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Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H_3PO_4

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Abstract

The present work reported the adsorption of Cr (VI) from aqueous solutions on activated carbon prepared from mango kernel, a seasonal waste from mango fruits. Kernels from dried mango fruit shells were taken out and pulverized in a micro-pulverizing mill. The powder thus obtained was activated with 40% H_3PO_4 and carbonized at 600 °C for 1 hour in an inert atmosphere. Physico-chemical characteristics such as elemental composition, surface area, functional groups and surface morphology of the activated carbon were analyzed using elemental analyzer, BET surface area analyzer, FTIR spectroscopy and SEM analysis respectively. Batch adsorption experiments were performed to investigate the effects of Cr (VI) concentration, carbon dose, pH, rate of agitation, time and temperature. The maximum adsorption capacity of Cr(VI) was found to be 7.8 mg g^{-1} at pH 2 and temperature 35 °C. The Langmuir adsorption isotherm best represented the equilibrium data and a pseudo-second order relation represented the adsorption kinetics.

Keywords: Removal; Activated carbon; Hexavalent chromium Cr (VI); Mango kernel

1. Introduction

Use of chromium is quite wide-spread and it is used as antifouling agent in cooling towers, chrome-plating, leather tanning, pigment, textile, and wood preservation, etc [1]. As a result its concentration in the environment, particularly in water bodies has increased from its natural abundance during last two decades [2]. Out of its two abundant forms Cr (III) and Cr (VI), the hexavalent form is toxic and is suspected to be carcinogenic. It affects the kidney and liver and causes dermatitis, diarrhea [3]. According to the WHO, its permissible level in surface water bodies is 0.05 mg/L and its concentration in industrial wastewaters varies from 0.5 to 270 mg/L [4]. Thus it is mandatory to treat the Cr-bearing wastewaters. Several chemical and physical methods have been developed to treat chromium bearing effluents to bring its level down to the permissible effluent standards [5–8].

A large number of researchers have tried to use conventional and non-conventional adsorbents such as carbonized biomass, un-carbonized powder biomass and activated carbon for removing chromium from wastewater. Table 1 gives a representative summary of the various unconventional adsorbents used by researchers for removing Cr (VI) from actual and synthetic wastewaters. In spite of this an effective substitute for commercial activated carbon is yet to be developed.

Activated carbons prepared from agro-wastes are likely to have properties comparable to those of commercially available activated carbon [23]. Actually, agro waste from crops and fruit production can be used as most suitable raw material for preparation of low cost activated carbons. If properly processed, the agro-wastes can serve as a good feed-stock for obtaining gaseous and liquid fuels along with activated carbon with good adsorption capacities [24–26]. Further, properly utilizing these can also help in saving trees that are currently being used for making activated carbon on a commercial scale. Wastes from various fruits can also serve as cheap raw material for making activated carbon for use in adsorption units. Activated carbons prepared from apricot stone [27], coconut shell [28], groundnut husk [10], pecan nut shell [29], Terminalia arjuna nuts [30], etc. were successfully used for water and wastewater remediation by several researchers. However, there is no published information available on the use of mango shell and/or mango seed kernel for removal of hexavalent chromium.

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Table 1
Summary of some adsorbents used for removal of Cr (VI) ions from aqueous solution.

Adsorbent	Solution pH	Maximum adsorption capacity (mg/g)	References
Coconut tree sawdust activated carbon	3.0	3.46	[9]
Groundnut husk activated carbon	3.0	7.0	[10]
Casuarina equisetifolia leaves activated carbon	3.0	17.2	[11]
Coconut shell activated carbon	4.0	10.88	[12]
Bael fruit shell activated carbon	2.0	17.27	[13]
Rubber wood sawdust	2.0	44.05	[14]
Sugarcane bagasse	2.0	1.76	[15]
Maize corn cob	2.0	0.28	[16]
Cactus	2.0	7.08	[17]
Peanut shell activated carbon	2.0	16.26	[18]
Erythrina variegata orientalis	3.0	6.32	[19]
Swietenia mahagoni fruit shell	3.0	2.309	[20]
Pineapple leaves activated carbon	2.0	18.77	[21]
Sal sawdust	3.5	9.55	[22]
Mango kernel activated carbon	2.0	7.8	Present study

