

Preparation of Porous Activated Carbons from Rice Husk with Alkali Activation

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Abstract

Activated carbons were prepared from rice husk by chemical activation using various alkali hydroxides (KOH, NaOH) as activating agent. The influences of activation parameters such as impregnation ratio, activation temperature and retention time on the final products were investigated, and the optimum preparation conditions were determined. The products were characterized by nitrogen gas adsorption isotherms at -196°C and the surface areas and pore volume of the carbon were estimated by BET method. The specific surface area and pore volume were as high as 2960, 2450 m^2/g and 2.159. 1.525 ml/g for activated carbons prepared using KOH, NaOH, respectively. Adsorption of Cr (VI) ions from solutions onto the resulting activated carbons have been studied. The effect of the solution pH on the adsorption was studied in the pH range 1-7 and $25\pm 2^{\circ}\text{C}$. The results show that the process was pH dependent. The experimental adsorption isotherm data were analyzed using three models, Freundlich, Langmuir and BET isotherm models and various adsorption parameters have been calculated. Equilibrium data were best represented by the Langmuir isotherm model. The results indicated that the prepared activated carbons are suitable adsorbent for the removal of Cr (VI) from wastewaters effluents.

Introduction

Activated carbon is one of the most important industrial carbon materials; it is being widely used to remove organic and inorganic contaminants from water and air due to its high adsorption capacity. Industrial applications of the activated carbon includes both gas phase adsorption such as air purification, respirators, and liquid phase adsorption as applied to the treatment of drinking water, ground water and in soft drink industry [1]. With the introduction of rigorous environmental regulations and the development of new applications, demands for porous carbons are expected to increase progressively.

The carbon precursors may be of botanical origin (wood, coconut shells, fruit seeds), mineral origin (coal, petroleum coke), or polymeric materials (rubber, tires, plastics). About 50% of industrial available activated carbons are derived from precursors of botani-

cal origin [2]. These precursors are usually low-cost agricultural residues almost usually used as fuels for energy generation. Almost numerous agro-waste biomaterials have been used for the production of activated carbons, including date pits, coconut shells, almond shells, peach stones, apricot stones, plum stones, cherry stones, apple pulp, and nutshells [3-5].

Activated carbons could be produced by either physical or chemical activation. Physical activation involves carbonization or calcinations of the raw materials at elevated temperatures ($500-900^{\circ}\text{C}$) in an inert atmosphere followed by mild oxidation (gasification) of the substance with steam and/or carbon dioxide at high temperatures ($700-1000^{\circ}\text{C}$) [6,7]. Simultaneous carbonization and activation can also be obtained chemically by impregnation with dehydrating agents such as phosphoric acid and zinc chloride [8,9].

Rice husk, an undesirable agriculture mass, is a byproduct of the rice milling industry. It represents about 20% of the whole rice produced, on weight basis of the whole rice [10]. For an estimated annual rice production of 500 million tons in developing countries, approximately 100 million tons of rice husk

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are generated annually for utilization in these countries alone [11]. Traditionally, rice husks have been used in manufacturing block employed in civil construction as panels, as fodder for livestock and was used by the rice industry itself as a source of energy for boilers [12]. However, the amounts of rice husk available are exceed by far any local uses and have posed disposal problems.

According to the statistics compiled by Egyptian Ministry of Agriculture, 500 thousand metric tons of rice husks are produced in Egypt annually [13]. These husks are used as fuel with low calorific values [14] or rejected to the environment. A better way to give this inexpensive by-product added value is to use it as precursor for the preparation of activated carbon.

Recently, the production of activated carbon from rice husk by alkali activation technique has become a research topic of a great interest due to the enhanced characteristics of the produced activated carbon compared to activated carbon produced by other traditional activation methods [15-17]. The present work investigates the production of a high quality activated carbon from rice husk by alkali activation technique with potassium or sodium hydroxide.

