Removal of hexavalent chromium from aqueous solutions using low cost adsorbents and ANN modeling for prediction

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Three low cost adsorbents such as groundnut seed cake powder, sesame seed cake powder and coconut cake powder were chosen for the bio-sorption of Cr(VI) from aqueous solutions and industrial effluent. Effect of contact time, pH, adsorbent dosage, temperature and initial metal concentration on the removal of Cr(VI) were investigated and optimized. Isothermal studies indicated that the bio-sorption of Cr(VI) followed Langmuir adsorption isotherm. Reaction kinetic studies indicated that removal of the chosen metal by the three adsorbents followed pseudo-second order kinetics. Artificial Neural Networks tool was used for modeling the adsorption of the metal on the chosen adsorbents. ANN was trained to predict the percent removal of the adsorbents. The percent error obtained between the ANN predicted value and experimental value percentage removal of Cr(VI) was found 0.8, implicating that the network and the algorithm used predicted the adsorption efficiency accurately. The three adsorbents chosen for the present study have not been so far used in the removal of heavy metals. And method was found to be economical, easy, and simple, can be applicable for industrial applications.

Keywords: Bio-sorption, Cr(VI), Artificial Neural Networks, adsorption isotherms, pseudo-second order kinetics, groundnut cake powder, sesame seed cake powder, coconut cake powder.

Introduction

Natural sources and manmade activities are responsible for water pollution due to hexavalent chromium. Chromium is found in rocks, animals, plants, soils, volcanic dusts and gases. Various industrial processes such as steel production, electroplating, leather tanning, nuclear power plants, textile industries, wood preservation, anodizing of aluminum, water-cooling and chromate preparation involve the use of Cr(VI). Discharge of wastes containing chromium occurs into environment; with its concentration varies between 5 and 200 mg/L. Such discharge ultimately contaminates soil and water[1–3]. US regulations have set limits for chromium discharge such as: 170 mg/L of Cr(III) and 0.050 mg/L of Cr(VI) and the USEPA drinking water regulations limit the total chromium in drinking water to less than or equal to 0.1 mg/L[4]. Chromite world mine production was estimated at a gross mass of 13×10^6 metric tons in 2002[5] and is one of the reasons for environmental contamination with Cr(VI). In nature chromium exists in two most stable oxidation states, i.e. trivalent and hexavalent forms in aqueous systems. Although at trace level, the trivalent form is considered as an essential nutrient[6–7] whereas hexavalent form of chromium is toxic, carcinogenic and mutagenic in nature[8–14]. Kowalski (1994) revealed that the hexavalent form is about 500 times more toxic than trivalent form. Furthermore, Cr(VI) is highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by skin[15].

Globally a variety of physical, chemical, mechanical and electrical methods were utilized in the removal of heavy metals from industrial effluents. In recent years research has been carried out in removing the heavy metals using low cost, renewable and abundant biomass. These include moss peat, algae, leaf mould, sea weeds, coconut husk, sago waste, peanut hull, hazelnut, bagasse, rice hull, sugar beet pulp, plant biomass, bituminous coal, and coffee powder[16–27].

The adsorption of Cr(VI) by a number of materials such as leaf mould[28], activated ground nut husk carbon[29,30], coconut husk and palm pressed fibers[31], coconut shell activated carbon[32], coconut shell, wood and dust coal activated carbons[33], coconut jute carbon[34], coconut tree sawdust carbon[35], sawdust and used tyres carbon[36], phosphate treated

sawdust[37], cactus, olive stone/cake, wool, charcoal and pine needles[38], rice husk carbon[39,40], moss[41], sphagnum moss peat[42], coconut fiber compost, maize cob, sugar beet pulp and cane bagasse[43], hazelnut shell carbon[44], almond shell carbon[45], corncob[46], quaternized wood[47], cow dung carbon[48], waste slurry[49] and carbon slurry[50] have been reported in the literature.