Mango is a seasonal tropical fruit produced in several countries. Its global production during 2013 was around 43 million metric tons and India being its largest producer had a production of 18 million metric tons during the same year [31]. The mango kernel is nearly 5% of the total fresh fruit weight. It is available almost throughout the country. At present the shell and its kernel are nothing but wastes having no value. Since it is primarily lingo-cellulosic in nature, it would be interesting to use it as a feed-stock for making activated carbon for adsorption of water pollutants including Cr (VI) to save the woody biomass currently being used for producing activated carbon on a large scale. In view of above, an effort has been made in the work to prepare activated carbon from mango-shell kernel with objective to use it as adsorbent for removing Cr(VI). The results of batch adsorption experiments including the effect of pertinent operating parameters like agitation, concentration, adsorbent dose, pH, temperature and time are presented in this paper.

2. Material and methods

2.1. Adsorbate: chromium (VI)

A stock solution of Cr (VI) was prepared (1000 mg/L) by dissolving required amount of Potassium dichromate salt, $K_2Cr_2O_7$ (SRL Pvt. Ltd., extra pure AR) in distilled water. The stock solution was further diluted to obtain desired concentration ranging from 20 to 100 mg L^{-1}.

2.2. Preparation of mango kernel activated carbon (MKAC)

The mango seeds were collected from local fruit-vendors and were dried over a period of time. Thereafter, the dried mango stones were broken-up to retrieve the fleshy mango kernels from inside. The kernels were further dried and then crushed in the disintegrator. The crushed powder of kernel was sieved in 14–22 mesh (BSS) fractions to obtain the desired particle size of 710–1000 μm and was selected for further operation. Then the powdered mango kernels were washed twice to remove soluble and insoluble lighter materials and dried in an oven at 60 °C for overnight. Chemical activation of the precursor (powdered kernel) was done with 40% H_3PO_4 (AR grade) using the procedure reported by others [32]. The impregnation ratio of 3:1 (weight of chemical: weight of powdered kernel, w/w) was used to ensure sufficient penetration and the mixture was kept undisturbed for 24 h at 35 °C. The kernel powder was then washed thoroughly with distilled water and dried in air oven at 75 °C for overnight.

The dried chemically activated kernel powder was carbonized at 600 °C in a laboratory muffle furnace (NSW India, NSW-101) [33]. Furnace temperature was raised at 20 °C/min to the final carbonization temperature 600 °C under inert atmosphere. The samples were maintained at the carbonization temperature for 1 h before cooling to room temperature. The cooled carbonized mass was washed thoroughly with distilled water until the pH of filtrate water reached 7 to ensure complete removal of residual acid and other organic and mineral matters, and then dried at 75 °C for overnight. The carbonized mango kernel activated carbon (MKAC) was kept in an airtight container for characterization and use in adsorption experiments. The activated carbon is abbreviated as "MKAC" throughout the manuscript.

2.3. Characterization of carbonized activated mango seed kernel powder

The MKAC was characterized in terms of chemical composition, functional groups, morphology, and surface area. The presence of various functional groups present on the surface of the adsorbent and their role in adsorption was analyzed using FTIR (Fourier transform infrared) spectrum within the range of 400–4000 cm^{-1} using Thermo-Fisher FT-IR analyzer (SCIENTIFIC, NICOLET 5700).

The pH value required to give zero net surface charge was measured for MKAC [34]. The surface is positively charged below this pH and negatively charged above this pH. A plot of the equilibrium pH versus initial pH yielded a curve from where the pHpzc was identified as the point at which the change of pH is zero.

The surface morphology of MKAC was investigated using a Scanning Electron Microscope (FEI™, QUANTA 200F) to study the surface texture and the porosity of the MKAC. The average pore size or diameter was also determined using SEM.

The elemental analysis of raw and activated mango kernel were determined with the help of an elemental analyzer (EURO-EA) and results are presented in Table 2. The surface area S_{BET} (Brunauer–Emmett–Teller Surface area) of the MKAC was determined from the N_2 adsorption at −196 °C and N_2 desorption at ambient temperature with degassing at 300 °C using Smart Sorb 92/93 surface area analyzer (Smart Instruments Co. Pvt. Ltd.).

Table 2
Elemental analysis of raw mango kernel and activated mango kernel.