Experimental

Preparation of Activated Carbons

Rice husk used in this study was obtained from Mecca Company for Rice Milling, Tanta, Egypt. The proximate and ultimate analyses are presented in Table 1.

Rice husk was thoroughly washed with water to remove impurities, dried at 110°C in an oven overnight. After drying the husk was carbonized at 450°C for 3 hrs in presence of nitrogen then cooled down to room temperature. The resulting char was heated, in the presence of chemical reagent (KOH or NaOH) with different ratios, from room temperature to a tem-

perature in the range of 600-900°C, followed by holding the samples at that temperature for different time intervals (0.5-3.5 hrs), before left to cool, then washed by different techniques as shown in Table 2. All samples were dried at 105°C overnight. The prepared activated carbon using KOH, NaOH are notated as ACKOH and ACNaOH respectively.

Table 2
Different washing techniques

Method 1	Washing with hot distilled water till pH 7.5	
Method 2	1-st stage	Washing with hot water
	2-nd stage	Washing with hot acidified water (1% HCl)
	3-rd stage	Rewashing with hot water to adjust pH to about 7
Method 3	HCl is replaced by 1% H ₃ PO ₄ in method 3	

Characterization of Activated Carbon

Specific surface areas and pore volumes of the activated samples were determined by gas adsorption. An automated adsorption apparatus (NOVA, model 2200, Micro Meritics 9320) was employed for these measurements. Adsorption of N₂, as probe species, was performed at -196°C.

The methylene blue (MB) test was adopted to assess the adsorption performance of the products. 0.1 dm³ of MB solution of 1 g/dm³ was added to flask which contains 1 g of activated carbon. The flask was then shaken for 24 hrs at 25°C to assure equilibrium adsorption of MB onto the carbon. The residual concentration was determined using UV adsorption (Bauc & Lomp Spectronic Model 501) by measuring absorbance at 660 nm.

Chromium (VI) Adsorption Study

Batch adsorption equilibrium experiments were undertaken by mixing 0.1 g of carbon with 0.1 dm³ of chromium (VI) solution in sealed glass bottles. The bottles were shaken in a thermostatic shaker operated at 100 rpm until the equilibrium was attained. The equilibrium concentrations of chromium in solutions were detected by standard spectrophotometric method at wavelength of 540 nm with 1,5-diphenyl carbazide reagent, which form pink complex in the presence of chromium ions in acidic solutions [18]. Influence of temperature and pH was studied

Table 1

Rice husk proximate and ultimate analysis

Proximate analysis, wt.%		Ultimate analysis, wt.%	
Volatiles	55	Carbon	44.9
Moisture	3-8	Hydrogen	5.6
Ash	15-17	Oxygen	49.3
Fixed carbon	22-25	Nitrogen	Nil

and the pH was adjusted using H_2SO_4 . Preliminary tests indicated that the adsorption equilibrium was essentially attained after 4 hrs. All the chemical used were of analytical grade. The initial chromium solutions were prepared with the concentration range of 50 to 1000 mg/dm^3 using potassium dichromate.

Results and Discussion

Preparation and Characterization of Activated Carbons

Series of activated carbons were prepared from rice husk as precursor with chemical activation using KOH, NaOH as activating agents. Effect of different preparation variables on the adsorption of methylene blue was studied.

Effect of Impregnation Ratio

The ratio of the chemical activator to the char has been found to be one of the important parameter in the preparation of the activated carbon using chemical activation [19]. The activation reaction between alkali hydroxide and char are [20]:

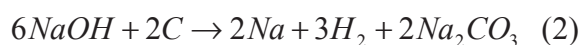
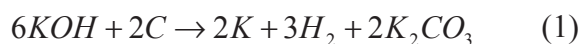


Figure 1 shows the effect of the impregnation ratio versus adsorption capacity of the methylene blue. It shows that an increase in alkali/char ratio produces a great enhancement of methylene blue adsorption, reaching maximum values (4:1, 3:1 for KOH, NaOH respectively) and above these values adsorption decreases with increasing the impregnation ratio. At high impregnation ratio the gasification of surface carbon atoms is the predominant reaction leading to increase in the development in micropores, through the removal of the carbon atoms on pore walls to widen the micropores [21].

