30–40° above the ambient temperature), which were then crushed into a fine powder in a mechanical grinder. The Neem Leaf Powder (NLP) was sieved and the fraction, $>53\ \mu$ and $<74\ \mu$, was selected as the adsorbent. This fraction was again washed a number of times with double distilled water till the washings are free of color and turbidity. After drying for several hours at room temperature, the Neem Leaf Powder (NLP) was preserved in glass bottles for use as an adsorbent.

2.2. Adsorption Experiments

The synthetic solutions of Cr (VI) for the present study were made from a stock solution containing 1000 mg of $K_2Cr_2O_7$ (Assay 99% $K_2Cr_2O_7$, E. Merck India, Mumbai) in 1 dm^3. The pH of the aqueous solutions of $K_2Cr_2O_7$ was $\sim$5.5, which did not change much with dilution. A series of experiments with pH of the initial Cr (VI) solution varying between 2.5 and 10.0 (by addition of drops of 0.1 M HNO_3 and 0.1 M NaOH solutions) showed that the adsorption of Cr (VI) was maximum around the natural pH ($\sim$5.5) of the Cr (VI) solutions. Consequently, all the experiments were done without adjusting the pH of the Cr (VI) solutions.

The batch adsorption was carried out in 100 ml borosil conical flasks by agitating a pre weighed amount of the NLP with 50 ml of the aqueous Cr (VI) solution of concentration 7.1, 10.6, 14.1, 17.7, 21.2 and 24.8 mg dm^{-3} (equivalent to $K_2Cr_2O_7$ concentration of 20, 30, 40, 50, 60 and 70 mg dm^{-3}). The conical flasks were kept in a constant temperature, water bath shaker (NSW, Mumbai) and the mixtures were agitated for a pre-determined time interval at a constant speed. Experiments were carried out by varying the adsorbent amount (from 1.6 to 14.0 g dm^{-3}), the adsorbate concentration (7.1 to 24.8 mg dm^{-3} with respect to Cr (VI)), the agitation time (60 to 300 min) and the adsorption temperature (300 to 323 K). After adsorption, the mixture was centrifuged (Remi Research Centrifuge, R24) when the adsorbent settled quickly and the metal ion remaining unabsorbed was determined spectrophotometrically.

2.3. Mathematical Models

Adsorption is normally accompanied by release of heat and a decrease in Gibbs energy and entropy. If a quantity q of adsorbate is adsorbed by a porous solid at constant temperature and the steady state equilibrium partial pressure is p (or concentration c) then the function $q(p)$ describes the adsorption isotherm. A variety of isotherm equations have been in use, some of which have a theoretical foundation and some being of mere empirical nature. Many of these equations are valid over small relative pressure or concentration changes but do not fit experimental data when tested over the full range of relative pressures or concentrations. In the present work, two of these isotherms only have been tested.

The Langmuir Isotherm. This isotherm is applicable when the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached. The isotherm assumes a dynamic equilibrium between the adsorbed phase and the vapor/liquid phase. Langmuir described chemisorption as the formation of an ionic or covalent bond between adsorbent and adsorbate (Langmuir, 1918). The isotherm equation gives the fractional coverage (θ) in the form

$$\theta = q_\mathrm{e}/q_\mathrm{m} = bC_\mathrm{e}/(1 + bC_\mathrm{e}) \tag{1}$$

where b is $k_\mathrm{a}/k_\mathrm{d}$ (where k_a and k_d are the respective rate constants for adsorption and desorption, respectively) and q_m is the quantity of adsorbate required to form a single monolayer on unit mass of the solid and q_e is the amount adsorbed on unit mass of the solid when the equilibrium concentration is C_e. The ratio $q_\mathrm{e}/q_\mathrm{m}$ can be measured and expressed in different ways. The most widely used form, known as the two-parameter equation for a single solute system, is of the form represented by (1).

Equation (1) can be rearranged to the form:

$$C_\mathrm{e}/q_\mathrm{e} = (1/bq_\mathrm{m}) + (1/q_\mathrm{m})C_\mathrm{e} \tag{2}$$

which shows that a plot of ($C_\mathrm{e}/q_\mathrm{e}$) vs. C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then give the values of q_m and b. These expressions have been shown to be valid in relatively higher concentration ranges (Dutta, 1999).

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L (Hall et al., 1966), also known as the separation factor, given by—

$$R_\mathrm{L} = 1/(1 + bC_\mathrm{e}) \tag{3}$$

where C_e is any equilibrium liquid phase concentration of the solute at which adsorption is carried out. The value of R_L lies between 0 and 1 for favorable adsorption, while $R_\mathrm{L} > 1$ represents unfavorable adsorption, and $R_\mathrm{L} = 1$ represents linear adsorption while the adsorption process is irreversible if $R_\mathrm{L} = 0$.

The Freundlich Isotherm. There is abundant evidence to show that, for many systems, the heat of adsorption decreases in magnitude with increasing extent of adsorption. This has been well taken care of by the Freundlich isotherm (Thomas and Crittenden, 1998), previously considered to be an empirical isotherm. This isotherm was later derived by Laidler (Thomas and Crittenden, 1998) who showed that for small values of θ, the following equation can be obtained:

$$\ln\theta = (\mathrm{RT}/Q_0)\ln\, p + \text{constant} \tag{4}$$

Q_0 is a constant related to the energy distribution of the adsorption sites. The above equation may be recast into the familiar Freundlich isotherm

$$\theta = K_f\, p^n \tag{5}$$

which is valid for $n < 1$ and K_f and n are known as Freundlich coefficients. For adsorption from solution, Eq. (5) takes up the form:

$$q_\mathrm{e} = K_f\, C_e^n \tag{6}$$

The Freundlich coefficients can be determined from the plots of log q_e versus log C_e on the basis of the linear form of the equation—

$$\log q_\mathrm{e} = \log K_f + n \log C_\mathrm{e} \tag{7}$$

Adsorption is usually an exothermic process and as the temperature increases, the amount adsorbed at a given concentration decreases in accordance with Le Chatelier's principle.

