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Batch equilibrium analysis for the removal of hexavalent chromium: analysis of uncertainties using numerical modelling

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ABSTRACT

Adsorbents like water hyacinth leaf, powdered activated carbon (PAC), PAC in combination with polymer beads (added to enhance the porosity) and a combination of PAC with water hyacinth leaves were used to remove hexavalent chromium from wastewater. Equilibrium was achieved after approximately 18 h. The maximum equilibrium sorption capacity ($q_{\max}$), determined from Langmuir isotherm, are: ADRB1: 9.638 mg/g; ADRB2: 31.46 mg/g; ADRB3: 55.926 mg/g; ADRB4: 33.575 mg/g for 1l wastewater solutions. The adsorption capacity of PAC (ADRB3) has been found more than the composite ADRB4 with a combination of WH (2 g) and PAC (1 g). However, ADRB4 could be used for applications where large quantity of wastewater (e.g. leather complexes) containing hexavalent chromium is disposed into a huge water body where plenty of water hyacinths are grown naturally. Simultaneously three isotherms namely Tempkin, Freundlich and Langmuir were parameterized. The parameters were estimated using the Levenburg and Marquardt optimization scheme, which is based on the minimization of the Sum of the Squares of the Residuals or Deviations (SSQ). The uncertainties associated with the estimated parameters and the range of confidence limits were computed. Close agreement was observed between the predicted Langmuir output and the experimental data for the system considered. This particular case satisfied experimental conditions with almost negligible interaction, constant energy of adsorption and equally likely competition between species. Hence Langmuir ranked first for three times out of four experiments.

Keywords: Adsorption; Hexavalent chromium; Water hyacinth; Isotherm; Parameter estimation; Nonlinear least square

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1. Introduction

Hexavalent chromium is a major pollutant present in the wastewater of the metal and mineral processing, leather processing and pulp and paper industries [1]. Hexavalent chromium usually exists in wastewater as oxy anions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) and does not precipitate easily using conventional methods [2]. Cr(VI) anions, including chromates (CrO_4^{2-}) and di-chromates ($Cr_2O_7^{2-}$) are highly soluble in aquatic systems and behave as hazardous contaminants in the environment due to their carcinogenic, mutagenic and teratogenic features in biological systems as indicated by Fendorf et al. [3]. Thus the presence of chromium ions in the environment is of serious concern. Cr(VI) is known to cause distinct health effects. When present as a compound in leather products, it can cause allergic reactions, such as

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skin rashes. After inhalation Cr(VI) can cause irritation to the mucous membrane. Other health hazards include skin rashes, gastric upsets, ulcers, respiratory problems, weakened immune systems, kidney and liver damages, changes to genetic material, lung cancer and death. Singh and Singh [4] demonstrate that Cr(VI) is highly mobile in soil and aquatic systems.

The maximum level permitted for trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] in wastewater is 5 mg/l and 0.05 mg/l [5] respectively. Maximum contamination levels (MCL) set by the US EPA for chromium is 0.1 parts per million (~mg/l) in the drinking water [6,7]. The toxicity to fish from hexavalent chromium is comparatively high (LC_{50} for fresh water fish = 250–400 mg/l, for sea fish = 170–400 mg/l and for trout = 10 mg/l). In chrome tanneries, the hexavalent chromium concentration in the treated wastewater has to be less than 45 mg/l, according to the General Standards for the Discharge of Environmental Pollutants of Central Pollution Control Board, India [8]. The Recommended Criteria for Hazardous Waste Disposal into Secured Landfill (SLF) defines the limit of total chromium to be less than 0.5 mg/l with specific effluent standards for tanneries demanding a limit of 2 mg/l of total chromium [8]. Lower permissible limits for hexavalent chromium are required for inland surface water and public sewers at 0.1 mg/l and 2.0 mg/l [9].

Cr(VI) are generally removed from wastewaters by chemical precipitation, ion exchange, membrane processes, electro-dialysis and adsorption [9,10]. Natural adsorbents can be comparatively easily regenerated without significant loss of adsorption capacity, even after three cycles [11–13]. Water hyacinth (*Eichhornia Crassipes*) is a floating macrophyte belonging to the family Pontederiaceae. It is found abundantly throughout the year and has been found to accumulate high concentrations of toxic metals as well as phenolic compounds from wastewater [14–16].

Batch adsorption of hexavalent chromium using natural adsorbents has been studied by a number of research groups [17–29]. Prigione et al. [30] and Srivastava et al. [31] described the chromium removal from a tanning effluent by autochthonous and allochthonous fungi. Namasivayam et al. [32] details the performance of coconut coir pith as a special natural sorbent in removing Cr(VI) from water and wastewater containing modified surfactants. Similarly Quintelas et al. [33] show the potential for a pilot-scale bioreactor in treating Cr(VI) solutions through a biofilm of *Arthrobacter viscosus* supported on GAC.

