

KINETICS AND EQUILIBRIUM STUDIES OF Cr(VI) METAL ION REMEDIATION BY *ARACHIS HYPOGAEA* SHELLS: A GREEN APPROACH

Garima Mahajan and Dhiraj Sud *

Arachis hypogea shells (ground nut shells), a lignocellulosic waste biomass, was evaluated for sequestering of Cr(VI) from synthetic wastewater. *Arachis hypogea* shells (AHS) were used in three different forms, viz. natural (AHSN), immobilized in the form of beads (AHSB), and in the form of activated carbon (AHSC). Batch experiments were performed for the removal of hexavalent chromium. Effects of pH adsorbent dose, initial metal ion concentration, stirring speed, and contact time were investigated. The removal of metal ions was dependent on the physico-chemical characteristics of the adsorbent, adsorbate concentration, and other studied process parameters. Maximum metal removal for Cr(VI) was observed at pH 2.0. The experimental data were analyzed based on Freundlich and Langmuir adsorption isotherms. Kinetic studies indicated that the adsorption of metal ions followed a pseudo-second-order equation.

Keywords: Waste water; Biosorption; Kinetics; *Arachis hypogea*; Cr(VI); Adsorption isotherms

Contact information: Department of Chemistry, Sant Longowal Institute of Engineering & Technology, Sangrur, 148001 INDIA; *Corresponding author: suddhiraj@yahoo.com

INTRODUCTION

Water pollution by chromium is of major environmental concern, as this metal is used in a number of industrial applications including steel production, electroplating, leather tanning, nuclear power plant, textile industries, wood preservation, anodizing of aluminum, water-cooling, and chromate preparation (Altundogan 2005). Chromium exists in trivalent and hexavalent forms in aquatic systems. The trivalent form is an essential nutrient (Rojas et al. 2005), but the hexavalent form is toxic, carcinogenic, and mutagenic in nature. It is highly mobile in soil and aquatic systems and also is a strong oxidant capable of being adsorbed by the skin (Singh and Singh 2002). The hexavalent form is 500 times more toxic than the trivalent form (Kowalski 1994). Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (Toxicological Profile for Chromium 1991; Cieslak-Golonka 1995). The tanning process is one of the major sources of chromium pollution at global scale. In the chromium tanning process, the leather takes up only 60 to 80% of the applied chromium, and the rest is usually discharged into wastewaters, causing serious environmental hazards. Chromium ion in liquid tanning wastes occurs mainly in the trivalent form, which gets further oxidized to the hexavalent form. The maximum levels permitted for trivalent chromium in wastewater are 5 mg/L and for hexavalent chromium are 0.05 mg/L (Acar and Malkoc 2004).

Numerous treatment methods such as ion exchange (Toxicological Profile for Chromium 1991); chemical reduction (Cieslak-Golonka 1995), chemical precipitation (Acar and Malkoc 2004), membrane separations (Patterson 1977; Tiravanti et al. 1997), electrochemical precipitation (Dahbi et al. 1999), photo-catalytic reduction (Kapoor et al. 1999), adsorption (Aksu 2001; Zhang et al. 1998; Demirbas 2005), and biosorption (Goel et al. 2005; Mohanty et al. 2006) have been tested to remove Cr(VI) from effluents to the permissible level. However, due to prohibitive cost, their use is limited in developing countries like India. So there is a need to develop low-cost and easily available adsorbents for the removal of heavy metal ions from the aqueous environment. An abundant source of potentially metal-sorbing biomass is lignocellulosic agricultural waste materials. These materials could be an inexpensive substitute for the treatment of heavy-metal laden wastewater (Sud et al. 2008). Biomass is widely available, inexhaustible, and inexpensive material that exhibits significant specificity for the heavy metal ions. *Arachis hypogea* shells, an agricultural waste material, are generated in large quantities in India. The majority of the shells are burned in the open field, dumped in forest areas, or blown into huge piles and left to naturally deteriorate. These shells are very rich in cellulose and hemicelluloses and comprise 68% of organic matter. They contain many polymeric materials that possess functional moieties that may help for the binding of metal ions. Various agricultural waste materials have been used, such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, *Cassia fistula* leaves, maize corn cob, jatropha-oiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, and cotton stalks, etc. (Annadurai et al. 2002; Cimino et al. 2000; Hashem et al. 2006; Macchi et al. 1986; Mohanty et al. 2005; Orhan and Buyukgungor 1993; Reddad et al. 2002; Tee and Khan 1988). Thus, in continuation with previous work done by our research group (Sud et al. 2008; Garg et al. 2007, 2008a,b), the present study explores the use of *Arachis hypogea* shells as sustainable adsorbents for chromium removal from aqueous systems under different experimental conditions. Experiments were performed in batch mode. *Arachis hypogea* shells were taken in three different forms, viz. natural, immobilized, and carbon forms. The results showed the potential removal of the Cr(VI) metal ion by biomass in matrix mode and carbon form as compared to the natural form under optimized conditions. Equilibrium and kinetic models were investigated and applied to the data to describe the overall adsorption process.