Elemental analysis (%)	Raw mango kernel	Activated mango kernel
C	44.71	78.56
H	6.42	2.05
N	5.05	1.23
S	0	0
O	44.53	18.16

2.4. Batch adsorption experiments

The batch adsorption experiments were performed in 250 mL Erlenmeyer flasks containing 100 mL solution of Cr (VI) of known concentration in a shaker incubator at controlled temperature for different periods. Adsorption experiments were conducted with different amounts of MKAC with known initial concentration of Cr (VI) solution. The residual concentration of adsorbate was determined by measuring the absorbance of the purple complex of Cr (VI) with 1, 5-diphenylcarbazide at 540 nm using an UV-spectrophotometer (ELICO, SL 159). The calibration curve for this purpose was prepared by using a standard solution of potassium dichromate. The difference in Cr (VI) concentration before and after the adsorption was used to calculate the percentage adsorption of Cr (VI) on activated carbon and it was expressed by Eq. (1):

$$Adsorption\ \% = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

The amount of adsorbed Cr (VI) per gram of activated carbon was calculated using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (2)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium concentration of Cr (VI) respectively, V(L) is the volume of solution, W (g) is the mass of activated carbon, q_e (mg g^{-1}) is the metal uptake capacity of activated carbon.

Effect of agitation speed of the shaker on the adsorption was studied through a separate set of experiments by varying the speed from 100 to 180 rpm. It was observed that up to 150 rpm marginal increase in the extent of adsorption was observed but after that practically no change was detected. Thus the agitation speed of 150 rpm was used in all experiments.

To evaluate the equilibrium contact time, adsorption experiments were performed for over 200 min using 20 mg L^{-1} initial Cr (VI) concentration with 0.25 g/100 mL adsorbent dose at pH 2, 35 °C operating temperature and 150 rpm. Experiments were performed to find out the effect of adsorbent dose on Cr (VI) uptake and percentage adsorption for initial Cr (VI) solution concentration 20 mg L^{-1}, pH 2, 35 °C operating temperature, 150 rpm and for 150 min. Effect of pH was investigated by performing adsorption experiments at different initial pH values of 2–8 using 20 mg L^{-1} initial Cr (VI) concentration and 0.25 g/100 mL adsorbent dose at 35 °C for 150 min equilibrium time. Effect of Cr (VI) concentration was investigated at different initial Cr (VI) concentrations with adsorbent dose

of 0.25 g/100 mL at pH, temperature 35 °C and for 150 min equilibrium time.

3. Result and discussion

3.1. Characterization of activated carbon

The pHpzc value of the MKAC was found to be 6.8, which indicates that at this pH the net surface charge of the adsorbent is zero, whereas at pH < 6.8, the adsorbent surface is positively charged and at pH > 6.8, it is negatively charged.

The FTIR spectrum of the adsorbent before (Fig. 1a) and after adsorption (Fig. 1b) are recorded. In Fig. 1a the spectrum reveals the complex nature of the adsorbent as evidenced by the presence of a large number of peaks. Absorption peaks around 3030.6 and 3423.0 cm^{-1} indicate the presence of free and inter-molecular bonded hydroxyl groups [35]. The peaks around 2720.5–1724.3 cm^{-1} can be assigned to the presence of aldehydes, carbonyls, carboxylic acids and esters on the surface [36]. The peaks appearing at 3371.7, 1510.6 and 555.5 cm^{-1} indicate the presence of N-H stretching showing presence of amines and amide groups, nitro compounds, and alkyl halides respectively [37,38]. The bands around 1254.0 and 876.9 cm^{-1} show the presence of aromatic, amines and hydrocarbons on the surface [39]. These functional groups have a high affinity toward hexavalent chromium. FT-IR spectra of Cr (VI) adsorbed MKAC show low transmittance intensity and the shifted peak locations at different frequencies due to Cr (VI) adsorption (Fig. 1b).

The SEM micrograph of MKAC before adsorption is shown in Fig. 2a. It is seen that MKAC has a highly porous structure with greater homogeneity and average pore diameter of 38.9 μm. Fig. 2b shows the SEM morphology of MKAC after Cr (VI) loading. From the figure it is clear that a layer is formed due to Cr (VI) adsorption on the surface and some Cr (VI) have occupied inside the pores of MKAC.