The objective of this work was to identify the most relevant adsorption isotherm for a system containing varied concentrations of hexavalent chromium along with various combinations of natural and chemical adsorbents. Adsorption behaviors were evaluated using some adsorption isotherm models. A number of well-known isotherm models (e.g. Tempkin isotherm, Freundlich isotherm and Langmuir isotherm) were considered to correlate the experimental data. Parameters for three different adsorption isotherms were estimated using a robust nonlinear least square scheme, based on the minimization of the Sum of the Squares of the Residuals or Deviations (SSQ), established by Levenburg and Marquardt. Uncertainties on the estimated parameters were also computed along with the confidence limits. These models were later ranked according to their performance.

2. Experimental methods

2.1. Chemicals

All chemicals used were analytical reagent grade (Make: MERCK, Germany).

2.2. Simulated wastewater

Artificial wastewaters were prepared in the laboratory for this experiment. Hexavalent chromium(VI) solution was prepared by dissolving potassium di-chromate ($K_2Cr_2O_7$) in double distilled water with chromium solutions ranging from 10 to 100 mg/l.

2.3. Adsorbents

Water hyacinths were collected from ponds around the metropolitan area of the city of Kolkata, India. Then they were washed thoroughly to remove all mud and particulates. The leaves and stem portions of the green hyacinth was then cut into small pieces for use in combination with other adsorbents like powder activated carbon (PAC). High density poly-propylene (HDPE) beads were used for their non-adsorbing properties to increase the porosity of the composite adsorbent bed. Morphological analysis of the water hyacinth leaf was done using a scanning electron microscope (SEM) (JEOL; Model: JSM 5800) at three different resolutions, see Fig. 1a–c. The adsorbing BET surface area of the water hyacinth leaves were measured using the BET surface area analyzer (Quantachrome; Model: NOVA 40003). The resulting area was found to be 1.03 m^2/g, with nitrogen as the adsorbate.

Zeta potential ranges for the water hyacinth leaves were measured using a Malvern Zeta Sizer, Nano Series (Nano-Z Model No; ZEN 2600). pH values for the leaf solution were adjusted from 2.0 to 9.0 by adding 0.1 M nitric acid (HNO_3) and 0.1 M potassium hydroxide (KOH) to the sample solution at 25 °C.

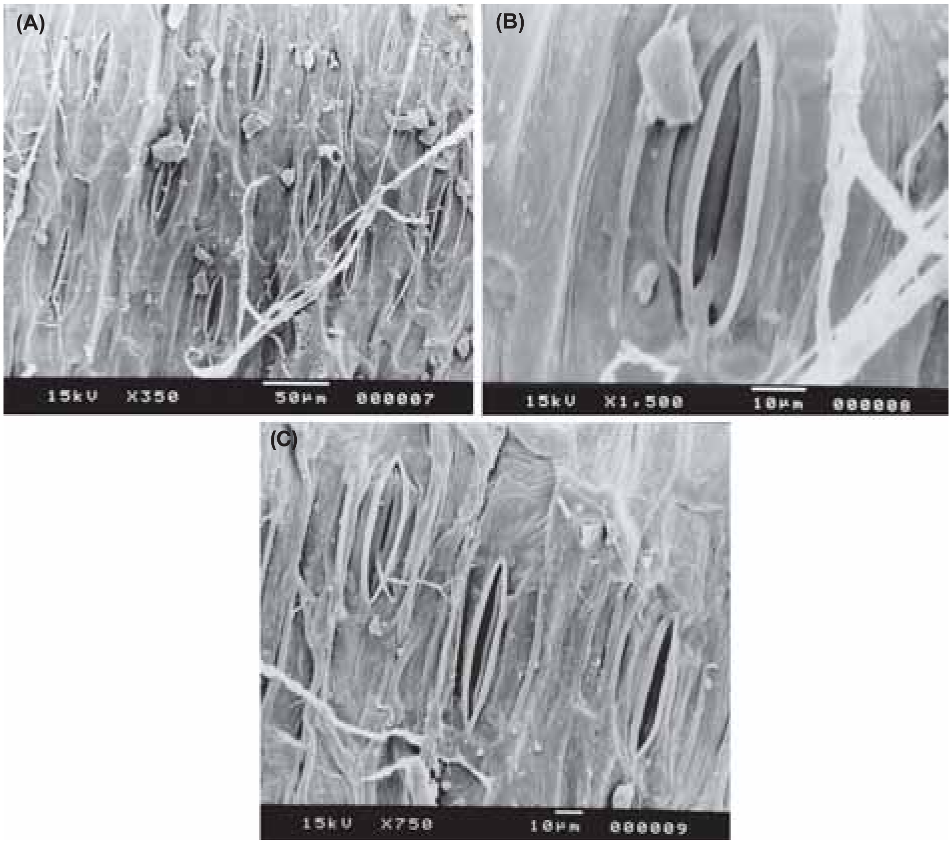

Fig.1. Scanning electron micrograph of water hyacinth (*E. crassipes)* leaf. (a) Resolution: 16 mm represents 50 µm; (b) resolution: 14 mm represents 10 µm; (c) Resolution: 7 mm represents 10 µm.