EXPERIMENTAL

Materials

Preparation of adsorbent

The selected agricultural waste material *Arachis hypogea* shells (AHS) was collected from the local area. Hot water treatment was given to them for one hour to remove the soluble organic components and sugars, and the material was dried at 120°C in hot air oven for 24 h. The material was then ground and sieved (150 MICs).

Immobilization of biomass in the form of beads was prepared by mixing sodium alginate (polymer) and biomass in different ratios of 1:1, 1:3, 1:5, 1:7, 1:9, and 1:11 in a pre-calculated amount of de-ionized water and dropped into a 2% solution of calcium chloride by use of a micropipette. The beads thus prepared were stirred in the CaCl_2 solution for 24 hours for hardening. Beads were then washed three times with de-ionized water and maintained in 2% CaCl_2 solution at 4°C. The carbon form of the biomass was prepared by heating the powder of biomass in a muffle furnace at 800°C for 2 hrs.

Preparation of adsorbate

A stock solution of chromium(VI) (1000 mg/L) was prepared by dissolving potassium dichromate in double-distilled water. The stock solution was diluted with distilled water to obtain Cr(VI) solutions of the desired concentration range. The pH of the solutions was adjusted using 0.01M NaOH/0.01M HCl using an Orion 420A pH meter. The Cr(VI) concentration was determined spectrophotometrically [Double Array UV-Vis Spectrophotometer, Agilent 8453] by the diphenyl-carbazide method (Zhang et al. 1998).

Methods

Adsorption experiments were carried out using 100 mL of chromium solution of the desired concentration (50 mg/L) at an initial pH of 2.0 and with 1.5 g of adsorbent in a 250 mL Erlenmeyer flask at 25 ± 1 °C (stirring speed 250 rpm). At predetermined time intervals (60 min), samples were separated by centrifugation at 4000 rpm for 10 min. The residual chromium concentration in the supernatant was determined as given earlier. All experiments were replicated three times for all the forms of adsorbents. The removal percentage (R %), defined as the ratio of difference in metal concentration before and after adsorption ($C_i - C_e$) to the initial concentration of chromium in the aqueous solution (C_i), was calculated using Eq. 1:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Composition

In terms of their structure, *Arachis hypogea* shells (AHS) can be regarded as a lignocellulosic agricultural waste material containing high amount of proteins and crude fibers. The composition of AHS is given in Table 1 (as per Standard Methods).

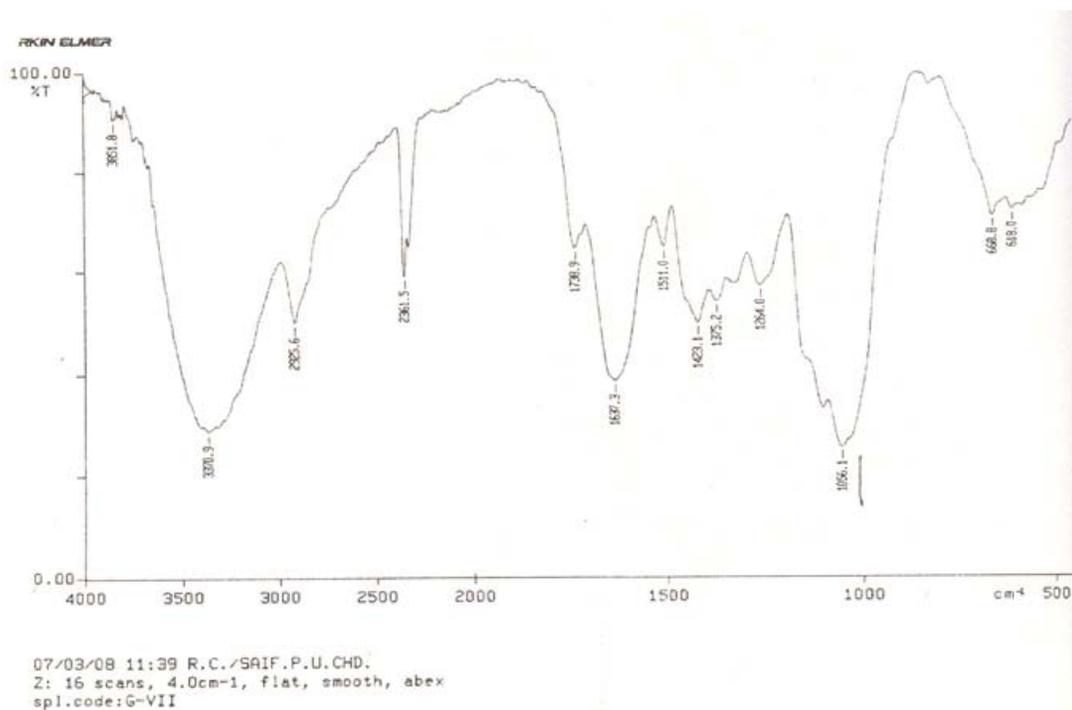
Fourier Transform Infrared Analysis of Adsorbent