Kinetics of Adsorption. The study of adsorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of the reactions. Any adsorption process is normally controlled by three diffusion steps: (i) transport of the solute from bulk solution to the film surrounding the adsorbent, (ii) from the film to the adsorbent surface, and (iii) from the surface to the internal sites followed by binding of the metal ions to the active sites. The slowest of these steps determines the overall rate of the adsorption process and usually it is thought that the step (ii) leads to surface adsorption and the step (iii) leads to intra-particle adsorption. It is generally acknowledged throughout the literature that the dominant rate-controlling step is not the actual physical attachment of adsorbate to adsorbent but rather intraparticle transport of the solute within the porous structure of the adsorbent to the available surface. Interparticle transport from bulk fluid to the external surface of the porous adsorbent may also have an effect on the overall rate of adsorption under some circumstances.

Therefore, the rate law describing the sorption system should address the requirements of knowledge of all the molecular details of the reaction including the energetics and the stereochemistry, interatomic distances and angles throughout the course of the reaction, and the individual molecular steps involved in the mechanism. Several kinetic models are in use to explain the mechanism of the adsorption processes. A simple pseudo first-order equation due to Lagergren was used by Ho and McKay (1998, 1999):

$$\mathrm{d}q_t/\mathrm{d}t = k_{\mathrm{ad}}(q_\mathrm{e} - q_t) \tag{8}$$

where q_e and q_t are the amount of adsorption at equilibrium and at time t respectively, and k_{ad} is the rate constant of the pseudo first-order adsorption process. The integrated rate law after application of the initial condition of $q_t = 0$ at $t = 0$, becomes

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e} - k_{\mathrm{ad}}/2.303.t \tag{9}$$

Plot of log $(q_\mathrm{e} - q_t)$ vs. t gives a straight line for first order adsorption kinetics, which allow computation of the adsorption rate constant, k_{ad}. This equation differs from a true first order equation in two ways: (i) the parameter k_{ad} $(q_\mathrm{e} - q_t)$ does not represent the number of available sites, and (ii) the parameter log (q_e) is an adjustable parameter and often it is found not equal to the intercept of the plot of log $(q_\mathrm{e} - q_t)$ vs. t, whereas in a true first order log q_e should be equal to the intercept (Ho and McKay, 1998). In such cases, applicability of the second order kinetics has to be tested with the rate equation—

$$\mathrm{d}q_t/\mathrm{d}t = k_2(q_\mathrm{e} - q_t)^2 \tag{10}$$

where q_e and q_t are the sorption capacities (mg g^{-1}) at equilibrium and at time t, respectively and k_2 is the second order rate constant (g mg^{-1} min^{-1}). From the boundary conditions, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation becomes:

$$1/(q_\mathrm{e} - q_t) = (1/q_\mathrm{e}) + k \cdot t \tag{11}$$

which can be written in the linear form,

$$t/q_t = 1/h + (1/q_\mathrm{e}) \cdot t \tag{12}$$

where $h = kq_\mathrm{e}^2$ can be regarded as the initial sorption rate as $t \rightarrow 0$. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows computation of q_e, k and h without having to know any parameter beforehand.

The variation in the amount of adsorption with time at different initial metal ion concentrations may be processed further for evaluating the role of diffusion in the adsorption of Cr (VI) on NLP powder. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates and then, diffusion of the solute molecules into the interior of the pores—which is likely to be a slow process and is therefore, rate determining. The intra-particle diffusion rate constant (k_p) is given by the equation (Weber and Morris, 1962):

$$q_t = k_p \cdot t^{1/2} \tag{13}$$

where k_p is the intra-particle diffusion rate constant. If a linear relation was observed (McKay et al., 1980), the k_p values could be determined from the slope.

3. Results and Discussion

Determination of the surface area of the powder was cumbersome, as the same could not be degassed properly due to temperature limitation. Measurement, with this limitation, yielded a value of ~1.3 m^2 g^{-1} for the surface area of the Azadirachta indica powder, which is much less compared to that of the conventional activated carbon powders. Electron micrographs of the powder revealed the particles to be non-uniform in size and shape and with a large number of steps and kinks on the external surface.

3.1. Effect of Agitation Time

The kinetics of Cr (VI) adsorption on Neem Leaf Powder (NLP) was studied by carrying out batch experiments with a constant Cr (VI) concentration of 14.1

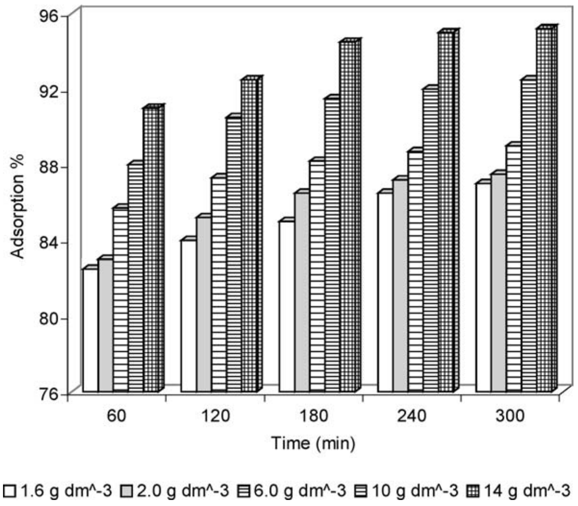


Figure 2. Influence of agitation time and NLP amount on adsorption of Cr (VI) (Initial Cr (VI) concentration 14.1 mg dm^{-3}, temperature of adsorption 300 K).