Effect of Time

Activation time plays an important role on the quality of the products. Figure 2 depicts the effect of activation time on adsorption capacity of methylene blue at optimum impregnation ratios for using KOH, NaOH. The adsorption capacity increases gradually until it reaches its maximum values at 1.5, 2 hrs for

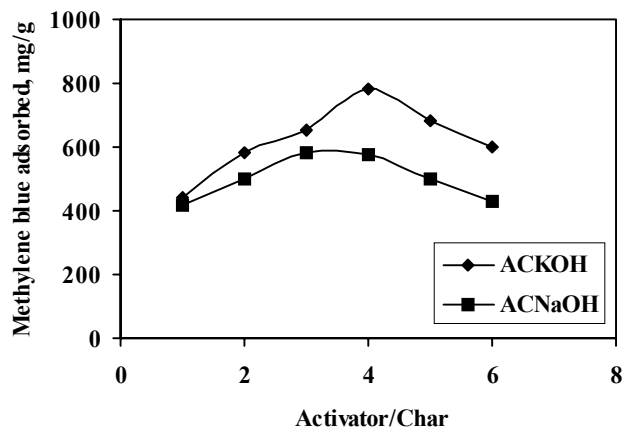


Fig. 1. Effect of impregnation ratio on the adsorption capacity of methylene blue on rice husk based activated carbon (1 h, 700°C, washing with acidified water).

ACKOH, ACNaOH respectively. Then, these slightly decreases by further increase of activation time. As the dwell times increases, the formation of K_2CO_3 or Na_2CO_3 increases which increase the number of created pores, and hence increases adsorption capacity. But longer carbonization time (1.5, 2.5 hrs for ACKOH, ACNaOH respectively) promoted reduction in both surface area and total pore volume, presumably due to collapse of the smaller pores as inferred from the decrease in micropore volume (9) and consequently the decrease of the adsorption of methylene blue.

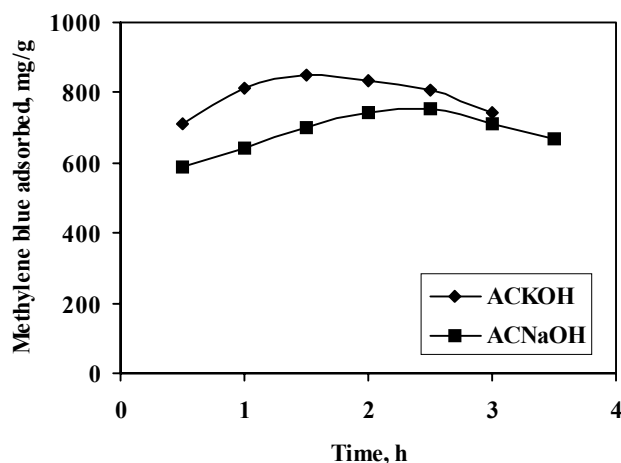


Fig. 2. Effect of activation time on the adsorption capacity of methylene blue on rice husk based activated carbon (700°C, KOH/C = 4/1, NaOH/C = 3/1, washing with acidified water).

Effect of Temperature

Activation temperature is the most important parameter for the process. The effect of activation

temperature on the adsorption capacity of methylene blue is shown in Fig. 3. Elevated heating temperature improved the adsorption capacities of the products, but temperature above 800°C for ACKOH, 700°C for ACNaOH, could lead to significant decrease. This increase in capacity with temperature can be attributed to pore enlargement caused by gasification [22], but with further increase in temperature, significant decrease in the adsorption capacities was observed. This phenomena probably results from the extensive gasification at high temperature leading to destroy of the pore walls between adjacent pores [23].