FT-IR analysis of the adsorbent before and after sorption of metal ions was performed to determine the vibrational frequency changes in the functional groups of the adsorbent in various forms. The spectra of adsorbents were measured in the range of 400 to 4000 cm^{-1} wave number. The FT-IR spectra showed a number of adsorption peaks, indicating the complex nature of the studied adsorbent.

Table 1. Structural Composition of *Arachishypogea* Shells

Structural components	Percentage
Crude protein	6.8
Carbohydrates	21.2
Proteins	7.3
Minerals	4.5
Lipids	1.2
Organic matter	68
Crude fiber	18.2
Ash content	7.1

In *Arachis hypogea* shells (AHS), the sorption peak at 3370.9 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed at 2925.6 cm^{-1} can be assigned to the stretching vibration of the C-H group. The peaks around 1738.9 cm^{-1} correspond to the -C=O group (Garg et al. 2007). The strong C-O band at 1056.1 cm^{-1} due to -OCH_3 groups also confirms the presence of lignin structures in *Arachis hypogea* shells. The additional peaks at 618 and 668.8 cm^{-1} can be assigned to bending modes of aromatic compounds. The C-O absorption peak was observed to shift to 1036.5 cm^{-1} when ASH was loaded with chromium. It seems that this functional group participates in metal binding (Fig. 1a & b).