From Table 2 it is seen that as expected the percent carbon content in activated carbon (78%) is substantially higher than
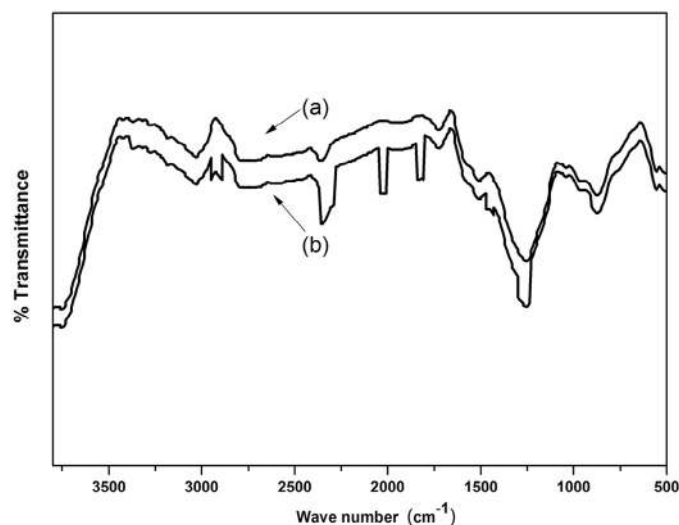

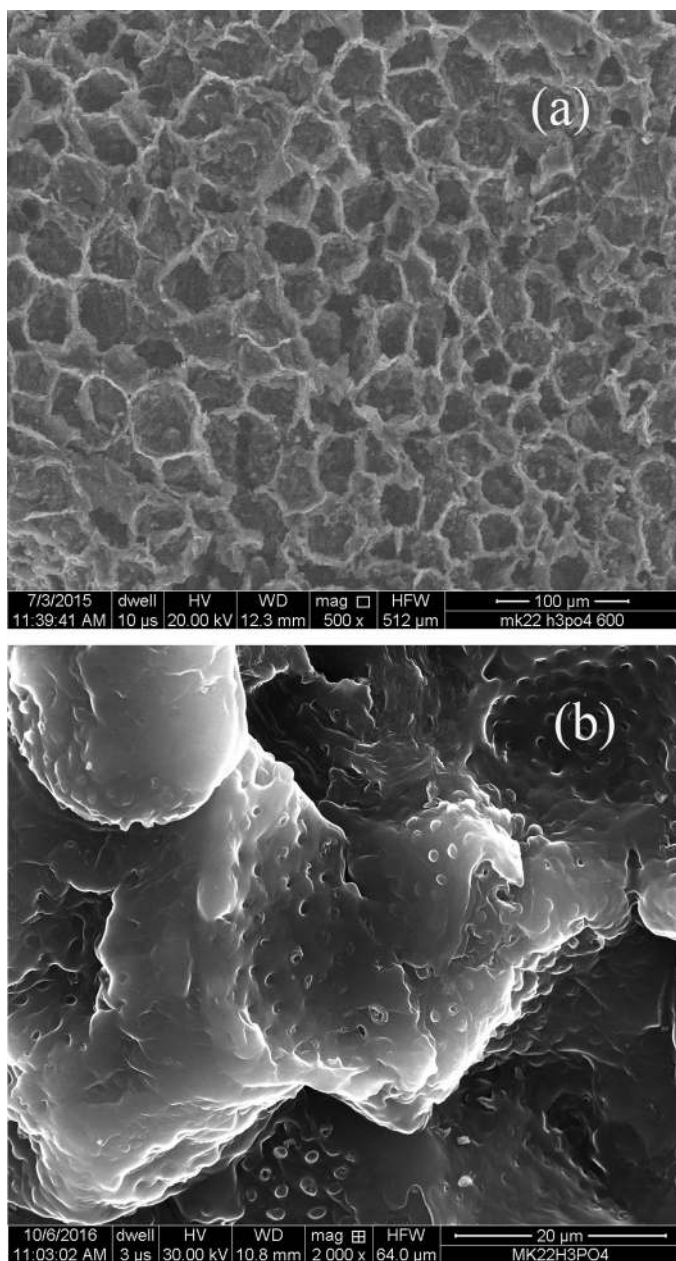Fig. 1. FTIR spectra of the MKAC (a) Before adsorption and (b) After Cr (VI) loading.

Fig. 2. SEM micrograph of MKAC (a) Before adsorption and (b) After Cr (VI) adsorption.

Table 3
The physical characteristics of the mango kernel activated carbon.