Measurements for each sample were taken to determine the average value of zeta potential for the water hyacinth leaf samples at different values of the pH. By measuring the zeta potential as a function of pH, the acidity or basicity of the leaf surfaces and point of zero charge (pH_{pzc} [1]) were determined. Zeta potential analysis is shown in Fig. 2. It was evident that the solution pH affected the surface charge of the water hyacinth's leaf. The optimum value of pH_{pzc} for water hyacinth's leaf was found to be 3.116. Thus a pH of approximately 5.9 was maintained for all the experiments of batch adsorption.

2.4. *Analytical procedure*

A 330–900 nm wavelength spectrophotometer (Perkin Elmer, Model: PRECISELY LAMDA 25 UV/Visible) equipped with a standard 10 nm path length sample cell was used for absorption measurements of hexavalent chromium. Hexavalent chromium was determined by reaction with 1,5 diphenyl carbazide (DPC) in an acidic solution to produce a violet colored (Magenta Chromagen) complex absorbing light at λ = 540 nm, as per Standard Methods [34]. Here, the required amount of filtrate (after adsorption) was

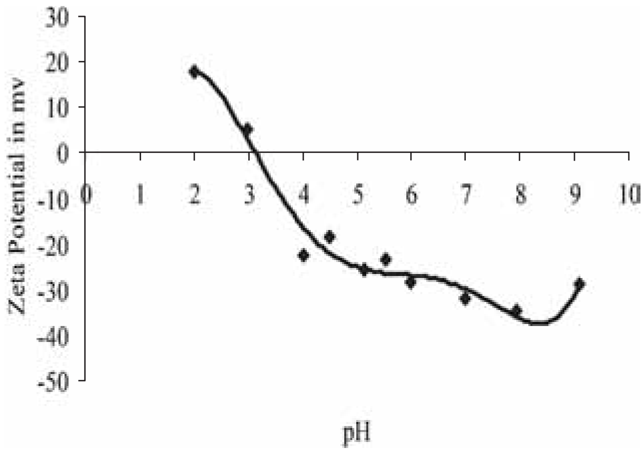

Fig. 2. Zeta potential versus pH of the solution before adsorption to find out the point of zero charge.

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[1] The point of zero charge (pHpzc) is the pH above which the total surface of the leaf is negatively charged.

taken to a 50 ml graduated make-up flask by Eppendorf automated pipette and the volume was made up with double distilled water. Concentrations of hexavalent chromium in each solution was calculated from a standard curve already developed.

Sulfuric acid was added prior to the addition of DPC to lower the pH of the solution.

The equilibrium adsorbate phase concentration was calculated after adsorption as given by the following equation:

$$q_e = (C_0 - C_E)V/m$$

where, q_e is the adsorbent phase concentration after equilibrium has been achieved in mg adsorbate/g adsorbent, C_0 is the initial concentration of adsorbate in mg/l; C_E is the final equilibrium concentration of adsorbate after adsorption in mg/l, V is the volume of liquid and m is the mass of the adsorbent in grams.

2.5. Design of experiment

In the current study, we attempted to find suitable adsorbent material/s those are cheap and easily available for the removal of chromium from wastewater. Thus, a series of adsorbent combinations including; PAC, water hyacinth, mixture of PAC and water hyacinth, PAC in combination with polymer beads, in different compositions were prepared. Adsorption capacities of these adsorbents were then examined.

Experiments were carried out in an incubator, keeping a constant temperature of 25 °C to optimize the equilibrium time. The adsorption equilibrium is reached within 18 h. Four sets of experiments were carried out with 10 samples per set. Each of these 10 samples had varying feed concentrations and a constant adsorbent quantity. After reaching the equilibrium in 18 h the mixtures were filtered using Whatman 589^2 (125 mm) filter papers. The standard DPC method was chosen as the specific analytical technique to determine hexavalent chromium.

Table 1 shows the details of experiments for the batch study to assess the amount of adsorption for a variety of dilutions of chromium samples, along with weight ratio for differing adsorbents.

2.6. Models for AadsorptionIisotherms

Adsorption, described through an isotherm, normally creates a film of adsorbate on the surface of the adsorbent, whether mon layer or multi layer. An isotherm can be generated by the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. There are many types of isotherms available for various systems. Most popular and useful isotherms are Freundlich, Langmuir, BET, Tempkin, Toth, Redlic-–Peterson, etc.

2.6.1. The Tempkin isotherm (Model 1)

Tempkin and Pyzhev [35] considered the effects of certain indirect adsorbate–adsorbate interactions on adsorption isotherms. They suggest that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to these interactions. The Tempkin isotherm has been used in the following form:

$$q = k_2 \log C = k_1 \tag{1}$$

Here q is the equilibrium solid phase concentration in mg per 100 ml per gm of adsorbent and C is the equilibrium liquid phase concentration in mg per 100 ml. The constant k_1 is related to the heat of adsorption.