**Fig. 1a.** FT-IR spectrum of AHS before use

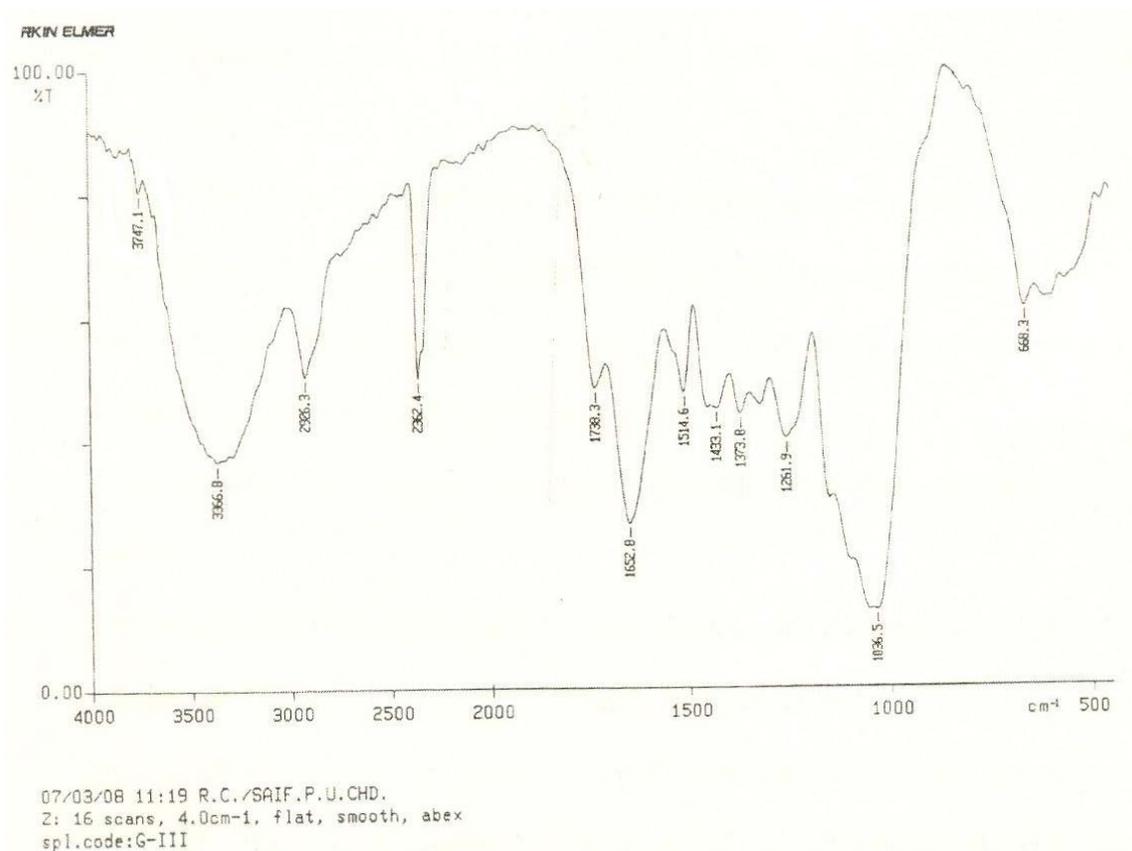


Fig. 1b. FT-IR spectra of AHS after use

Effect of Polymer and Biomass Ratio

For the formation of beads, biomass was bonded with sodium alginate in the ratio 1:9 of binding agent to biomass. This particular ratio was selected after a series of trials with different ratios, viz. 1:1, 1:3, 1:5, 1:7, 1:9, and 1:11. The adsorption increased with increase in the ratio of biomass to binding agent. Maximum adsorption was achieved with a ratio of 1:9, as compared to 1:11, which was attributed to a lack of stability in the latter. So the adsorption experiments were further performed with beads prepared by using the ratio 1:9. The amount of biomass present in a given quantity of beads was also calculated, and it was found that 10.00 g of beads contained 0.80 g of biomass (Fig. 2).

Effect of pH

pH is an important controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and the ionic form of the metal ion in solution. Adsorption experiments were carried out in the pH range 2 to 10, while keeping all other parameters constant (chromium concentration = 50mg/L; stirring speed = 250 rpm; contact time = 60 min, adsorbent dose = 15g/L, temp. = 25 °C). The pH of the chromium solution was adjusted after adding the adsorbent (Garg et al. 2004 and 2007; Bansal et al. 2009). The maximum adsorption of chromium was 99, 97, and 95% for AHSC, AHSB, and AHSN, respectively at pH 2 (Fig. 3) (Garg et al. 2004).