In the present study, three low cost adsorbents such as groundnut seed cake powder (GNSCP), sesame seed cake powder (SSCP) and coconut cake powder (CCP) were chosen for the removal of hexavalent chromium from aqueous solutions. These materials were used in their native form as it is, without any chemical pretreatment. The details are presented hereafter.

Materials and methods:

All the chemicals used were in analytical grade. Double distilled water was used throughout the experiment. Bruker advanced D8 PXRD instrument was used for XRD analysis. Bruker model ALPHA II- FTIR instrument was used for FTIR analysis.

Preparation of Cr(VI) solution:

A stock solution of (100 mg/L) Cr(VI) was prepared by dissolving adequate amount of potassium dichromate in one litre of double distilled water. By appropriate dilutions, a series of required concentrated solutions were prepared for the study.

Preparation of adsorbent:

Groundnut seed cake powders (GNSCP), coconut cake powder (CCP) and sesame seed cake powder (SSCP) were used as adsorbents for the bio-sorption of Cr(VI) ions. Samples of adsorbent cakes were collected from local markets. These samples were dried under sunlight for twenty four hours. The dried samples are crushed and ground into fine powder by using crusher and ball mill. The powders were sieved by sieve analysis method to get particles of homogeneous size. The sieved powders were stored.

Characterization of adsorbents:

GNSCP, CCP, SSP samples were found to have higher surface area 470, 480, 490 $m^2 \, g^{-1}$. These powders have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high capacity for adsorption. The sample structure and the presence of carbonyl and OH groups were estab-

lished by using XRD analysis and FTIR analysis (Supplementary data). The FTIR spectra of the three adsorbents showed similar bands. Some important bands observed are at 3270.8 cm^{-1} for N-H stretching in amines, 2921 cm^{-1} for -OH stretching in -COOH, 1743.2 cm^{-1} for C=O stretching in amides or aldehydes or ketones. From these data it is found that the adsorbent materials contain lignin, protein, amines and carboxylic acid groups in them. XRD patterns of the adsorbents before and after adsorption process clearly depicts the presence of metal ion in the adsorbent after experimentation.

Adsorption experiment:

The adsorption experiment of Cr(VI) was performed using batch adsorption technique. The different adsorbents are weighed and dissolved into 50 ml Cr(VI) solution. The pH of the solutions was adjusted by using 0.1 N H_2SO_4 until it gets stabilized. Then the resultant solution was agitated for one hour at room temperature until equilibrium attained. After the attainment of equilibrium the mixture is filtered through a Whatmann 1 filter paper. Residual concentration of the metal ions in the filtrate was determined by AAS.

Results and discussion

Effect of pH:

As pH determines the surface charge, degree of ionization of the adsorbent and speciation of adsorbate, pH of the solution is one of the significant factors in adsorption of heavy metals by bio-adsorbents. The results of effect of pH were shown in Fig. 1 and show the effect of pH on the removal of Cr(VI) from aqueous solution using the three adsorbents. From the results it was found that, as the pH of the solution increased till 4 a significant increase in the equilibrium capacity of Cr(VI) removal by the different adsorbents. At a higher initial pH (> 6) precipitation of chromium ions was found. From the results it was clear that the adsorption was effective at a pH value of 2 with the three adsorbents used, pH of 2 was fixed as optimum pH for the present study. These results were in agreement with those that reported in literature.