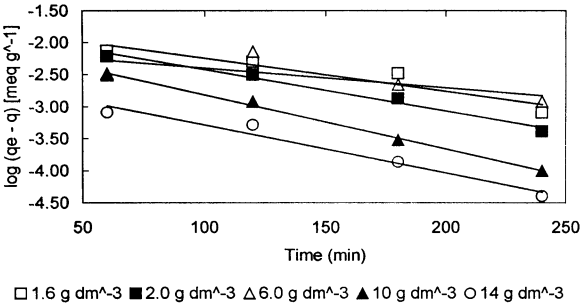


Figure 3. Pseudo first order plot for adsorption of Cr (VI) on five different amounts of the adsorbent, NLP (Initial Cr (VI) concentration 14.1 mg dm^{-3}, temperature of adsorption 300 K).

mg dm^{-3} at 300 K with five different NLP amounts of 1.6, 2.0, 6.0, 10.0 and 14.0 g dm^{-3} when the agitation time was varied from 60 to 300 min at intervals of 60 min in each case. A gradual increase in the extent of adsorption with time was observed (Fig. 2). The Cr (VI) adsorption increased from 82.5 to 87% in the time interval of 60 to 300 min for an amount of 1.6 g NLP per dm^3. In the same interval of time, Cr (VI) removal increased from 91.0 to 95.2% if the NLP amount was increased to 14.0 g dm^{-3}. Such behaviour is expected in a batch reactor with either constant adsorbent amount and varying initial adsorbate concentration or vice versa (Chu, 2002). An increase in the adsorbent amount should result in a decrease in the time required to reach apparent equilibrium while the fraction of the metal removed from the aqueous phase should increase with an increase in the adsorbent amount. For the same batch of experiments, the amounts of Cr (VI) adsorbed in meq per g of NLP (Table 1) also increased with increasing agitation time, but the amount adsorbed in meq decreased with increasing amount of NLP per dm^3 although there was an actual increase in the extent of adsorption.

The nature of the adsorbent and its compactness affected the time needed to reach equilibrium. In the present case, the extent of adsorption changed very little after 180 min (Table 1) and equilibrium conditions could be assumed at 300 min for applying Lagergren pseudo first order kinetics. The linearity of the Lagergren plots (Fig. 3, R^2 values in the range of 0.89 to 0.99), obtained by plotting log $(q_e - q_t)$ (meq g^{-1}) vs. agitation time for adsorption of Cr (VI) from a solution of concentration 14.1 mg dm^{-3} at 300 K for all the six different amounts of the adsorbent, showed that the adsorption process might be following the pseudo first order kinetics. The rate constants, calculated from the slopes of the best-fit lines, were in the range of 6.91×10^{-3} to 19.58×10^{-3} min^{-1} with a mean value of 14.1×10^{-3} min^{-1}. Dakiky et al. (2002) have reported very similar values for Cr (VI) removal on a variety of adsorbents (wool 3.96×10^{-3} min^{-1}, cactus

Table 1. Variation in the amount of Cr (VI) adsorbed on NLP at 300 K with increasing agitation time (initial Cr (VI) concentration 14.1 mg dm^{-3}).

	Amount adsorbed $q_e = x/m$ (meq g^{-1}) for NLP amount				
Time (min)	1.6 g dm^{-3}	2.0 g dm^{-3}	6.0 g dm^{-3}	10.0 g dm^{-3}	14.0 g dm^{-3}
60	0.1398	0.1125	0.0387	0.0239	0.0176
120	0.1424	01155	0.0395	0.0245	0.0179
180	0.1441	0.1173	0.0399	0.0248	0.0183
240	0.1466	0.1182	0.0401	0.0250	0.0184
300	0.1474	0.1186	0.0402	0.0251	0.0184

leaves 6.80×10^{-3} min^{-1}, sawdust 9.00×10^{-3} min^{-1}, almond 8.80×10^{-3} min^{-1}, olive cake 8.99×10^{-3} min^{-1}) at pH 2 and 30°C.

Lagergren equation has been adequate to describe the adsorption process in a large number of cases (Ho and McKay, 1998, 1999) although this equation does not provide a concrete picture about the mechanism of the adsorption process. Besides, log q_e values obtained from the intercepts of Lagergren plots do not match with the experimental log q_e values of the present work as shown below:

NLP amount (g dm^{-3})	1.6	2.0	6.0	10.0	14.0
log q_e (meq g^{-1}) Experimental	−0.832	−0.926	−1.396	−1.600	−1.734
log q_e (meq g^{-1}) Lagergren plots	−1.733	−1.774	−2.097	−1.969	−2.535

(For initial Cr (VI) concentration of 14.1 mg dm^{-3}, temperature 300 K).

The first order kinetics are thus inadequate to give a good account of the kinetics of Cr(VI) adsorption on NLP. Application of second order kinetics by plotting t/q_t vs. t (Eq. (15) yielded better results (Fig. 4) with the second order rate constant, k_2. in the range of 2.65 to 28.93 g meq^{-1} min^{-1} (R for the lines ≈ 0.99). There is also now good agreement between experimental q_e values and those obtained from the slopes of the second order plots as given below:

NLP amount (g dm^{-3})	1.6	2.0	6.0	10.0	14.0
q_e (meq g^{-1}) Experimental	0.1474	0.1186	0.0402	0.0261	0.0184
q_e (meq g^{-1}) Second order plots	0.1478	0.1191	0.0410	0.0252	0.0185

(For initial Cr (VI) concentration of 14.1 mg dm^{-3}, temperature 300 K).