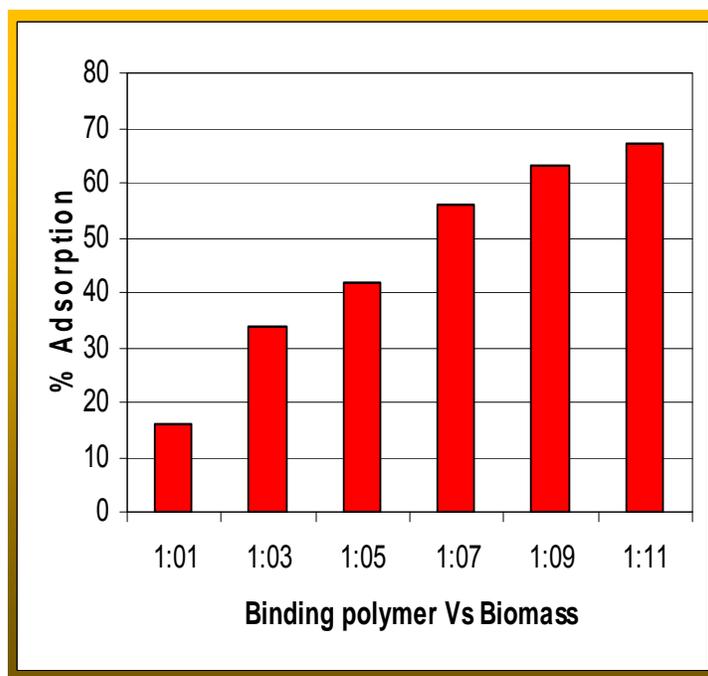


Fig. 2. Binding agent and biomass ratio

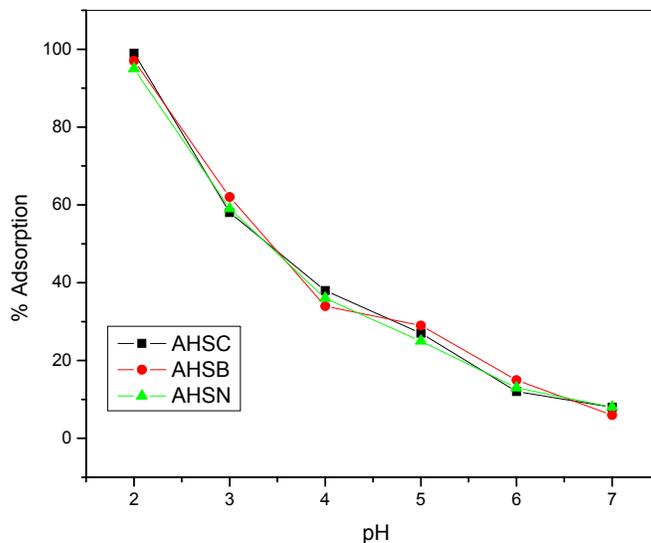


Fig. 3. Effect of pH on chromium removal by different forms of adsorbent (Cr conc.= 50 mg/l; stirring speed = 250 rpm; contact time = 60 & 30 min; adsorbent dose = 15 g/L, 12 g/L, & 5 g/L (AHSN, AHSB, AHSC))

There was a sharp decline in per cent adsorption with increase in pH of the aqueous solution. Chromium adsorption by AHSN was decreased from 95 to 28% as the pH was increased from 2 to 5. Chromium adsorption by AHSB was decreased from 97

to 24% as pH was increased from 2 to 5. Similarly, chromium adsorption by AHSC was decreased from 99 to 31% as pH was increased from 2 to 5. Maximum adsorption was observed at pH 2.0, and hence it was taken as the optimal pH value for further adsorption experiments. Our results are consistent with those of other workers (Kapoor et al. 1999; Aksu 2001; Zhang et al. 1998; Goel et al. 2005; Mohanty et al. 2006; Hamadi et al. 2001; Garg et al. 2004), who observed that the removal of Cr(VI) decreases with the increase of pH. The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution (Mohanty et al. 2006). In the pH range of 1.0 to 6.0, chromium ions co-exist in different forms, such as Cr_2O_7^- , HCrO_4^- , $\text{Cr}_3\text{O}_{10}^{2-}$, and $\text{Cr}_4\text{O}_{13}^{2-}$, of which HCrO_4^- predominates. As the pH of the solution increases, the predominant species become CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. More adsorption at acidic pH suggests that the lower pH results in an increase in H^+ ions associated with the adsorbent surface, resulting in sufficiently strong electrostatic attraction between a positively charged adsorbent surface and negatively charged chromate ions. Lesser adsorption of Cr(VI) at pH values greater than 6.0 may be due to the dual competition of both the anions CrO_4^{2-} and OH^- to be adsorbed on the surface of the adsorbent, noting that OH^- adsorption is favored by higher pH. This is in accordance with the earlier studies that have reported the removal of Cr(VI) by different adsorbents (Mohanty et al. 2006).

Adsorption Kinetics

Studies comparing the three forms of biosorbents were conducted by varying the contact time from 5 to 120 min at a fixed initial chromium concentration (50 mg/L), stirring speed (250 rpm), temperature (25°C), and pH (2.0). Maximum chromium was sequestered from the solution within 60 min by the different forms of adsorbent (Fig. 4).

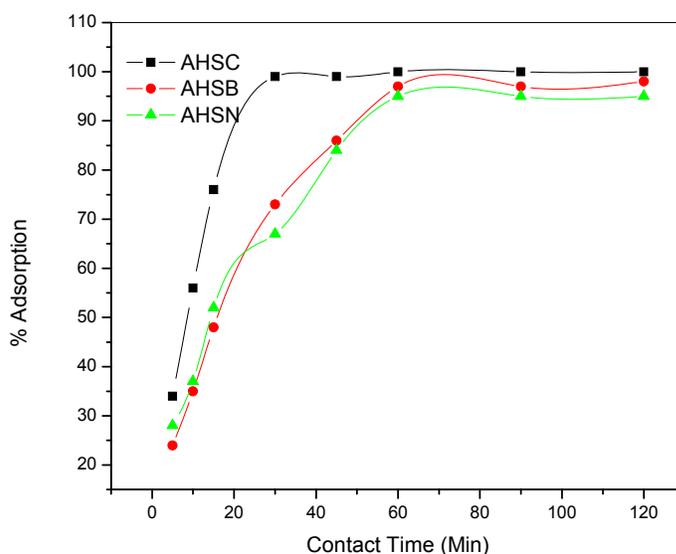


Fig 4. Effect of contact time (in min) of chromium on its removal by different forms of adsorbents (adsorbent dose = 15 g/l, 12 g/l, 5 g/l) chromium concentration = 50 mg/l, stirring speed = 250 rpm, pH 2.0, and temperature = 25 °C).