Effect of contact time:

The effect of contact time on the removal efficiency of chromium ions from aqueous solution using different adsorbents was studied; the results were shown in Fig. 2. The rate of uptake of metal ions was found to be quite rapid.
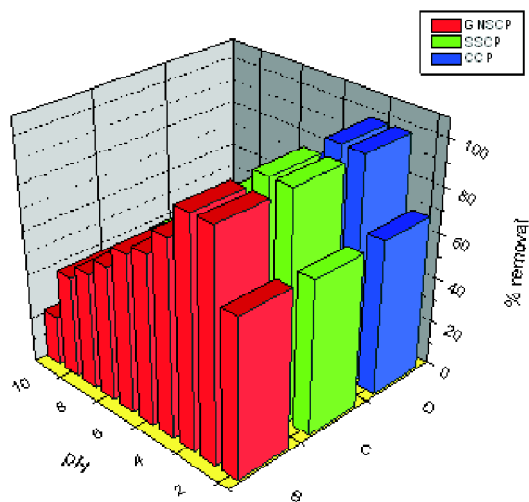
Fig. 1. Effect of pH on the removal of Cr(VI) using the three adsorbents.
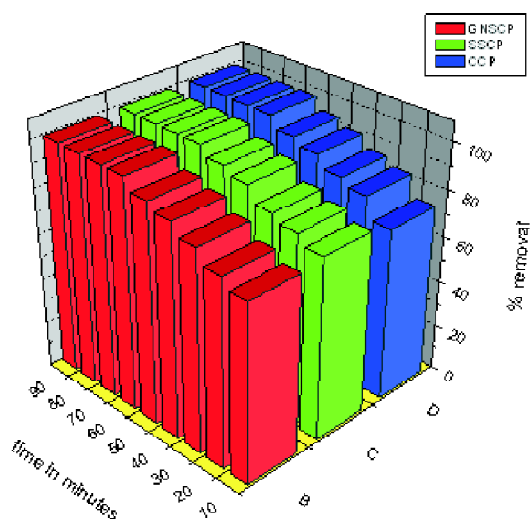

Fig. 2. Effect of contact time on the removal of Cr(VI) using the three adsorbents.

A series of experiments were carried out to establish the equilibrium time for the effective removal of chromium ions using the adsorbents. By fixing the adsorbent dosage batch experiments were carried out at varying time intervals. From the results obtained 99.7% of removal of chromium ions was found at time of 1 h.

Effect of adsorbent dosage:

A series of experiments were carried out to establish the optimum dose of the adsorbent for the removal of Cr(VI) by the three adsorbents. The experiments were conducted by

taking 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 g of the adsorbents for batch studies. The results obtained were shown in Fig. 3. From the results it was found that removal of chromium ions from aqueous solution was effective with 0.6 g of the three adsorbents. And the same was fixed as optimum adsorbent dosage.
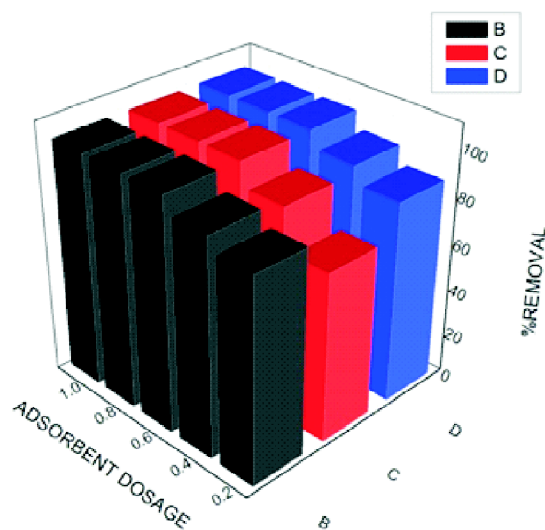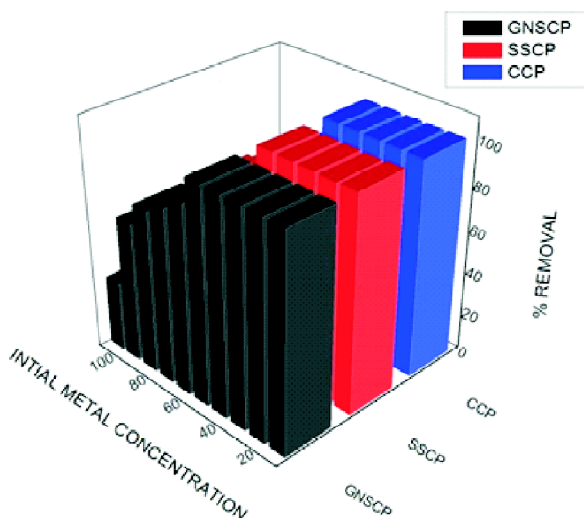

Fig. 3. Effect of adsorbent dosage on the removal of Cr(VI) using the three adsorbents.