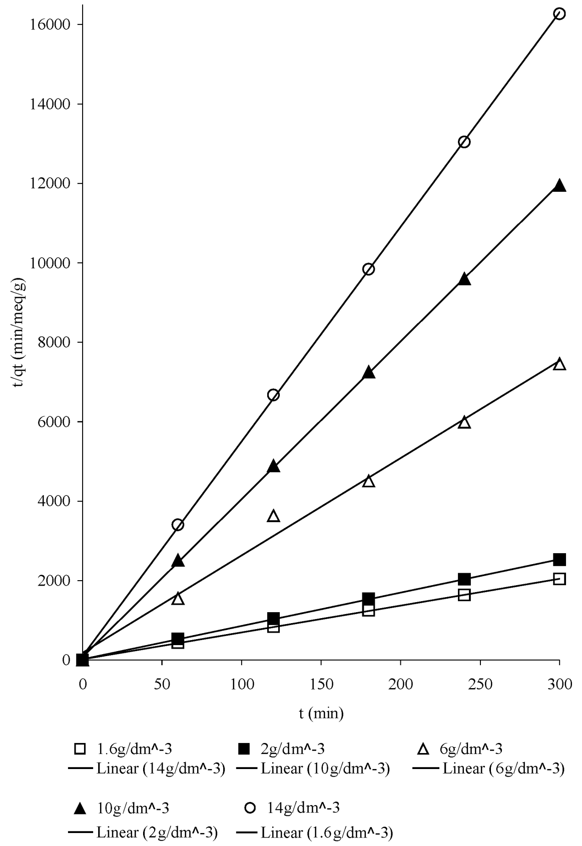


Figure 4. Second order plots for adsorption of Cr (VI) on five different amounts of the adsorbent, NLP (Initial Cr (VI) concentration 14.1 mg dm^{-3}, temperature of adsorption 300 K).

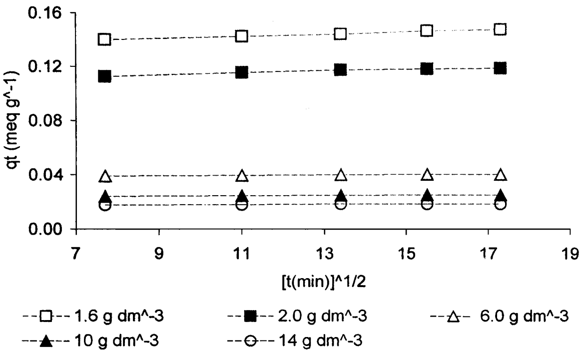


Figure 5. Plots of q_t (meq g^{-1}) vs. $t^{1/2}$ for adsorption of Cr (VI) on five different amounts of NLP (Initial Cr (VI) concentration 14.1 mg dm^{-3}, temperature 300 K).

The intra-particle diffusion mechanism of adsorption (Weber and Morris, 1962) suggests that the approach towards equilibrium is governed by the function $(D \cdot t/r^2)^{1/2}$, where r is the radius of the particle and D is the diffusivity within the particle. The initial rates of intra-particle diffusion are obtained from the Eq. (16) from the plots of q_t (amount adsorbed in meq per unit mass (g) of the adsorbent after a contact time of t minutes) vs. $t^{1/2}$ (Fig. 5). The values of the constant, k_p, covered a wide range of 9.0×10^{-5} to 8.0×10^{-4} meq g^{-1} min$^{-1/2}$ with a mean value of 3.4×10^{-4} meq g^{-1} min$^{-1/2}$. The intra-particle diffusion is thus a slower process compared to the initial rate of adsorption by a factor of more than 10 although its importance could not be ignored. After initial adsorption of the metal ions on the surface of the NLP particles, the ions might slowly diffuse into the interior of the particles, and the overall kinetics of the adsorption should be discussed on the basis of both surface adsorption and intra-particle diffusion (Wu et al., 2000). The plots of q_t vs. $t^{1/2}$ should have zero intercept as per Eq. (16), but the lines in the present work (Fig. 5) have intercepts in the range of 0.017 to 0.134 meq g^{-1}. This further proves that intra-particle diffusion is not the only mechanism for the adsorption of Cr(VI) on NLP.

Panday et al. (1984) has suggested that adsorption of chromium (VI) on a homogeneous mixture of fly ash and wollastonites take place through initial diffusion followed by surface compound formation. A similar situation cannot be ruled out in the present case as well. The metal ions arrive at the exterior surface of the NLP particles at a comparatively high speed, then slowly diffuse into the interior surface and eventually bind to the surface through chemisorptive bond formation.

3.2. *Effect of pH*

The solution pH is one of the parameters having considerable influence on the adsorption of metal ions (Sanches-Polo and Rivera-Utrilla, 2002), because the surface charge density of the adsorbent and the charge of the metallic species present depend on the pH. In the present work, the extent of Cr (VI) adsorption was investigated in the pH-range 2.0 to 10.0 with a constant NLP amount of 1.6 g dm^3 for a Cr (VI) solution of concentration 17.7 mg dm^{-3} at 300 K. The results are shown in Fig. 6. The adsorption of Cr (VI) was maximum in the pH-range 4.5 to 7.5.

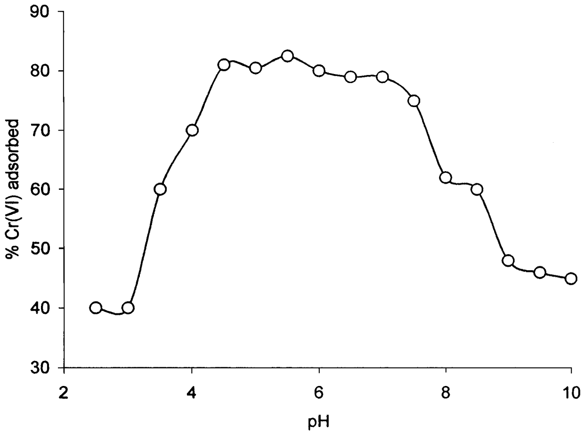


Figure 6. Influence of solution pH on adsorption of Cr (VI) on the adsorbent NLP (Initial Cr (VI) concentration 17.7 mg dm^{-3}, NLP 1.6 g dm^{-3}, agitation time 180 min, temperature 300 K).