2.6.2. The Freundlich isotherm (Model 2)

The Freundlich expression assumes that the adsorbate concentration increases with the concentration of adsorbate on the adsorbent surface

$$q = k_1 (C)^{k_2} \tag{2}$$

In this equation k_1 and k_2 are the Freundlich constants. This expression is characterized by the heterogeneity factor, k_2. Hence this isotherm may be used to describe various heterogeneous systems [36, 37]. The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wider range of concentrations cannot be fitted with a single set of constants.

2.6.2. The Langmuir isotherm (Model 3)

The theory for Langmuir isotherms assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Therefore, at equilibrium a saturation point is reached where no further adsorption can occur. This takes place at specific homogeneous sites within the adsorbent. In the following equation, k_1, k_2 are the Langmuir constants

$$q = \frac{k_1 C}{k_2 + C} \tag{3}$$

Table 1
Details of the experiments for the batch adsorption of hexavalent chromium in various combinations of adsorbents

Expt	Adsorbent combinations used	Adsorbent ID	Equilibrium time (h)		Experimental result q_e = amount Adsorbed (mg/100 ml of solution)/amount of adsorbent used (g) C_e = equilibrium chromium concentration (mg/100 ml of solution)									
1	Water hyacinth leaf (4 gm)	ADRB1	18	C_e	1.021	1.628	2.698	3.687	5.014	5.259	6.58	8.887	9.315	9.888
				q_e	0.066 (±0.0002)	0.149 (±0.0006)	0.132 (±0.00007)	0.136 (±0.0005)	0.109 (±0.0003)	0.157 (±0.0003)	0.506 (±0.0002)	0.335 (±0.0005)	1.352 (±0.0015)	0.783 (±0.0010)
2	Powder activated carbon (4 gm)	ADRB2	18	C_e	0.004	0.006	0.011	0.020	0.035	0.044	0.062	0.108	0.194	0.708
				q_e	0.320 (±0.0001)	0.555 (±0.0015)	0.804 (±0.0027)	1.053 (±0.0003)	1.354 (±0.0013)	1.461 (±0.0025)	2.137 (±0.0143)	2.530 (±0.0089)	3.6382 (±0.0124)	3.0777 (±0.0039)
3	Powder activated carbon (2 g) in combination with polymer beads(HDPE 1 g)	ADRB3	18	C_e	0.003	0.019	0.020	0.024	0.048	0.109	0.161	0.247	0.372	0.813
				q_e	0.559 (±0.0002)	1.137 (±0.000)	1.577 (±0.0005)	1.669 (±0.0003)	2.182 (±0.0002)	3.362 (±0.0006)	3.851 (±0.0003)	4.487 (±0.0012)	5.406 (±0.0007)	5.533 (±0.0011)
4	Powder activated carbon(1 g) in combination with water hyacinth leaf (2 g)	ADRB4	18	C_e	0.007	0.062	0.072	0.101	0.139	0.338	0.796	1.05	1.696	2.168
				q_e	0.371 (±0.0143)	0.743 (±0.0001)	1.034 (±0.0089)	1.087 (±0.0015)	1.424 (±0.0124)	2.165 (±0.0027)	2.356 (±0.0039)	2.725 (±0.0003)	3.162 (±0.0013)	3.570 (±0.0025)

3. Parameter Estimation

The nonlinear Levenbur–Marquardt parameter estimation method, as described in the function LMF of MATLAB Version 7.0 was used to obtain the parameters in each of the three models described in eqs. (1)–(3). In this method, we usually define a merit function, sum of the squares of the deviations (SSQ) and determine the best-fit parameters by its minimization. Given a set of empirical data pairs of independent and dependent variables, (x_i, y_i), we optimize the parameters β of the model curve $f(x,\beta)$ so that the SSQ becomes minimal.

$$S(\beta)=\sum_{i=1}^{m}\left[y_i-f\left(x_i,\beta\right)\right]^2 \tag{4}$$

The parameters are iteratively adjusted, due to nonlinear dependences, to minimize the SSQ in order to achieve a global minimum (Refer Appendix1A). We start with a set of trial values for the parameters to be estimated, which are gradually improved. The procedure is then repeated until the SSQ decreases no further. A gradient (sensitivity) matrix was derived for the three models for the adsorption functions (amount adsorbed/unit amount of adsorbent used versus equilibrium C (VI) concentration) with respect to the parameters k_1 and k_2.