The chromium removal was 99% by AHSC, 97% by AHSB, and 95% by AHSN within 60 min of contact time. In the case of AHSC there was very fast adsorption; so keeping these observations in view, 30 min contact time was chosen for AHSC and 60 min for the AHSB and AHSN forms for further experiments.

Effect of Adsorbent Dose

The per cent adsorption of Cr(VI) on different forms of adsorbent was studied at different adsorbent doses (250, 500, 1000, 1500, and 2000 mg/100 mL, respectively), keeping chromium concentration (50 mg/L), stirring speed (250 rpm), pH (2.0), temperature (25 °C), and contact time (30 and 60 min as obtained by kinetic studies) constant. The results showed that with increase in the adsorbent dose, the percentage adsorption of chromium was increased, and the maximum removal was observed with adsorbent dose of 5.0 g/L of AHSC, 12 g/L of AHSB, and 15 g/L of AHSN (Fig. 5). Increase in the percentage adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites (Garg et al. 2004). But unit adsorption was decreased with increase in adsorbent dosage. As the adsorbent dose was increased from 2.5 to 20.0 g/L, the unit adsorption for AHSC, AHSB, and AHSN was decreased significantly. In the case of AHSN it decreased from 1.74 to 0.30. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Namasivayam et al. 1998). The order of percentage removal of chromium by studied adsorbent forms was: AHSC > AHSB > AHSN.

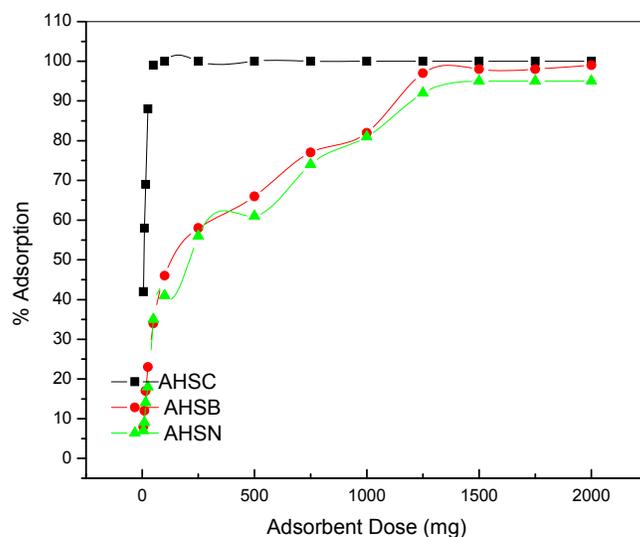


Fig 5. Effect of adsorbent dose on chromium removal by different forms of adsorbent (Chromium conc. = 50 mg/l; stirring speed = 250 rpm; pH 2.0; temperature = 25 °C and contact time = 60 & 30 min).

Effect of Initial Concentration

The percent adsorption of Cr(VI) with different adsorbents was studied by varying the chromium concentration (5, 10, 25, 50, 75, 100, 250, and 500 mg/L), while keeping the adsorbent dose (15 g/L of AHSN, 12 g/L of AHSB, 5 g/L of AHSC), stirring

speed (250 rpm), pH (2.0), temperature (25 °C), and contact time (60 min and 30 min) constant. Higher concentrations of metal ions were used to study the maximum adsorption capacity of the adsorbents (Mohanty et al. 2006; Karthikayn et al. 2005). The percent chromium adsorption was decreased with increase in initial chromium concentration (Fig. 6). But the actual amount of chromium adsorbed per unit mass of the adsorbent was increased with increase in chromium concentration in the test solution (Fig. 7). As the chromium concentration in the test solution was increased from 5.0 to 500 mg/L, the unit adsorption of chromium on AHSC, AHSB, and AHSN increased from 10.00 to 904 mg g⁻¹, 0.416 to 18.16 mg g⁻¹, and 0.332 to 31.26 mg g⁻¹, respectively (Table 2).