Summers and Roberts (1988) have reported for the granulated activated carbon (GAC) adsorbent that the chemical nature of the surface is influenced by solution pH, which therefore plays an important role in the adsorption of solutes from aqueous solutions. At a lower pH, the molecular form is the predominantly adsorbed species, while at a higher pH, the ionized form is preferentially adsorbed. For adsorption on bentonite surface, Khan et al. (1995) have suggested that the Cr (VI) ions bind to OH-groups in the anionic form as $HCrO_4^-$ at very low pH as the surface gets positively charged, while cationic adsorption takes place at increasing pH. On a variety of low cost adsorbents like wool, olive cake, sawdust, pine needles, almond, coal, cactus leaves, etc., Dakiky et al. (2002) found maximum adsorption of Cr (VI) at pH 2.0 when the dominant species were likely to be $HCrO_4^-$ (Namasivayam and Yamuna, 1995). The following mechanism proposed by Bayat (2002) for adsorption of Cr(VI) at different pH is likely:

$$2H^+ + 2HCrO_4^- \overset{2H^+}{\Leftrightarrow} 2H_2CrO_4 \Leftrightarrow 2H_2O + Cr_2O_7^{2-} \overset{2H^+}{\Leftrightarrow} 2CrO_3 + H_2O$$

The H_2CrO_4 and CrO_3 probably exist as polynuclear species, along with their anhydrous forms, at high chromium concentration and at low pH. The pH of the aqueous solutions of Cr (VI), used in the present set of experiments, was 5.5 and therefore, the surface of the NLP particles can be considered as almost amphoteric in nature with the result that Cr (VI) adsorbed mostly in the cationic form.

3.3. *Effect of Adsorbate and Adsorbent Mass*

Cr (VI) adsorption was influenced by the amount of NLP. With Cr (VI) concentration of 7.1 mg dm^{-3}, the adsorption increased from 89.1 to 100% in the NLP range of 1.6 to 14.0 g per dm^3 for a constant agitation time of 180 min at 300 K (Table 2). On the other hand, for NLP amount of 1.6 g dm^{-3}, the adsorption decreased from 89.1 to 78.4% when Cr (VI) concentration increased from 7.1 to 24.8 mg dm^{-3} with the same agitation time and adsorption temperature.

Table 2. Variation in the percentage of Cr (VI) adsorbed on NLP at 300 K with a constant agitation time of 180 min.

	Percentage of Cr (VI) adsorbed on NLP amount				
Cr (VI) (mg dm^{-3})	1.6 g dm^{-3}	2.0 g dm^{-3}	6.0 g dm^{-3}	10.0 g dm^{-3}	14.0 g dm^{-3}
7.1	89.1	90.1	95.5	98.9	100.0
10.6	87.1	88.0	89.6	94.6	96.5
14.1	85.0	86.5	88.7	91.5	94.5
17.7	82.0	84.5	85.0	90.5	92.5
21.2	80.5	82.0	83.5	88.0	91.1
24.8	78.4	79.5	80.0	86.0	90.0

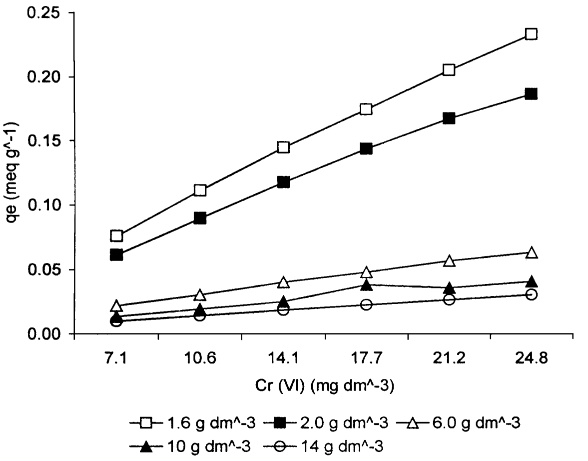


Figure 7. Influence of Cr (VI) concentration and NLP amount on amount adsorbed after a constant agitation time of 180 min (temperature of adsorption 300 K, Cr (VI) from 7.1 to 24.8 m dm^{-3}, NLP from 1.6 to 14.0 g dm^{-3}).

The amount of Cr (VI) adsorbed per unit mass increased gradually with increase in Cr (VI) concentration for a constant adsorbent amount (Fig. 7). This may be due to an increase in the number of Cr (VI) ions per unit mass of NLP leading to higher uptake of the ions. If the adsorbent amount was increased for constant Cr (VI) concentration, the amount adsorbed per unit mass showed a decrease due to availability of less number of Cr (VI) ions per adsorbent unit mass.

NLP has a larger adsorption capacity than a number of unconventional adsorbents. Dakiky et al. (2002) have found that pine needles and cactus leaves can respectively remove 42.9 and 19.8% of Cr (VI) from a 100 ppm solution at 303 K in 2 hrs at pH 2.0. The cellulose-based plant materials with a large number of OH-groups on the surface can bind easily to Cr (VI) ions. The large adsorption capacity of the NLP may be similarly attributed to easily accessible surface OH and other groups for metal ion uptake. The main chemicals present in the Neem leaves, viz, azadirachtin, salannin, meliantriol, nimbidin, and nimbin, contain a large number of OH-groups, which are likely to be the possible sorption sites for the metal ions. Neem leaves contain a number of fatty acids like oleic acid, steric acid, palmitic acid, linoleic acid, etc. (Skellon et al., 1962). FTIR measurements also showed the presence of a large number of functional groups, —OH, —COOH, =C=O, >C=C<, >S=O, etc., in Neem leaves and these groups may contribute to the excellent sorption properties of NLP.