The sensitivity *matrix* can be written as:

For Model 1:

$$\frac{\partial q}{\partial k_1}=1.0 \tag{5a}$$

$$\frac{\partial q}{\partial k_2}=\log C \tag{5b}$$

For Model 2:

$$\frac{\partial q}{\partial k_1}=C^{k_2} \tag{6a}$$

$$\frac{\partial q}{\partial k_2}=k_1C^{k_2}\log C \tag{6b}$$

For Model 3:

$$\frac{\partial q}{\partial k_1}=\frac{C}{(k_2+C)} \tag{7a}$$

$$\frac{\partial q}{\partial k_2}=-\frac{k_1C}{(k_2+C)^2} \tag{7b}$$

3.1 Evaluation of the Three Models

Evaluation of the following statistical parameters is necessary to infer the estimated parameters:

1. The minimized SSQ function, $S(\beta)$ as given in Eq. (4), which is the least-squares measure of the fit (the smallest SSQ gives the best model).
2. The uncertainties associated with the estimate of each parameter, formally termed as the standard error σ. These are the square-root of the error term covariance matrix C_{ij} of the fit. The closer this value is to zero, the better the fit.
3. The correlation coefficient (r^2). The higher the %, the better is the fit.

4. Results

Table 1 shows details for the experiments for the batch study to determine the amount of adsorption at varied dilutions of hexavalent chromium samples. Table 2 gives the adsorption capacity of various adsorbents used for the removal of hexavalent chromium. Parameter estimation results are given in Table 3 where the uncertainties and confidence intervals of each parameter are presented for each of the models for various samples.

Models are ranked according to their performance in the nonlinear least square fit with their respective values of SSQ (see Table 3). The overall performance for all the three models is given in Table 4. Model 1 (based on Tempkin isotherm) was ranked 1st for only 1 case (see Table 4), while Langmuir ranked first for three cases out of four. Fig. 1–c clearly reveal the surface texture and different levels of porosity within the water hyacinth leaves under study.

Fig. 3a shows how the amount of hexavalent chromium adsorbed, per unit amount of adsorbent varies with the equilibrium hexavalent chromium concentrations for the sample ADBR1, with respect to each of the three models. The performance of model 3 was the best with a rank 1 out of 3 based on the estimate of minimum SSQ (= 0.5274) and a comparatively low value of uncertainties on k_1 (= 0.25) and k_2 (= 2.99). Widths of the 95% confidence interval for both the model parameters look relatively narrow. The confidence interval for k_1 ranges from –0.153 to –0.1233 while that for k_2 varied from 0.7934 to 0.8106. In Fig. 3b residual concentrations (Residual Concentration = Predicted Concentration – Measured Concentration) are plotted against the equilibrium chromium concentrations with respect to the three models tested. This shows no serious departures from the model assumptions. Models 1 and 2 show higher values of SSQ than for Model 3. Thus it could be concluded that

Table 2
Adsorption capacity of various adsorbents used for the removal of hexavalent chromium

S.No.	Adsorbent	Maximum adsorbent capacity, q_m (mg g^{-1})	Reference
1	Activated neem leaves	62.97	[38]
2	Activated carbon	57.7	[39]
3	Bentonite clay	49.75	[40]
4	Sawdust	41.52	[41]
5	Activated tamarind seeds	29.7	[38]
6	Coconut husk fiber	29	[42]
7	Tea factory waste	27.24	[43]
8	Leaf mould	25.9	[44]
9	Pine needles	21.5	[45]
10	Coconut shell based activated carbon	20	[46]
11	Sugar beet pulp	17.2	[47]
12	Palm pressed-fibers	15	[42]
13	Maize cob	13.8	[47]
14	Sugar cane bagasse	13.4	[47]
15	Activated charcoal	12.87	[48]
16	Almond	10	[45]
17	Polymer grafted sawdust	9.4	[49]
18	Maple sawdust	8.2	[50]
19	Activated alumina	7.44	[48]
20	Cactus	7.08	[45]
21	Coal	6.78	[45]
22	Biomass residual slurry	5.87	[51]
23	Distillery sludge	5.7	[52]
24	Calcined bauxite	2.02	[53]
25	Fly ash impregnated with aluminum	1.8	[54]
26	Waste tea	1.55	[55]
27	Fe(III)/Cr(III) hydroxide	1.43	[51]
28	Walnut shell	1.33	[55]
29	Agricultural waste biomass	0.82	[56]
30	Rice husks	0.6	[57]
31	Soya cake	0.28	[58]
32	River bed sand	0.15	[59]

Model 3 (based on Langmuir Isotherm) and the corresponding regression parameters could be accepted for the adsorption analysis of the sample ADRB1.

Similarly Fig. 4a shows the predicted isotherms along with the observations for ADRB2. Model 3 performed best with Model 1 ranking second. The uncertainties on k_1 and k_2 are 0.033 and 0.0034, respectively for Model 3. Corresponding confidence intervals for k_1 ranges from –3.64 to 3.856 while that for k_2 varied from 0.2442 to 0.2658. Fig. 4b shows very small values of residuals ranging from –0.26 to +0.49. In case of ADRB3, Model 3 again ranked first with the lowest value of SSQ = 0.5628. The uncertainties on the fitted parameters were also very low (uncertainty on k_1 = 0.0083 and that on k_2 =0.0002). Figs. 5a and 5b support these results. The same trend was not found for ADRB4. Here Model 2 performed better (SSQ = 0.269) as compared to the other two Models (SSQ_{Model1} = 0.7587; SSQ_{Model3} = 0.5024). Figs. 6a and 6b support this observation.