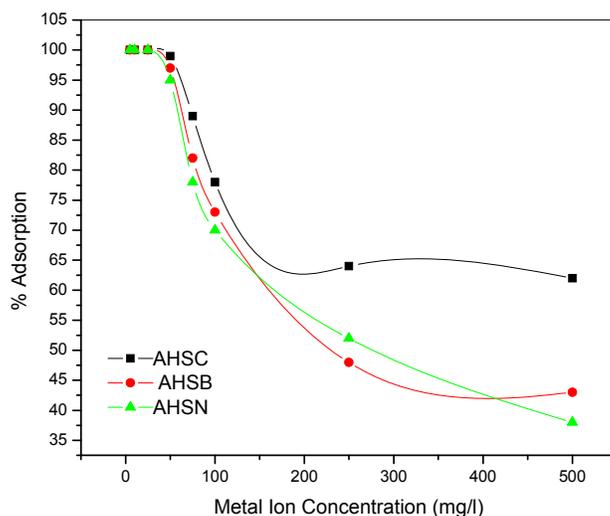


Fig. 6. Effect of initial concentration of Cr on its removal by different forms of adsorbent (dose = 20 g/l, stirring speed = 250 rpm, pH 2.0, temperature = 25 °C, and contact time = 60 min)

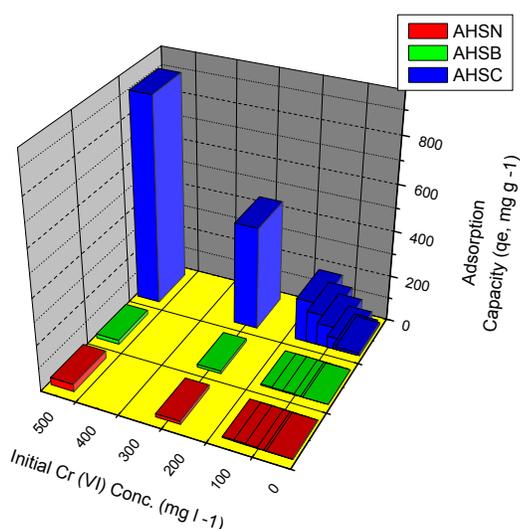


Fig. 7. Effect of adsorption of chromium per unit mass of adsorbent

The adsorption capacity of an adsorbent, which is obtained from the mass balance on the sorbate in a system with solution volume V , is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of chromium(VI) ions at equilibrium were calculated from the following equation (Goel et al. 2005),

$$q_e (\text{mg g}^{-1}) = \left[\frac{C_i - C_e}{M} \right] \times V \quad (2)$$

where C_i is the initial concentration in at equilibrium, V is the volume of solution (in L), and M is the mass of the adsorbent. The order of percentage removal of chromium for different metal ion concentration was AHSC > AHSB > AHSN. Moreover, literature studies also show a wide variety of natural waste materials as biosorbents for the removal of hexavalent chromium. The results of present study have been compared with other materials in Table 3.

Table 2. Adsorption Capacity of Different Forms Adsorbent at Different Initial Chromium Concentration

Initial chromium concentration (mg l^{-1})	AHSN (q_e) (mg g^{-1})	AHSB (q_e) (mg g^{-1})	AHSC (q_e) (mg g^{-1})
5	0.332	0.416	10
10	0.666	0.833	20
25	1.666	2.083	50
50	3.2	4.166	96
75	4.46	4.416	138
100	5.66	05.00	184
250	15.06	11.166	448
500	31.26	18.16	904

Table3. Agricultural Products as Biosorbents and their Sorption Capacities

Agricultural product in Activated Carbon form (AC)	Sorption Capacity (mg g^{-1})	Reference
Almond Shell (AC)	190.3	Demirbas et al. 2003
Hazelnut Shell (AC)	170	Kobyas 2004
Hevea <i>brasiliensis</i> (AC)	65.78	Karthikeyan et al. 2001
Fir wood (AC)	315.6	Khezami and Capart 2005
Terminalia <i>arjun</i> nut (AC)	28.43	Mohanty et al. 2005
Coconut Shell (AC)	20	Alaerts et al. 1989
Commercial (AC)	11.1	Huang and Wu 1977
Pomegranate husk (C)	35.2	Nemr 2009
Rice Husk (C)	48.31	Bansal et al. 2009
Arachis hypogea Shells (AC)	904	Present Study