Parameters	Value
Bulk density (g cm^{-3})	1.43
Porosity	0.576
BET Surface area (m^2 g^{-1})	490.43
Average particle size (μm)	781.5
Average pore size (μm)	38.9
pH at the point of zero surface charge (pHpzc)	6.8

to the surface functional groups and chemistry of the adsorbate metal ion-solvent interaction that vary with the pH. The hexavalent chromium ions can exist as hydrogen chromate ($HCrO_4^-$) or chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) depending upon the pH of the solution. At acidic pH 2, the dominant form of Cr (VI) is $HCrO_4^-$ and higher pH other forms CrO_4^{2-} or $Cr_2O_7^{2-}$ predominate. Observed higher adsorption at lower pH can be attributed to the strong electrostatic attraction between positively charged surface groups and $HCrO_4^-$. Reduced adsorption above pH 6 can be attributed to the competitive adsorption of CrO_4^{2-} and OH^- ions. Earlier works have also reported similar behavior using other adsorbents [43–45].

3.3. Effect of contact time

As shown in Fig. 4, the extent adsorption increases steeply with increasing contact time up to around 50 minutes and there after it reduces and tends to a constant value. In the beginning all the active sites on the adsorbent are vacant hence adsorption proceeds at a faster rate and desorption at a lower rate, the net effect is faster increase in the extent of adsorption. As the active sites get occupied, the rates of adsorption and desorption tend to be equal and extent of adsorption reduces and eventually becomes nearly constant at equilibrium. Any further adsorption beyond this is through intra-particle diffusion which is a much slower process [46,47]. For the given situation adsorption equilibrium time is observed to be 150 min.

that of green mango seed kernel. This is nearly comparable to the carbon content reported for olive pits (64.42%) [40], sugar beet bagasse (70–80%) [41] and hazelnut-husk (80.41%) [42]. BET surface area of the adsorbent was found to be 490.43 m^2 g^{-1} (Table 3) which indicates MKAC to be a very good adsorbent for efficient adsorption of Cr (VI) and other pollutants from wastewater .The other physical properties like bulk density, porosity, average pore size of prepared activated carbon are given in Table 3 which may affect the adsorption capacity.

3.2. Effect of solution pH on adsorption

It was found that uptake of Cr (VI) decreases with increasing pH which is shown in Fig. 3. The adsorption of metals is related
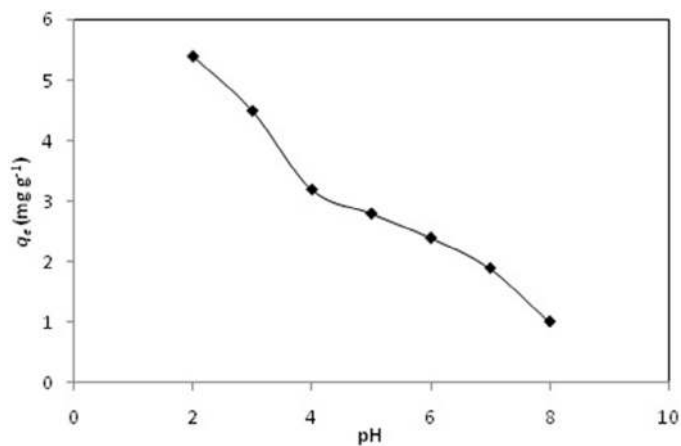

Fig. 3. Effect of solution pH on Cr (VI) adsorption by MKAC (Initial concentration: 20 mg/L; Agitation speed: 150 rpm; Dose: 0.25 g/100 mL; Temperature: 35 °C; time: 190 minutes).
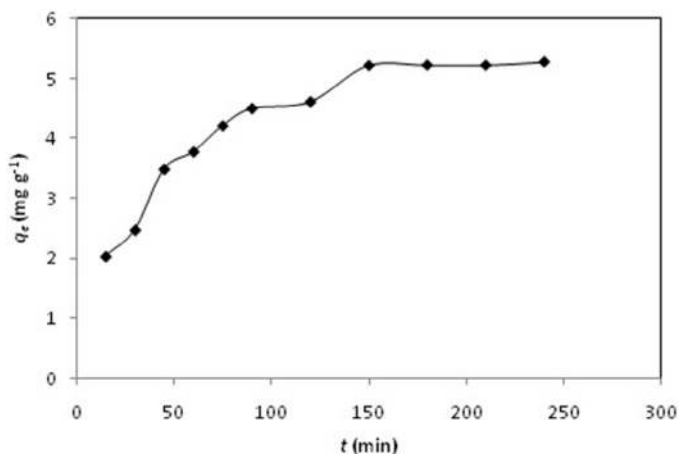
Fig. 4. Effect of contact time on Cr (VI) adsorption by MKAC (Initial concentration: 20 mg/L, Solution pH: 2, Agitation speed: 150 rpm, Dose 0.25 g/100 mL, Temperature: 35 °C).
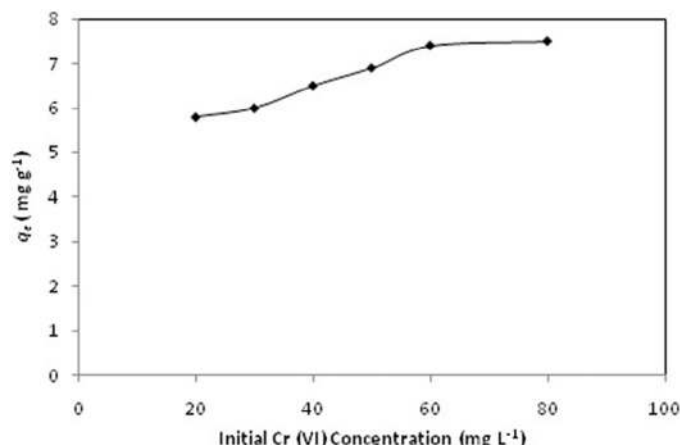