5. Discussion

Removal of hexavalent chromium from wastewater by biomaterials has been reported by many researchers including Park et al., [60–62] and Massara et al.[63]. Further, Lu et al. [15] demonstrate the phyto-remediation potential of water hyacinth *E. Crassipes* for the removal of heavy metals. The accumulation of cadmium and zinc in shoots and roots increased with the initial concentration and also with the passage of time. Plants treated with 4 mg/l of cadmium accumulated the highest concentration of metals in roots (2049 mg/kg) and in shoots, approximately 113.2 mg/kg after 8 days. On the other hand, the plants treated with 40 mg/l of Zn, showed an uptake value of 9652.1 mg/kg in the roots and 1926.7 mg/kg in the shoot after 4 days. Abdel-Halim et al. [64] report that the percentage removal of lead was 100% by bone powder, 90% by active carbon, 80% by plant powder from water hyacinth and 50% by commercial carbon. The maximum equilibrium sorption capacity (q_{max}) of our adsorbent samples, determined from Langmuir isotherm, are: ADRB1: 9.638 mg/g; ADRB2: 31.46 mg/g; ADRB3: 55.926 mg/g; ADRB4: 33.575 mg/g for 1 l wastewater solutions. The adsorption capacity of PAC (ADRB3) has been found more than the composite ADRB4 with a combination of WH (2 g) and PAC (1 g). However, this particular combination of ADRB4 could be very successfully applied for special cases where the wastewater is disposed into an inland surface waterbody where loads of water hyacinths are naturally grown.

Depending on the nature of each sample and range of concentration levels the isotherm model developed

Table 3
Parameter estimation using levenburg-marquardt algorithm and uncertainty analysis

Sample	Model	k_1	k_2	d.f.	SSQ	Uncertainties on		Rank	95% Confidence limits (k_1)		95% Confidence limit (k_2)	
						k_1	k_2		Lower	Upper	Lower	Upper
ADRB1 (4 g water hyacinth leaf)	1	–0.1383	0.802	8	0.8783	0.0047	0.0028	2	–0.153	–0.1233	0.7934	0.8106
	2	0.0662	0.895	8	0.916	0.0042	0.0327	3	0.053	0.0793	0.7931	0.9968
	3	–0.4247	–14.24	8	0.5274	0.2549	2.9922	1	–1.2187	0.3693	–23.5592	–4.9208
ADRB2 (4 g PAC)	1	3.832	1.5222	8	1.343	0.0048	0.0012	2	3.817	3.8471	1.5183	1.5261
	2	4.394	0.385	8	3.223	0.010413	0.0008	3	4.361	4.4265	0.3823	0.3876
	3	3.752	0.255	8	0.5024	0.0334	0.0034	1	3.6479	3.8560	0.2442	0.2658
ADRB3 (2 g PAC+ 1 g polymer beads)	1	5.803	2.421	8	1.510	0.0032	0.0003	2	5.7936	5.8139	2.4198	2.4222
	2	6.987	0.408	8	2.348	0.0076	0.0004	3	6.3332	7.6408	0.4065	0.4095
	3	6.0827	0.075	8	0.5628	0.0083	0.0002	1	6.0568	6.1086	0.0741	0.0759
ADRB4 (1 g PAC+ 2 g water hyacinth leaves)	1	2.716	1.348	8	0.7587	0.0014	0.0005	3	2.7113	2.7206	0.5840	0.5872
	2	2.656	0.390	8	0.2691	0.0013	0.0001	1	2.6519	2.6601	0.3895	0.3905
	3	3.752	0.255	8	0.5024	0.0061	0.001	2	3.733	3.771	0.2515	0.2585