Effect of initial metal ion concentration:

Experimentation was carried out to fix the initial metal ion concentration by varying the metal ion concentration and by fixing adsorbent dosage, pH and contact time. A series of chromium ion solutions of concentration 10, 20, 30, 40, 50, 60, 70, 80, 90 mg L^{-1} were mixed in separate flasks with 0.6 g of each of the adsorbent powder. This mixture was agitated for 1 h at pH 2. Concentration of Cr(VI) ions in the filtrate was determined after the predetermined time of 60 min. The results obtained were shown in Fig. 4. From the results it was found that the removal of chromium ion from aqueous solution decreases as the metal ion concentration increases. It may be due to the absence of adsorption sites in the adsorbent. The maximum removal of chromium using the adsorbents was found at a metal concentration of 50 mg L^{-1}.
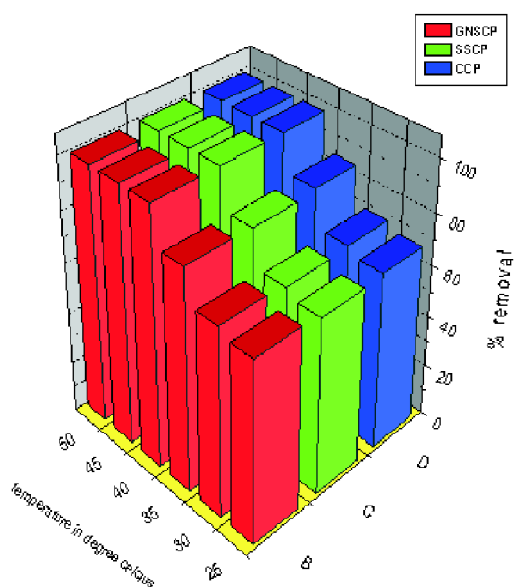
Effect of temperature:

The effect of temperature on the removal efficiency of chromium ions from aqueous solution using different

Fig. 4. Effect of initial metal concentration on the removal of Cr(VI) using the three adsorbents.

adsorbents was studied. The results were shown in Fig. 5. A series of experiments were carried out to establish the equilibrium temperature for the effective removal of chromium ions using the adsorbents. By fixing the adsorbent dosage, contact time, pH and initial metal concentration batch experiments were carried out at varying temperatures. From the results obtained 99.7% of removal of chromium ions was found at a temperature of 40°C.

Fig. 5. Effect of temperature on the removal of Cr(VI) using the three adsorbents.

Adsorption isotherms:

These isotherms are significant to describe the behavior of adsorbate-adsorbent interaction. This is in turn useful for the purposes of designing an adsorption process. There are many adsorption isotherms are used for this purpose. Langmuir adsorption isotherm, Freundlich adsorption isotherm and Temkin isotherms were adopted in the present study.

Langmuir adsorption isotherm:

$$q_e = \frac{q_m K C_e}{1 + K C_e}$$

(or)

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where q_m and K are Langmuir constants related to the sorption capacity and sorption energy respectively. C_e is the equilibrium concentration in mg L^{-1} and Q_e is the amount of adsorbate adsorbed per unit weight of adsorbent. The adsorption of Cr(VI) on different adsorbents gives a straight line (Fig. S1, supplementary data). It is clear that a linear fit if fairly good. This enables the Langmuir adsorption isotherm model's applicability.