Daneshvar et al. (2002) have suggested that during adsorption on soya cake, Cr (VI) is reduced to Cr (III) by groups like —NH$_2$ and —COOH. A similar situation is unlikely in Cr (VI) adsorption on NLP as identical functional groups are not known to be in abundance and also Cr (III) was not detected after adsorption.

3.4. The Adsorption Isotherms

Cr (VI) adsorption on NLP followed both Langmuir isotherm (Fig. 8) and Freundlich isotherm (Fig. 9). The adsorption coefficients and the correlation coefficients are given in Table 3. The Langmuir plots have good linearity (R: 0.95 to 0.99). The Langmuir monolayer adsorption capacity (q_m) increased from 14.35 to 145.77 meq g^{-1} for the NLP amount varying from 1.6 to 14.0 g dm^{-3}. The adsorption equilibrium parameter, b, showed a decreasing trend of 0.407 to 0.032 dm^3 meq^{-1} with the increase in NLP amount. The dimensionless parameter, R_L, remained between 0.122 and 0.637 ($0 < R_L < 1$) consistent with the requirement for a favourable adsorption process.

Table 3. Adsorption coefficients for Cr (VI)—NLP interactions at 300 K (Agitation time 180 min, Cr (VI) concentration 7.1 to 24.8 mg dm^{-3} for each different amount of NLP).

	Langmuir isotherm			Freundlich isotherm			
NLP amount (g dm^{-3})	R	q_m (meq g^{-1})	b (dm^3 meq^{-1})	R_L	R	K_f (dm^3 g^{-1})	n
1.6	0.95	14.38	0.407	0.122	0.99	0.876	0.58
2.0	0.99	19.49	0.283	0.166	0.99	0.733	0.57
6.0	0.98	38.00	0.078	0.419	0.97	0.162	0.41
10.0	0.98	83.62	0.046	0.554	0.99	0.128	0.42
14.0	0.97	145.77	0.032	0.637	0.99	0.101	0.40

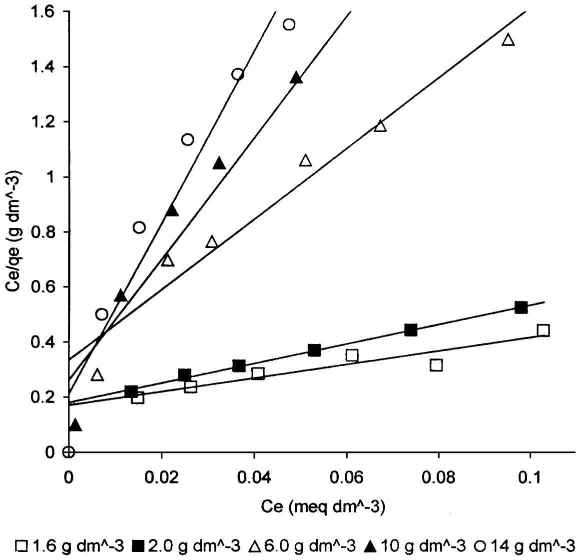


Figure 8. Langmuir plots for adsorption of Cr (VI) on NLP at 300 K (Agitation time 180 min, NLP amounts from 1.6 to 14.0 g dm^{-3}, *C* is the equilibrium concentration corresponding to initial Cr (VI) concentration of 7.1, 10.6,14.1,17.7, 21.2, and 24.8 mg dm^{-3} for each NLP amount).

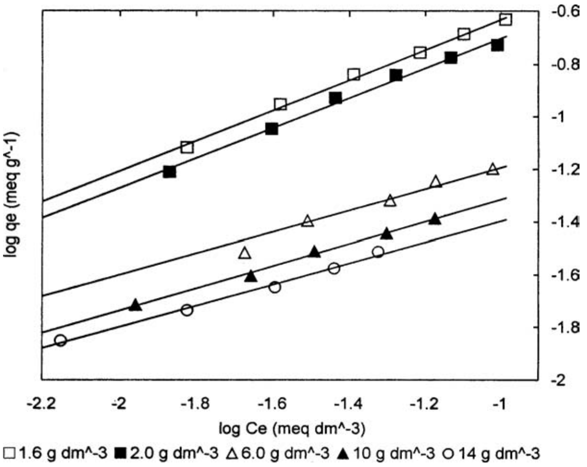


Figure 9. Freundlich plots for adsorption of Cr (VI) on NLP at 300 K (Agitation time 180 min, NLP amount from 1.6 to 14.0 g dm^{-3}, C is the equilibrium concentration corresponding to initial Cr (VI) concentration of 7.1, 10.6, 14.1, 17.7, 21.2, and 24.8 mg dm^{-3} for each NLP amount).