Adsorption Isotherms

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Classical adsorption models, such as the Langmuir and Freundlich models, have been extensively used to describe the equilibrium established between adsorbed metal ions on the biomass (q_e) and metal ions remaining in solution (C_e) at a constant temperature. The experimental results obtained for the adsorption of chromium on AHSC, AHSB, and AHSN at constant temperature (25 ± 1 °C) under pre-defined conditions of pH, adsorbent dose, and stirring speed obeyed the Freundlich adsorption isotherm. The Freundlich isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and concentration of the metal ion in solution at equilibrium (C_e),

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where K_f ($L g^{-1}$) is an indicator of adsorption capacity, and n (dimensionless) indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity (dimensionless). The plot of $\log(x/m)$ versus $\log C_e$ for various initial concentrations was linear (figures not given), indicating the applicability of the classical adsorption isotherm to the AHSC-Cr(VI), AHSB-Cr(VI), and AHSN-Cr(VI) systems. The adsorption capacities (K_f) and the Freundlich constant (n) are given in (Table 4)

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation,

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

where C_e is the equilibrium concentration (mg/L), q_e the amount adsorbed at equilibrium time ($mg g^{-1}$), Q_0 is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface ($mg g^{-1}$), and b is a constant related to the affinity of binding sites with the metal ions ($l mg^{-1}$) (Goel et al. 2005). The plots of $C_e/(x/m)$ versus C_e are linear, which shows that the adsorption of Cr(VI) followed a Langmuir isotherm model. The correlation coefficient (r) values were very high for all the adsorbents (Table 3) indicating that the data fitted reasonably well to the Langmuir isotherm in the present adsorption studies. The fact that the value of the slope was less than unity implied that significant adsorption took place at low metal ion concentration.

Table 3. Freundlich and Langmuir Models Regression Constants for Different Forms of Adsorbents

Biosorbent	Freundlich Isotherm			Langmuir Isotherm		
	$K_f(l g^{-1})$	n	R^2	$Q_0 (mg g^{-1})$	$b (l mg^{-1})$	R^2
AHSN	0.6762	1.13	0.6379	2.94	0.03825	0.7906
AHSB	0.7182	0.0019	0.9846	3.46	0.0484	0.8828
AHSC	1.1047	0.00166	0.8930	1.42	0.0223	0.9838

Adsorption Kinetics

Pseudo 1st & 2nd order equations

The kinetics of adsorption is important, as it controls the process efficiency. For evaluating the adsorption kinetics of heavy metals the pseudo-first order equation of Lagergren has been used to test experimental data,

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (5)$$

where Q_e (mg/g) and Q_t (mg/g) are the amount adsorbed of heavy metal ions at equilibrium and at time t , respectively, and K_1 (min^{-1}) is the rate constant of pseudo 1st order adsorption. The application of this equation to the data of selected biosorbent (data not shown) indicated the inapplicability of the model. The pseudo 2nd order kinetic model is linearly expressed as (Ho and McKay 1998),

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \quad (6)$$

where K_2 (g/mg min) is the pseudo 2nd order rate constant, which can be calculated from the intercept of the straight line obtained from plotting t/Q_t vs. t . Also, the initial sorption rate can be calculated using the relation (Koynucu 2008):

$$K_o = K_2 Q_e^2 \quad (7)$$

The perfect fit of the experimental data of AHS indicates the applicability of model for the adsorption of heavy metal ions on the selected biosorbent.

CONCLUSIONS

The potential use of *Arachis hypogea* shells in its various forms as a biosorbent for sequestering of chromium (VI) was studied. This new biosorbent was able to remove Cr(VI) ions from aqueous solutions, and the sorption capacity was strongly dependent on the adsorbent nature, the amount used, the initial metal ions concentration, and the initial pH. The experimental data fitted well to the Freundlich and Langmuir equations, with good correlation coefficients. The experimental data also showed that the process followed a pseudo-second-order equation and both adsorbate and adsorbent were significant in determining the sorption rate. Chromium was adsorbed due to the strong interactions with the active sites of the adsorbent. Further, the utilization of biosorbent in immobilized form will also overcome the problem of release of soluble organic materials, while utilizing biomass in its natural form. Moreover, the natural form is not mechanically strong and has a wide size distribution, which can lead to the problems in the operations of reactors by blocking flow lines and clogging filters, while separation of biomass and effluent can be difficult and expensive. Thus, these results can be helpful in designing a wastewater system for the removal of such toxic heavy metal ions. Further work is in progress, in which modifications in the natural form of the biosorbent can lead to the enhanced removal and recovery of the metal ions from aqueous solutions.

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