Freundlich adsorption isotherm:

The Freundlich isotherm is defined as $q_e = K_F C_e^{1/n}$ and in linearized form

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where C_e is the equilibrium concentration in mg L^{-1}, q_e is the amount of adsorbate adsorbed per unit weight of adsorbent in mg g^{-1} and "k" is parameter related to the temperature and "n" is a characteristic constant for the adsorption.

Temkin isotherm:

Temkin isotherm model can be represented as

$$Q_e = \left(\frac{RT}{b}\right) \ln (K_T C_e)$$

This equation can also be represented as

$$Q_e = \left(\frac{RT}{b}\right) \ln K_T + \left(\frac{RT}{b}\right) \ln C_e$$

Table 1. Optimization parameters for the adsorption process

Sr. No.	Parameter	Name of the adsorbent		
		GNCSP	SSCP	CCP
1.	pH	2	2	2
2.	Temperature (°C)	40	40	40
3.	Adsorbent dosage (g)	0.6	0.6	0.6
4.	Initial metal concentration (mg/L)	50	50	50
5.	Contact time (min)	60	60	60
6.	Q_{max} (mg/g)	7.82	7.2	7.81

K_T is the equilibrium binding constant (L/mg); b is the Temkin isotherm constant; B is the constant related to heat of sorption (J/mol); R is the universal gas constant; T is the absolute temperature. Table 2 enumerate the results of the various adsorption isotherm parameters. Adsorption of Cr(VI) by the three adsorbents fit aptly to Langmuir adsorption isotherm type with R^2 value of 0.9997, 0.9997 and 0.9997 with GNSCP, SSCP and CCP respectively. Freundlich and Temkin adsorption isotherms were graphically represented as Figs. S2 and S3 as supplementary data files.

From Langmuir isotherm the adsorption capacity is calculated as 0.98 mg/g. Equilibrium parameter or separation factor R_L can be calculated using the formula

$$R_L = 1/(1 + K_L \times C_0)$$

From the calculations it was found that the value of R_L lied in between 0 and 1, indicates the feasibility of adsorption of Cr(VI) by the three adsorbents.

It was found that Temkin isotherm for the adsorption of Cr(VI) by the adsorbents showed R^2 value greater than 0.85 indicating that the adsorption is of chemisorption type.

Kinetic models of the present study:

Kinetic models helps in understanding the mechanism of metal adsorption and evaluate the performance of various adsorbents for the removal of metals. Among the many kinetic models developed mostly used are the Lagargren's pseudo-first order kinetics and pseudo-second order model. The sorption kinetics of pseudo-first order was

$$\log (q_e - q) = \log q_e - kt/2.303$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent, q is the amount of solute adsorbed at any time and k is adsorption constant.

The pseudo-second order kinetic model is described by the following equation

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

where q_t and q_e are the sorption quantity at time t and equilibrium respectively, k is the rate constant. Thus a plot of t/q_t vs t gives the pseudo-second order adsorption. Pseudo-second order rate constant was determined from the respective plots.

The results obtained were tabulated in Table 3. Graphical representation for the pseudo-second order kinetic models was presented in Fig. 6. From the results it was found that the adsorption of Cr(VI) followed pseudo-second order kinetics. The plot drawn between t against t/q_t fitted a linear plot with R^2 value of 0.995. This was graphically represented in Fig. 6.