Table 4
Overall model performance

Rank	Model 1	Model 2	Model 3
1	0	1	3
2	3	0	1
3	1	3	0

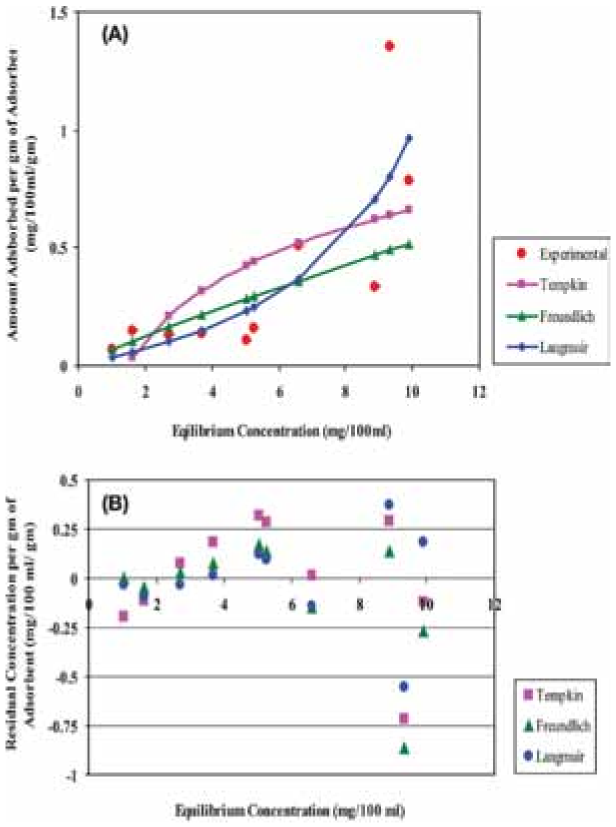

Fig. 3. (a) Plot of amount adsorbed/amount of adsorbents (mg/100 ml/g) vs. equilibrium concentration (mg/100 ml) using ADRB1 as the adsorbent material. (b) Plot of residual concentrations for the different isotherm models developed using ADRB1 as the adsorbent material.

by Langmuir fitted the data well on most occasions. Major assumptions within the Langmuir model are: (1) the surface of the adsorbent is uniform, i.e. all the adsorption sites are equivalent, (2) adsorbed molecules do not interact, (3) all adsorption occurs through the same mechanism and (4) At maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on those molecules already adsorbed but only get adsorbed on the free surface of the adsorbent. For the adsorbent combinations used in this study, the surface of both the commercial activated carbon and water hyacinth leaves were found to be notably smooth (see Fig. 1a–c). Further, adsorbed molecules did not interact since they comprised of hexavalent chromium only and no other compounds, i.e., conditions (3) and (4) were naturally satisfied.

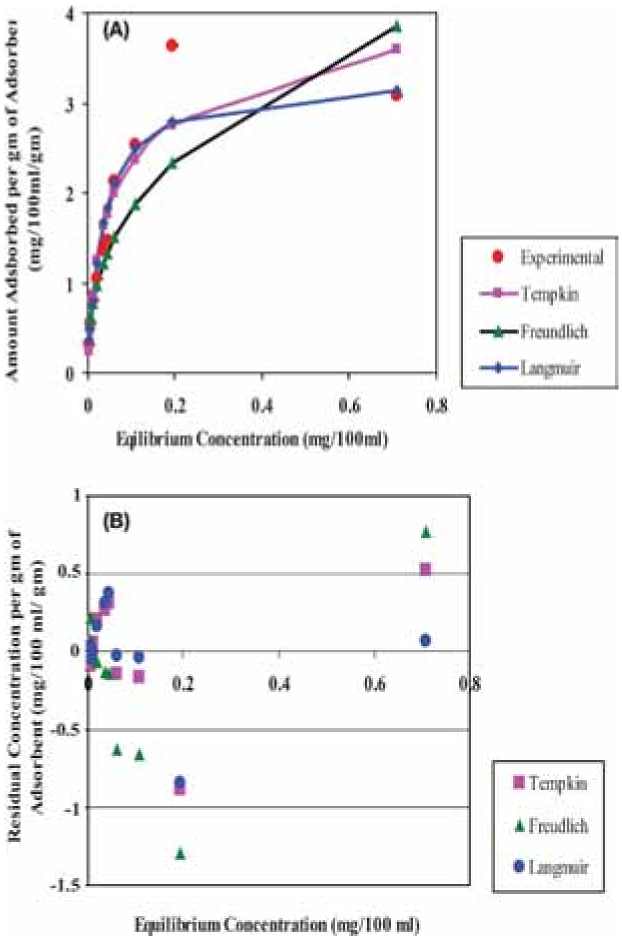

Fig. 4. (a) Plot of amount adsorbed/amount of adsorbents (mg/100 ml/g) vs. equilibrium concentration (mg/100 ml) using ADRB2 as the adsorbent material. (b) Plot of residual concentrations for the different isotherm models developed using ADRB2 as the adsorbent material.

6. Conclusion

The equilibrium adsorption of hexavalent chromium for varied combinations of adsorbents has been assessed. Specifically some of the established isotherms like the Tempkin, Freundlich and Langmuir models were fitted and their respective parameters were estimated using nonlinear least square technique, with SSQ as the merit function. The over-