The Freundlich plots also have similar linearity (*R:* 0.97 to 0.99). The adsorption coefficients are in the same trends as those of the Langmuir coefficients. The adsorption affinity, n, remained between 0.40 and 0.58. The adsorption capacity, K_f, showed a decrease from 0.876 to 0.101 dm^3 g^{-1} with an increase in the NLP amount. The values of the adsorption coefficients agree well with values reported by other authors for a variety of materials. Gupta et al. (2001) reported values of 0.31 (n) and 2.24 × 10^{-4} (K_f) for the Freundlich coefficients, and 4.36 × 10^{-4} mol g^{-1} (q_m) and 400 L mol^{-1} (b) for Cr (VI) adsorption on red mud at 303 K. Thus, the red mud has a smaller monolayer capacity of 0.436 meq g^{-1} compared to the NLP value of 14.38 meq g^{-1} (NLP amount 1.6 g dm^{-3}). But b is larger for red mud (400 dm^3 mol^{-1}) than for NLP (21.16 dm^3 mol^{-1}, NLP 1.6 g dm^{-3}). Similar is the case for Langmuir coefficients of q_m: 0.192 meq g^{-1} and b: 12.4 dm^3 meq^{-1}) (Dantas et al., 2001) for Cr (VI) adsorption on diatomite. Dakiky et al. (2002) have reported q_m: 0.13 to 0.79 meq g^{-1}, b: 0.244 to 0.598 dm^3 meq^{-1}, n: 0.44 to 0.69, and K_f: 0.094 to 2.23 dm^3 g^{-1} for adsorption of Cr (VI) on low cost adsorbents such as wool, olive cake, sawdust, pine needles, almond, coal and cactus at 303 K and pH 2.0. NLP has larger monolayer capacity (q_m) than these adsorbents. The coefficients obtained in this work compare reasonably with those obtained by Aksu et al. (2002) for adsorption of Cr (VI) on dried activated sludge (Langmuir (q_m: 1.83 meq g^{-1}, b: 0.286

dm^3 meq^{-1}; Freundlich n: 0.62, K_f. 1.60 dm^3 g^{-1}). Adsorption of Cr (VI) on soya cake, yielded Langmuir coefficients (q_m: 14.56 meq g^{-1}, b: 0.623) and Freundlich coefficients (n: 0.20, K_f. 1.4×10^{-4}), which agree well with the values obtained for NLP in this work.

4. Conclusions

The present study shows that a biological resource, known for its traditional medicinal applications, can also be useful as an adsorbent to remove toxic pollutants from water. The Neem Leaf Powder, which has been tested in this work for adsorbing toxic Cr (VI) ions from aqueous solution, has been found to be very effective. A small amount of the powder has been found to be sufficient to make water free from Cr (VI) at much higher levels of concentration than is usually found in effluents.

The adsorption has been found to be spontaneous and relatively fast. The adsorption process follows pseudo first order kinetics and the use of Freundlich and Langmuir isotherms shows that NLP has an adsorption capacity much larger than those reported in the literature for non-conventional and low cost adsorbents. In a recent study, Yabe and Oliveira (2003) have shown that a commercial adsorbent like alumina can remove about 80% of Cr (VI) from an industrial effluent containing Cr (VI) < 0.0044–0.08 mg dm^{-3}. The present work used synthetic effluent containing Cr (VI) at a much higher concentration and achieved nearly 100% removal. Other adsorbents like activated carbon, sphagnum moss peat, and leaf mold, etc., (Sharma and Forster, 1993, 1994, 1996) also cannot be said as better adsorbents than the NLP used in this work. One other advantage with the NLP is that no acid or alkali needs to be added to obtain maximum adsorption as the pH of the Cr (VI) solutions (5.5) fall within the optimum range of pH.

Acknowledgment

The authors are grateful to the two reviewers for their helpful comments and suggestions.

References

Aksu, Z., U. Acikel, E. Kabasakal, and S. Tezer, "Equilibrium modeling of individual and simultaneous biosorption of chromium (VI) and Ni (II) onto dried activated sludge", *Water Res.*, **36**, 3063–3073 (2002).

ATSDR, "Chromium Fact Sheet, Agency for Toxic Substances and Disease Registry (ATSDR)", USA (http://www.atsdr.cdc.gov), 2001.

Bailey, S.E., T.J. Olin, R.M. Bricka, and D.D. Adrian, "A Review of Potentially Low Cost Sorbents for Heavy Metals", *Walter Res.*, **33**, 2469–2479 (1999).

Bayat, B., "Comparative Study of Adsorption Properties of Turkish Fly Ashes. II. The Case of Chromium (VI) and Cadmium (II)", *J. Hazardous Materials*, **95**, 275–290 (2002).

Chattopadhyay, R.R., R.N. Chattopadhyay, and S.K. Maitra, "Possible Mechanism of Anti-Inflammatory Activity of Azadirchta Indica Leaf Extract", *Indian J. Pharmacol*, **25**, 99–100 (1993).

Chopra, R.N., S.L. Nayer, and I.C. Chopra, *Glossary of Indian Medicinal Plants*, p. 31, C.S.I.R., New Delhi, 1956.

Chu, K.H., "Removal of Copper from Aqueous Solution by Chitosan in Prawn Shell: Adsorption Equilibrium and Kinetics", *J. Hazardous Materials*, **B90**, 77–95 (2002).

Cieslak-Golonka, M., "Toxic and Mutagenic Effects of Chromium (VI)", *Polyhedron*, **15**, 3667–3689 (1995).

Dakiky, M., M. Khamis, A. Manassra, and M. Mereb, "Selective Adsorption of Chromium (VI) in Industrial Wastewater Using Low-Cost Abundantly Available Adsorbents", *Advances in Environmental Research*, **6**, 533–540 (2002).

Daneshvar, N. D. Salari, and S. Aber, "Chromium Adsorption and Chromium (VI) Reduction to Trivalent Chromium in Aqueous Solutions by Soya Cake", *Journal of Hazardous Materials*, **B94**, 49–61 (2002).

Dantas, T.N. De Castro, A.A. Dantas Neto, and M.C.P. De A. Moura, "Removal of Chromium from Aqueous Solutions by Diatomite Treated with Microemulsion", *Water Res.*, **35**, 2219–2224 (2001).

Dutta, M., "Adsorption of Certain Beta-Lactam Antibiotics on Activated Carbon/Polymeric Resins: Equilibrium and Kinetic Studies", Ph.D. thesis (unpublished), Gauhati University, India, 1999.