Fig. 6. Effect of initial Cr (VI) concentration on metal uptake (mg g^{-1}) by MKAC (Solution pH: 2; Agitation speed: 150 rpm; Dose: 0.75 g/100 mL; Temperature 35 °C; Time: 150 min).

3.4. Effect of adsorption dose

The adsorption results for adsorbent doses of 0.25 g/100 mL to 1.0 g/100 mL are shown in Fig. 5. It is seen that the adsorption % has increased from 65 to 100 that can be directly linked to the availability of increasing adsorption sites with increasing amount of adsorbent. At higher adsorbent dose, there are not enough Cr (VI) in the solution to occupy the active sites and hence the adsorption tends to become constant [48,49]. In view of this observation, for all other experiments the adsorbent dose was fixed at 0.25 g/100 mL.

3.5. Effect of initial concentration of Cr (VI)

It can be seen from Fig. 6 that in the beginning the Cr (VI) uptake increased with increasing Cr (VI) concentration that gradually reduced at higher concentrations and eventually became constant. After a certain level of increase in initial Cr (VI) concentration, all the active sites on the adsorbent surface get occupied and finally establish a form of dynamic equilibrium between the processes of adsorption and desorption [50,51].

3.6. Adsorption isotherm study

The equilibrium adsorption data for MKAC were tested with Langmuir [52] and Freundlich [53] to know which isotherm is better suited. A further analysis of Langmuir isotherm can be made using the dimensionless equilibrium parameter R_L which is presented in Table 3. The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, for $R_L = 1$ adsorption is linear and if $R_L = 0$, it is irreversible. The dimensionless parameter, R_L is found in the range of 0–1, which confirms the favorable adsorption process for Cr (VI) removal. The Freundlich constants, K_f and n cab are calculated by plotting the graph between lnq_e versus lnC_e as shown in Fig. 7. The adsorption isotherm parameters of both isotherms are shown in Table 4, together with the isotherm equations. Langmuir equation is shown as C_e/q_e versus C_e plot in Fig. 8. The values of q_m are obtained as 7.5, 7.8 and 7.9 mg g^{-1} at the temperature of 25, 30 and 35 °C, respectively. The coefficient of correlation for Freundlich isotherm model is much lower than that of Langmuir isotherm model as given in
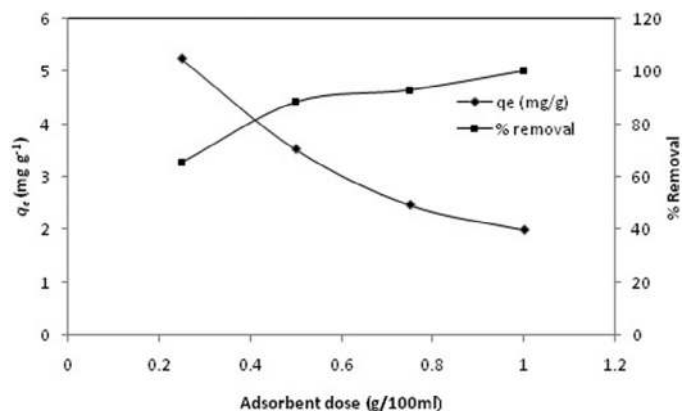