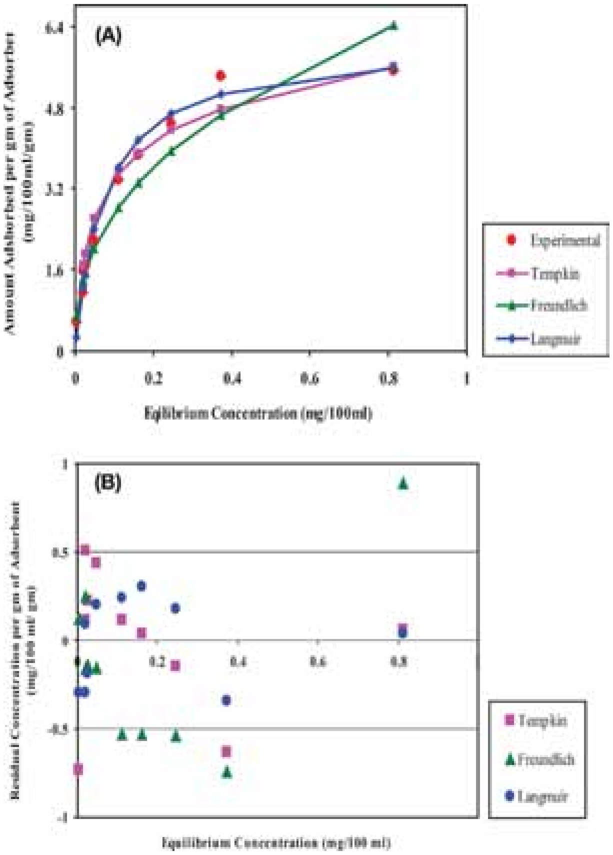

Fig. 5. (a) Plot of amount adsorbed/amount of adsorbents (mg/100 ml/g) vs. equilibrium concentration (mg/100 ml) using ADRB3 as the adsorbent material. (b) Plot of residual concentrations for the different isotherm models developed using ADRB3 as the adsorbent material.

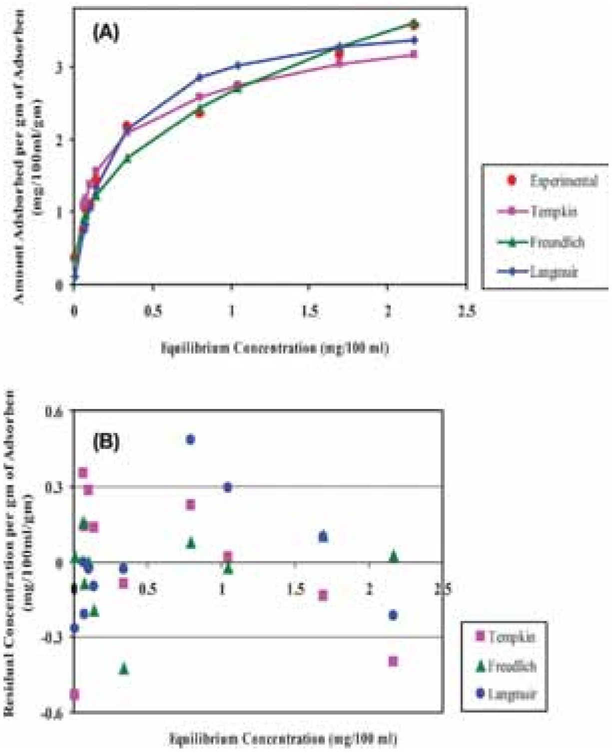

Fig. 6. (a) Plot of amount adsorbed/amount of adsorbents (mg/100 ml/g) vs. equilibrium concentration (mg/100 ml) using ADRB4 as the adsorbent material. (b) Plot of residual concentrations for the different isotherm models developed using ADRB4 as the adsorbent material.

all performance of these models was tested with the experimental data. The water hyacinth leaves were found to be very effective adsorbent in combination with another standard adsorbent like PAC. The quantity of adsorption was predicted using three different isotherms, fitted with the well known Levenburg–Marquardt parameter estimation technique, based on SSQ minimization. The Langmuir isotherm yields the best fit for three out of four adsorbent combinations as compared to Freundlich and Tempkin isotherms. Some agreement was observed between the predicted Langmuir output and experimental data for the system considered. The basic assumptions of the extended Langmuir model like the extended constant energy of adsorption, no interaction and equally important competition between species could be perfectly maintained during the experiments.

The maximum equilibrium sorption capacity (q_{max}) of ADRB4 has been found to be 33.575 mg/g for 1 l wastewater solution. The adsorption capacity of ADRB3, though more than that of the composite ADRB4, could be used for applications where large quantity of wastewater (e.g. leather complexes) containing Hexavalent chromium is disposed into a huge water body where plenty of water hyacinths are grown naturally. Muslin bags could be packed with proportional quantity of PAC and hanged from the water hyacinth shoots, which could be regenerated later.

The measurements should account for the extreme variability in the chromium contents of the samples, source type, its composition, pH, etc. It is important to determine the magnitude and distribution of such variability and its impact on the treatment process in order to design an accurate wastewater treatment technology which provides a coherent picture of the entire plant.

Symbols

C_0	initial concentration (mg/l)
C_e	final equilibrium concentration (mg/l)
q_e	sorption capacity after equilibrium has been reached (mg/100 ml solution/gm of adsorbent)

$q_{\max}$	maximum sorption capacity equilibrium has been reached (mg/100 ml solution/g of adsorbent)
V	volume of liquid (l)
m	mass of the adsorbent (g)
q	equilibrium solid phase concentration (mg/100 ml/g
C	equilibrium liquid phase concentration (mg/100 ml)
k_1	adsorption isotherm constant
k_2	adsorption isotherm constant
σ	standard error
C_{ij}	covariance matrix
λ	wavelength (nm)

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