Effect of Washing Stage

The washing stage is the last step in the preparation of a chemically activated carbon. The pyrolyzed mixture is leached in water or acid solutions to remove the activating agent. Figure 4 presents the adsorption capacity of methylene blue on the ACKOH at optimum parameters, corresponding to the different washing techniques. The plot clearly shows that, washing with water acidified with H_3PO_4 has the best washing efficiency. Thus it has a higher ability to dissolve any residues of carbonates salts which form during the course of activation. This may be attributed to the strong acidity of H_3PO_4 as compared to HCL. Also, H_3PO_4 dissolves any residues of silica in the activated carbon thus enhancing the efficiency of the activation. But the selection between the different techniques methods depends on the economic considerations.

The nitrogen adsorption for ACKOH & ACNaOH at $-196^\circ C$ are shown in Figs 5, 6. Analysis of the

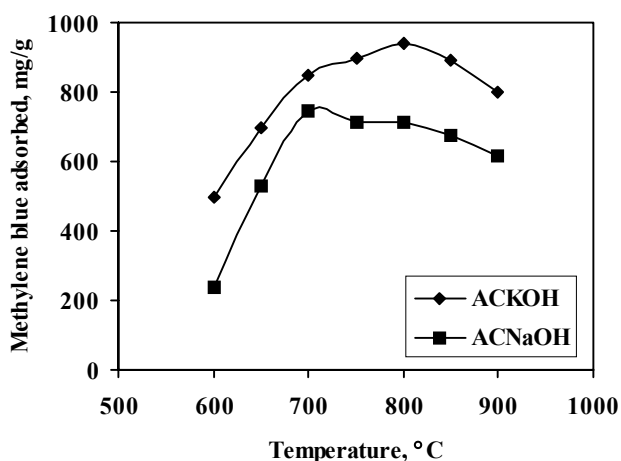


Fig. 3. Effect of activation temperature on the adsorption capacity of methylene blue on rice husk based activated carbon (time 1.5, 2 hrs for ACKOH, ACNaOH, impregnation ratio $KOH/C = 4/1$, $NaOH/C = 3/1$, washing with acidified water).

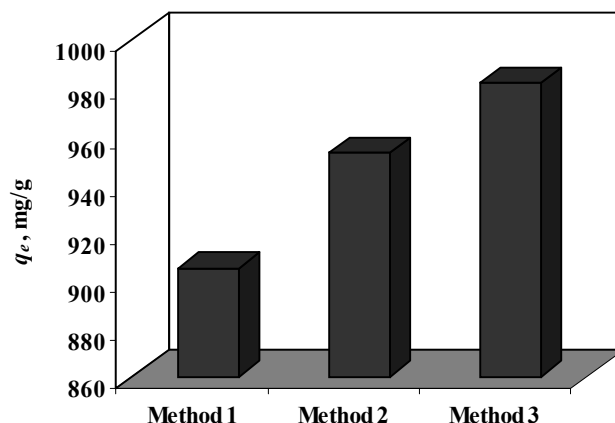


Fig. 4. Effect of washing technique on the adsorption capacity of methylene blue onto ACKOH.

adsorption isotherms was carried out by applying the BET equation to get the specific surface area (S_{BET}) and pore characterization of the prepared activated carbons, at optimum parameters, have been measured and listed in Table 3.

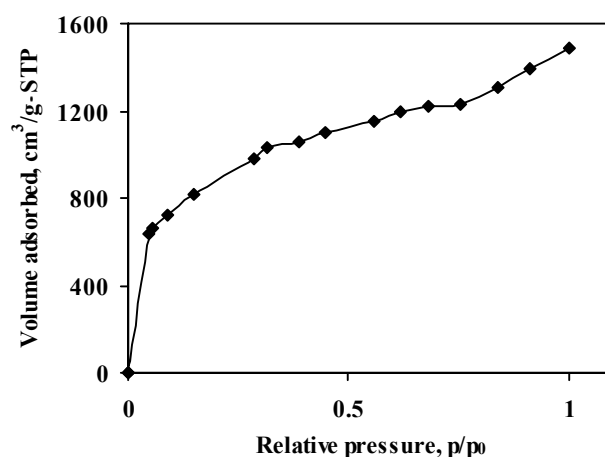


Fig. 5. Adsorption isotherm of N_2 on ACKOH.