Fig. 5. Effect of adsorbent dose on metal uptake and percentage metal removal by MKAC (Initial conc.: 20 mg/L; Solution pH: 2; Agitation speed: 150 rpm; Temperature: 35 °C; Time: 150 min).
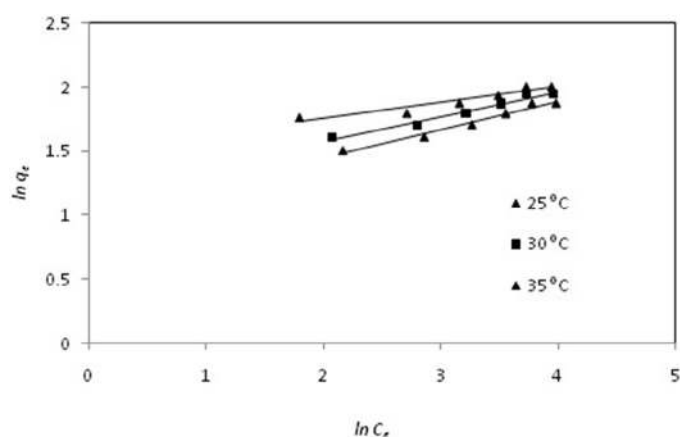

Fig. 7. Freundlich isotherm model for the Cr (VI) adsorption onto MKAC (Solution pH: 2; Agitation speed: 150 rpm; Dose: 0.25 g/100 mL; Time: 150 min).
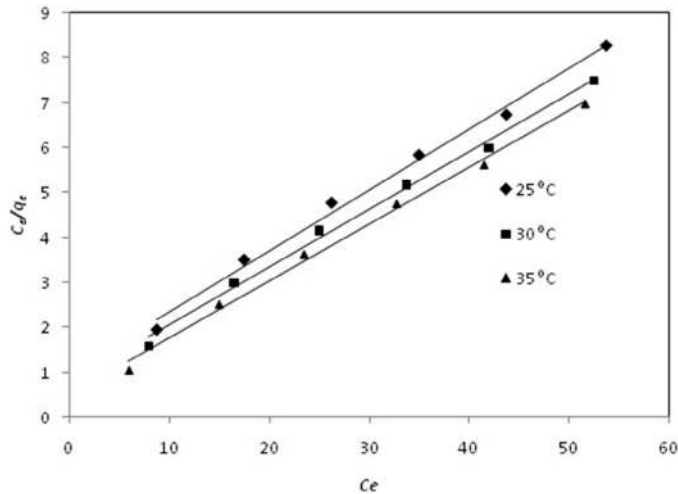
Fig. 8. Langmuir isotherm model for the Cr (VI) adsorption onto MKAC (Solution pH: 2; Agitation speed: 150 rpm; Dose: 0.25 g/100 mL; Time: 150 min).

Table 4 .This indicates that Langmuir model fits the data more closely.

3.7. Kinetic study

The kinetics of Cr (VI) sorption on the MK activated carbon as adsorbent was analyzed using two kinetic models. The linearized form of pseudo-first-order kinetic model [54] and the pseudo-second-order sorption kinetics [55] can be expressed as shown in Table 4. Figs. 9 and 10 show the plots of experimental data at different initial concentration of Cr(VI) for pseudo-first order and second order, models, respectively. The calculated kinetic parameters are presented in Table 5. Closure agreement between experimental and calculated kinetic constants and coefficient of correlation closure to unity indicated that the pseudo second order model better represents the experimental data.

4. Conclusions

Activated carbon from mango (*Mangifera indica*) seed kernel was prepared and characterized. It showed high surface area and porosity and had functional groups useful in adsorption. Its adsorption efficacy was tested for removal of Cr (VI) from aqueous solution. The adsorption of Cr (VI) was found to