Table 2. Adsorption isotherm characteristics for the removal of Cr(VI) using the chosen three adsorbent

Sr. No.	Adsorbent	Langmuir adsorption isotherm			Freundlich adsorption isotherm			Temkin adsorption isotherm		
		q_{max}	K	R^2	K_F	n	R^2	b_T	A	R^2
1.	GNSCP	0.97	14644	0.9997	26.5	2.23	0.453	413060	996.25	0.856
2.	SSCP	0.975	14643	0.9997	26.2	2.21	0.453	413060	996	0.854
3.	CCP	0.97	14644	0.9997	26.5	2.23	0.453	413060	996.2	0.854

Table 3. Kinetic parameters for the adsorption of Cr(VI) using the three adsorbents

Sr. No.	Adsorbent	Pseudo-first order kinetics			Pseudo-second order kinetics		
		q_e	K_1	R^2	q_e	K_2	R^2
1.	GNSCP	0.000011	24.51	0.148	0.602	2.542	0.995
2.	SSCP	0.0000117	24.512	0.15	0.6002	10.408	0.995
3.	CCP	0.0000117	24.512	0.148	0.595	3.407	0.997

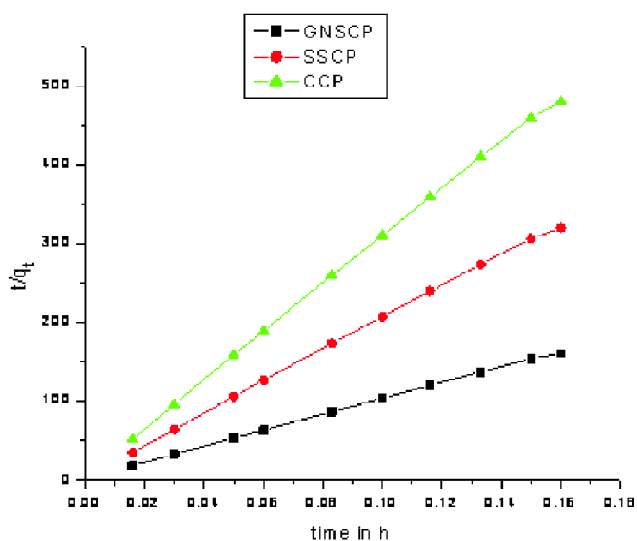GNSCP – groundnut seed cake powder; SSCP – sesame seed cake powder; CCP – coconut cake powder.

Fig. 6. Pseudo-second order kinetics for the removal of Cr(VI) using the chosen adsorbents.

Comparison of adsorption of Cr(VI) with other adsorbents:

A comparative study was carried out for the adsorption of Cr(VI) between the literature cited adsorbents and the adsorbents chosen in the present study. All the adsorbents cited in literature are either chemically derived or chemically pretreated. These possess the highest adsorption capacities. Although, some of the adsorbents like iron(III) hydroxide[51], activated red mud[52], waste tea[53], distillery sludge[54] and saw dust[55] were found to have lower adsorption capacities than that reported in the present study. Hence the adsorbents chosen for the present study gave better results than those mentioned above.

Application of the chosen adsorbents to real samples:

A comparative study was conducted by taking a real sample from aluminum coating factory [50 mg/L of Cr(VI)] and laboratory simulated sample [50 mg/L of Cr(VI)]. The experimentation was carried out by fixing Cr(VI) concentration first and second by varying the concentration. The results showed that the percent removal of Cr(VI) from the labora-

tory simulated sample was the highest when compared to that of the real sample. The reason may be attributed to the presence of other metal ions in the real sample. A comparative table is presented in Table 4.

*Adsorption modeling using Artificial Neural Networks (ANN):*

Feed forward architecture namely MLP (multilayer perception) is the most commonly used model of system in ANN. Input layer, hidden layer(s) and output layers are the three components of the network. Neurons are the elementary processing units in each layer. Each neuron in the input layer is connected to its hidden layer through weights. When an input is introduced to the neural network, the synaptic weights between the neurons are simulated and these signals propagate through layers and the output is result is formed. Closest approach to the experimental or expected value with the predicted value is the main objective of a neural network. Various algorithms are available for the purpose. Among these algorithms feed forward back propagation is the most widely used[56]. This algorithm is specially used in solving prediction problems. Hence for the present study back propagation algorithm was chosen for the prediction of percentage removal of Cr(VI). Fig. 6 presents a schematic representation of the ANN. Determination of optimal set of input variables is the pre requisite in performing the ANN in the best possible way[57,58]. In literature it was cited that a reduction of the input set size by 50% i.e. eight-four input variables improved the performance of the ANN by 1.2–9%. It was also mentioned that the variables must be predicted but not correlated. Correlated variables will degrade the performance of the ANN[59].