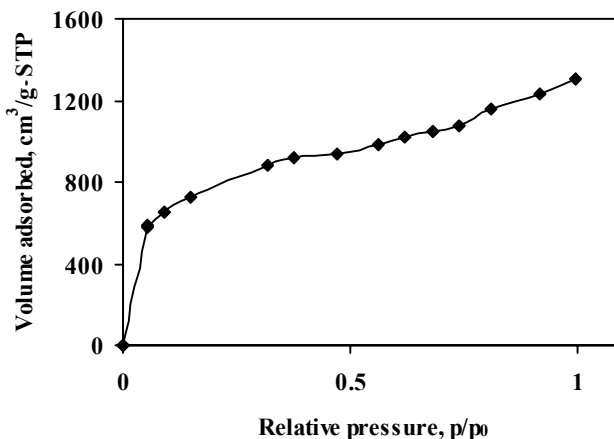


Fig. 6. Adsorption isotherm of N_2 on ACNaOH.

Table 3
Pore characteristic of the activated carbons

Activator	Surface area S_{BET} , m^2/g	Pore volume, ml/g	Average pore radius, \AA
KOH	2960	2.159	15.5
NaOH	2450	1.525	14.6

Adsorption Studies

Effect of Contact Time

Adsorption isotherms are usually determined under equilibrium conditions. Figure 7 shows the effect of contact time of Cr (VI) adsorption by prepared activated carbons (ACKOH & ACNaOH). The figure reveals that increased contacting time increased the uptake of chromium ions and attained equilibrium in 2 hrs; thereafter it remains almost unchanged with respect to time, for both types of activated carbons. However, the experimental data were measured at 5 hrs for the rest of the batch experiments to make sure that full equilibrium was attained.

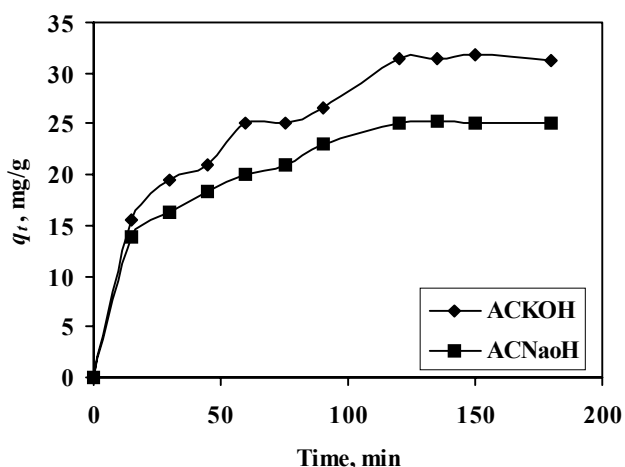


Fig. 7. Effect of contact time on the adsorption capacity of Cr (VI) on ACKOH, ACNaOH.

Effect of pH on the Adsorption Equilibrium

The pH is one of the most important parameters controlling the metal ion sorption process [24]. Figure 8 shows the effect of initial solution pH on the amount of chromium adsorbed (mg/g) at equilibrium time, on both ACKOH and ACNaOH at an initial Cr (VI) solutions concentration of $60 \text{ mg}/\text{dm}^3$, and temperature $25 \pm 2^\circ\text{C}$. For ACKOH the amount adsorbed increases from 15 to 53 mg/g as the pH decreases

from 7 to 1. While for ACNaOH, the amount adsorbed increases from 6.36 to 50 mg/g as the pH decreases from 7 to 2. This indicates that the adsorption capacity of the adsorbent is clearly pH dependent. It is obvious that pH determines the extent of the Cr (VI) removal as well as provides a favorable adsorbent surface charge for the adsorption to occur [25].