be strongly dependent on pH, adsorbent dose, contact time and initial Cr (VI) concentration. The pH 2.0, biomass dose 2.5 g/100 mL and equilibrium time 150 min were found to be the optimum conditions for the adsorption of maximum Cr (VI) uptake of 7.8 mg g^{-1}. Langmuir isotherm fitted the equilibrium data well.
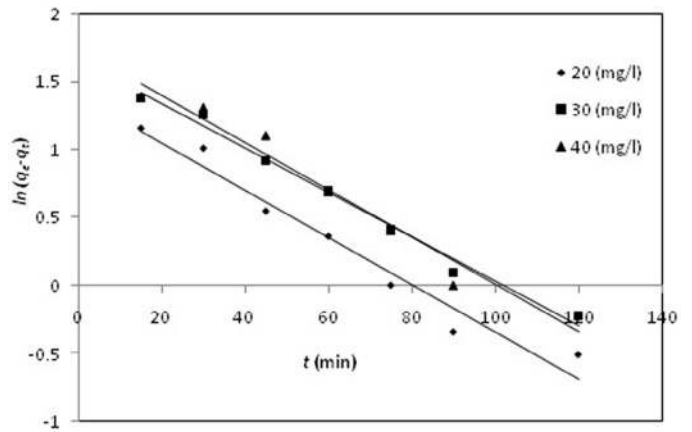

Fig. 9. Pseudo-first-order kinetic model for removal of Cr (VI) by MKAC (Solution pH: 2; Dose: 0.25 g/100 mL, Agitation speed: 150 rpm; Temperature 35 °C).
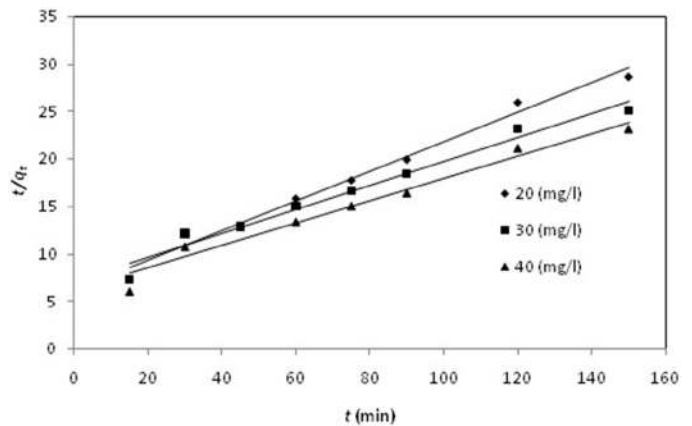

Fig. 10. Pseudo-second-order kinetic model for removal of Cr (VI) by MKAC (Solution pH: 2; Dose: 0.25 g/100 mL, Agitation speed: 150 rpm; Temperature 35 °C).

Table 4
Adsorption isotherm parameters for Cr (VI) removal using MKAC.

Adsorption isotheres	Parameters	Temperature		
		25 °C	30 °C	35 °C
Langmuir isotherm	q_m	7.42	7.83	7.96
$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$	b	0.135	0.166	0.2634
	R^2	0.993	0.994	0.995
$R_L = \frac{1}{1+bC_0}$	R_L	0.2702	0.2312	0.157
Freundlich isotherm	K_f	1.24	1.21	1.198
	n	0.99	0.84	0.76
$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e$	R^2	0.974	0.971	0.974

Table 5
Kinetic parameters for the adsorption of Cr (VI) on MKAC at different initial concentration.

Kinetic model	Parameters			
Pseudo first-order model	C_0	K_1	q_e	R^2
$\ln(q_e - q_t) = \ln q_e - k_1 t$	20	0.017	4.04	0.961
	30	0.016	5.25	0.957
	40	0.017	5.60	0.965
Pseudo second-order model	C_0	$K_2 \times 10^{-3}$	q_e	R^2
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	20	3.87	6.45	0.985
	30	2.19	8.01	0.984
	40	2.21	8.54	0.981

Abbreviations

b	Langmuir isotherm constant (L mg^{-1})
C_e	equilibrium concentration of Cr (VI) (mg L^{-1})
C_t	concentration of Cr (VI) at any time t (mg L^{-1})
C_0	initial concentration of Cr (VI) (mg L^{-1})
K_1	rate constant of pseudo-first order sorption (min^{-1})
K_2	rate constant of the pseudo-second order sorption (g · mg^{-1} · min^{-1})
K_f	Freundlich isotherm constants (mg · g^{-1} (L · mg^{-1})$^{1/n}$)
n	adsorption intensity
q_e	sorption capacities at equilibrium (mg g^{-1})
q_m	quantity of adsorbate required a single adsorption layer on unit mass of adsorbent (mg g^{-1})
q_t	sorption capacities at any time t (mg g^{-1})
R_L	separation factor
t	time (min)
V	volume of Cr(VI) (L)
W	weight of activated carbon(g)

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