Gupta, V.K., M. Gupta, and S. Sharma, "Process Development for the Removal of Lead and Chromium from Aqueous Solutions Using Red Mud—An Aluminum Industry Waste", *Water Res.*, **35**, 1125–1134 (2001).

Hall, K.R., L.C. Eagleton, A. Acrivos., and T. Vermeulen, "Pore and Solid Diffusion Kinetics in Fixed Bed Adsorption under Constant Pattern Conditions", *Ind. Eng. Chem. Fund.*, **5**, 212–219 (1966).

Ho, Y.S. and G. Mckay, "A comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents", *Trans. IChemE.*, **76B**, 332–340 (1998).

Ho, Y.S. and G. Mckay, "Comparative Sorption Kinetic Studies of Dyes and Aromatic Compounds onto Fly Ash", *J. Environ. Sci. Health*, **A34,** 1179–1204 (1999).

Khan, S.A., R. Rehman and M.A. Khan, "Adsorption of Cr (III), Cr (VI) and Ag (I) on Bentonite", *Waste Mgmt.*, **15**, 271–282 (1995).

Kraus, W., "Biologically Active Ingredients", in *The Neem Tree*, H. Schmutterer (Ed.), pp.35–92, VCH, Weinheim, 1995.

Langmuir, K., *J. Chem. Soc.*, **40**, 1361 (1918).

Majumdar, A.M., A.S. Upadhyay, and A.M. Pradhan, "Effect of Azadirachta Indica Leaf Extract on Carbontetrachloride-Induced Hepatic Damage in Albino Rats", *Indian J. Pharm. Sci.*, **60**, 363–367 (1998).

Namasivayam, C. and R.T. Yamuna, "Adsorption of Chromium (VI) by a Low Cost Adsorbent: Biogas Slurry", *Chemosphere*, **30**, 561–578 (1995).

National Research Council, *Neem: A Tree for Solving Global Problems*, Report of an adhoc panel of the Board on Science and Technology for International development, National Academy Press, Washington, D.C., 1992.

Neem Foundation, *Chemical composition of Neem Tree*, from the website http://www.neemfoundation.org, 1997.

Norseth, T., "The Carcinogenicity of Chromium and its Salts", *Br. J. Ind. Med.*, **43**, 649–651 (1986).

Panday, K.K, G. Prasad, and V.N. Singh, "Removal of Cr(VI) from Aqueous Solution by Adsorption on Fly Ash Wollastonites", *J. Chem. Technol. Biotechnol. A-Chemical Technology*, **34**, 367–374 (1984).

Rawat, N.S., "Neem Plantation for Better Pesticides for Reducing Poverty and for Protecting Environment in India", *Indian J. Environ. Protection*, **14**, 433–439 (1994).

Sanches-Polo, M. and J. Rivera-Utrilla, "Adsorbent-Adsorbate Interactions in the Adsorption of Cd(II) and Hg(II) on Ozonized Activated Carbons", *Environ. Sci. Technol.*, **36**, 3850–3854 (2002).

Schmutterer, H., "The Tree and its Characteristics", in *The Neem Tree*, H. Schmutterer (Ed.), PP.1–34, VCH, Weinheim, 1995.

Sharma, D.C. and C.F. Forster, "Removal of Hexavalent Chromium Using Sphagnum Moss Peat", *Water Res.*, **27**, 1201–1208 (1993).

Sharma, D.C. and C.F. Forster, "The Treatment of Chromium Wastewaters Using the Sorptive Potential of Leaf Mold", *Bioresource Technol.*, **49**, 31–40 (1994).

Sharma, D.C. and C.F. Forster, "Removal of Hexavalent Chromium from Aqueous Solutions by Granular Activated Carbon", *Water SA*, **22**, 153–160 (1996).

Skellon, J.H., Thorburn, S., Spence, J., and Chatterjee, S.N. (1962). The Fatty Acids of Neem Oil and their Reduction Products, *Journal of Scientific Food Agriculture*, **13**, 639–643 (1962).

Summers, R.S. and P.V. Roberts, "GAC Adsorption of Humic Substances II. Size Exclusion and Electrostatic Interactions", *J. Colloid. Interface. Sci.*, **122**, 382–397 (1988).

Thomas, W. John, "Crittenden, Barry", in *Adsorption Technology and Design*, Butterworth, Heinemann, Oxford, 1998.

US Department of Health and Human Services, *Toxicological Profile for Chromium*, Public Health Services Agency for Toxic Substances and Disease Registry, Washington DC, 1991.

Venugopal, P.V. and T.V. Venugopal, "Antidermatophytic Activity of Neem (Azadirachta indica) Leaves In Vitro", *Indian J. Pharmacol.*, **26**, 141–143 (1994).

Vogel, A.I., *Textbook of Quantitative Inorganic Analysis*, p. 791, 3rd edn., ELBS, 1969.

Weber, W.J. and J.C. Morris, "Kinetics of Adsorption on Carbon Solution", *J. San. Eng. Div. ASCE*, **89**, 31–59 (1963).

WHO, Technical Report Series, No. 546 (Assessment of Carcinogenicity and Mutagenicity of Chemicals—Report of a WHO Scientific Group), World Health Organization, Geneva, 19 p. 1974.

Wu, Feng-Chin, Tseng, Ru-Ling, and Juang, Ruey-Shin. "Comparative Adsorption of Metal and Dye on Flake- and Bead-Types of Chitosans Prepared from Fishery Wastes", *J. Hazard. Materials*, **B73**, 63–75 (2000).

Yabe, Maria Josefa Santos and de Oliveira, Elisabeth. "Heavy Metals Removal in Industrial Effluents by Sequential Adsorbent Treatment", *Advances in Environmental Research*, **7**, 263–272 (2003).