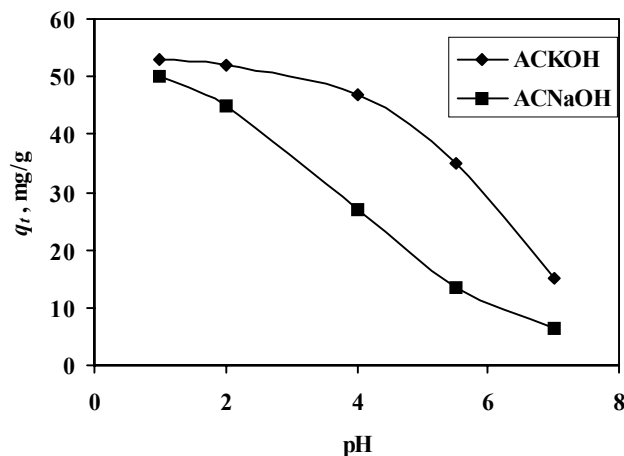


Fig. 8. Effect of the initial pH of the Cr (VI) solution on the adsorption capacities of ACKOH, ACNaOH.

The maximum adsorption of Cr (VI) species was found in the pH range below 7 and the sorbed amount was found to be negligible in the pH value over 8. Similar results were reported in other articles concerned the study of the adsorption of Cr (VI) by different activated carbons types [26-28]. They interpreted the decrease of adsorption capacity with pH increase by the increase of the negative charge on the carbon surface, thus the electrostatic force of attraction between the adsorbent surface and the adsorbate ions were decreased. Also, Das and Mahapatra [29], suggested that the sharp decrease in adsorption capacity above pH 5 may be due to the occupation of the adsorption sites by anionic species like $\text{Cr}_2\text{O}_7^{2-}$ ions for potassium dichromate solution which retards the further approach of such ions toward the sorbent surface [26]. Figures 9, 10 depict the adsorption isotherms measured at different pH values for the prepared activated carbons.

Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an im-

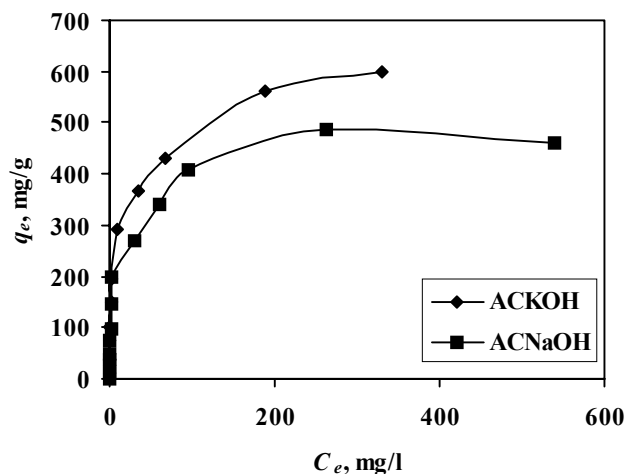


Fig. 9. Adsorption isotherms of Cr (VI) onto ACKOH, ACNaOH at pH = 2.

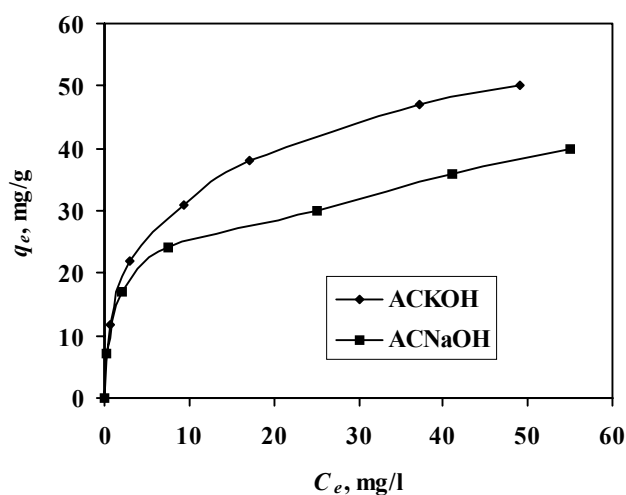


Fig. 10. Adsorption isotherms of Cr (VI) onto ACKOH, ACNaOH at pH = 5.5.

portant step to find the suitable model that can be used for design purposes [30]. Adsorption isotherm study was carried out on three isotherm models:

- Freundlich isotherm model, eq. 3.