The input variables for the modeling of the Cr(VI) removal are (a) initial pH, (b) adsorbent dosage, (c) name of the adsorbent and (d) contact time.

Among the data set of variables 60% of the data points were used for training, 20% for cross validation, the nest 10% for testing and the rest used for prediction. The network

Table 4. Comparison between real samples and laboratory simulated samples

Sr. No.	Adsorbent dose	Real sample	Simulated sample	Cr(VI) concentration	Real sample	Simulated sample
1.	0.4	54.8	99.7	20	45.8	99.8
2.	0.6	54.7	99.8	30	55.8	99.8
3.	0.8	55.8	99.6	40	65.8	99.7
4.	1.0	65.8	99.7	50	68.6	99.8
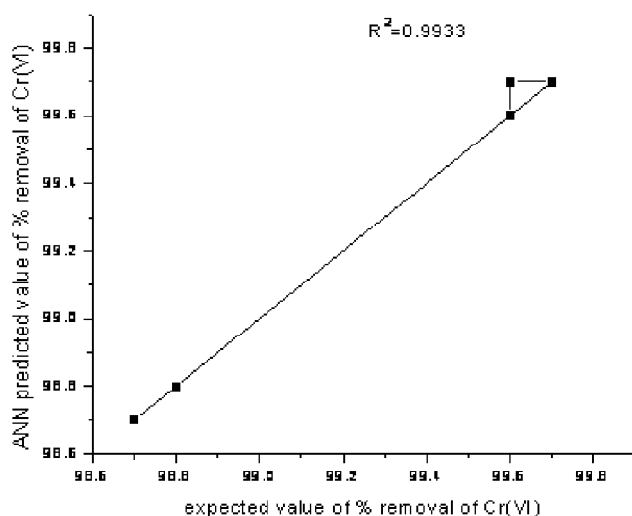
Fig. 7. Correlation between the expected and ANN predicted values of % removal of Cr(VI).

was trained until the number of epoch should be the least possible. The maximum number of epoch were kept at 30,000.

After training and testing the network was simulated and the predicted results were recorded. A comparative plot for the percentage removal between experimental and predicted values was presented in Figs. S5 and S6 (Supplementary data). This implicates that the algorithm chosen and the network trained were apt in predicting the removal of Cr(VI) using the three adsorbents. Correlation between the experimental and ANN predicted values were presented in Fig. 7. A strong positive correlation with R^2 value of 0.9993 infers that the modeling methodology adopted using ANN fits perfect and such model can efficiently be used to study the adsorption process.

Conclusions

Adsorptive removal of Cr(VI) ions from aqueous solutions using GNSCP, SSCP and CCP was demonstrated in the present study. These adsorbents were used in their native form without any chemical pretreatment and found to have a Q_{max} value 7.82, 7.2, 7.81 mg/g. The process of adsorption is optimized at a pH of 2, temperature of 40°C with 0.6 g of all the three chosen adsorbents. Adsorption kinetics for the present study was also investigated and found that the adsorption of Cr(VI) on these adsorbents followed pseudo-second order kinetics. It was found from the isothermal studies

that the adsorption process fit to Langmuir type. The value of R_L was found in between 0 and 1 implicating that the process of adsorption is favorable. Back propagation L-M algorithm was used for the prediction of adsorption using ANN. These results suggested that the predicted values were well in accordance with experimental results obtained. This enumerates the suitability of the algorithm in predicting the adsorption process.

Acknowledgements

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