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

- Langmuir isotherm model, eq. 4.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (4)$$

- BET isotherm model, eq. 5.

$$\frac{c_e}{(c_s - c_e)(q_e)} = \left(\frac{1}{BQ} \right) + \left(\frac{B-1}{BQ} \right) \left(\frac{c}{c_s} \right) \quad (5)$$

where q_e is the equilibrium solid-phase concentration (mg/g), c_e is the liquid-phase concentration (mg/dm³), K_f , n are the Freundlich isotherm constants, K_L , a_L are the Langmuir isotherm constants. c_s is the saturation liquid-phase concentration (mg/dm³), B , Q are the BET isotherm constants and R_L is the dimensionless constant separation factor, $R_L = 1/(1 + a_L C_0)$, which indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R^2 values.

The obtained isotherm parameters are listed in Tables 4, 5. From Tables 4, 5 it was observed that, the values of the Freundlich constant, n , are greater than one and the values of the dimensionless constant separation factor, R_L , in the range of 0 to 1, which confirms the favorable uptake of the chromium process.

The three models have good correlation between the model prediction and the experimental data. Obviously, it can be seen that Langmuir isotherm model yields a somewhat better fit than, Freundlich and BET models.

Conclusions

From the results presented in this study, it can be concluded that the rice husk is promising precursor to prepare activated carbon. Chemical activation with KOH produces porous carbon having BET surface

Table 4

Isotherm model constants for adsorption of Cr (VI) onto prepared activated carbon using KOH

Parameter	pH = 2		pH = 5.5	
	Value	R^2	Value	R^2
Freundlich isotherm				
K_f , dm ³ /g	129.21	0.98	14.18	0.99
n , -	3.516		2.97	
Langmuir isotherm				
a_L , dm ³ /mg	0.09	0.99	0.20	0.99
K_L , dm ³ /g	57.47		10.85	
R_L , -	$11 \cdot 10^{-3}$		$24 \cdot 10^{-3}$	
BET isotherm				
Q , mg/dm ³	251.89	0.98	12.18	0.93
B , -	-132.22		-14.40	

Table 5

Isotherm model constants for adsorption of Cr (VI) onto prepared activated carbon using NaOH

Parameter	pH = 2		pH = 5.5	
	Value	R^2	Value	R^2
Freundlich isotherm				
K_f , dm ³ /g	99.54	0.93	12.29	0.98
n , -	3.49		2.36	
Langmuir isotherm				
a_L , dm ³ /mg	0.12	0.99	0.26	0.98
K_L , dm ³ /g	56.82		10.37	
R_L , -	$8.2 \cdot 10^{-3}$		$18 \cdot 10^{-3}$	
BET isotherm				
Q , mg/dm ³	257	0.99	10.30	0.92
B , -	-389		-20.96	

area and pore volume as high as 2960 m²/g and 2.159 ml/g at optimum conditions of 4:1 impregnation ratio (activator:char), 800°C activation temperature and 1.5 hrs retention time. While, using NaOH as chemical activator produces activated carbon having BET surface area and pore volume as high as 2450 m²/g and 1.525 ml/g at optimum conditions of 3:1 impregnation ratio, 700°C activation temperature and 2.5 hrs retention time.

The resulting activated carbons are effective adsorbents for the removal of Cr (VI) ions from solutions in the concentration range from 50-1000 mg/l at equilibrium time of 5 hrs. The process is highly pH dependent. The Langmuir isotherm provides the best correlation fit for the Cr (VI) removal by the prepared samples.

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