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A comparative study of surface modification in carbonized rice husk by acid treatment

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ABSTRACT

Water pollution by heavy metals is a major environmental problem because of their toxicity and its removal is highly essential. In this present investigation, two types of adsorbents were prepared viz. activated carbon from acid treated rice husk (ACARH) and activated carbon from rice husk followed by acid treatment (ACRHA). Characterization of the adsorbents was performed by BET analyzer, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and EDAX analysis to determine their surface area and morphological behavior. Adsorption studies were conducted to optimize the process variables such as initial metal ion concentration, adsorbent dosage, pH of the solution and temperature on the percentage removal of hexavalent Cr ions from aqueous solution. It is found that ACARH adsorbent is highly effective for the removal of metal ions than ACRHA. Various kinetic and isotherm models were fitted with the experimental data obtained from ACARH adsorbent to evaluate the solute interaction behavior.

Keywords: Rice husk; Acid treatment; Activated carbon; Cr (VI) ions; Adsorption; Isotherms; Kinetics

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1. Introduction

The rapid modernization in this era has resulted in industrialization and urbanization that leads to increase the rate of discharge of domestic and industrial effluents to water streams. Most of these effluents contain toxic and non-biodegradable substances especially heavy metals. The presence of heavy metals is of major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment [1]. One of the heavy metals that have been a major focus in water and wastewater treatment is chromium which is released to the environment through a large number of industrial operations, such as textile dyeing, leather tanning, electroplating and metal finishing industries [2]. Chromium exists in two main oxidation states-hexavalent chromium (Cr (VI) ions) and trivalent chromium, (Cr (III) ions). Among these; Cr (VI) ion is more hazardous, carcinogenic and mutagenic to living organisms. In addition, it causes allergic and asthmatic reactions, diarrhea, stomach and intestinal bleedings, cramps, liver and kidney damage [3]. Chromium concentration in industrial wastewater ranges from 0.5 to 270,000 mg l^{-1}. The tolerance limit for the discharge of Cr (VI) ions into inland surface water is 0.1 mg l^{-1} and in potable water is 0.05 mg l^{-1} [4].

Treatment processes for heavy metal removal from waste water includes precipitation, coagulation, electrochemical processes, reduction, membrane filtration, ion exchange, solvent extraction and co-precipitation [5]. However, these methodologies have their own

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shortcomings and limitations. Adsorption is quite popular due to its simplicity as well as the availability of a wide range of adsorbents. Moreover it's been proved to be an effective and attractive process for removal of non-biodegradable pollutants from wastewater. It is a sludge free clean operation and result in complete removal even from dilute solutions [6,7]. Activated carbon is the most widely used adsorbent because of its extensive surface area, micro porous structure, high adsorption capacity, and high degree of surface reactivity [8]. Commercially available activated carbon is highly expensive. This has led to the search for cheaper substituent. A lot of adsorption studies have been carried out using agro waste because of its low cost, easy availability and easiness of handling. Rice husk is one of the cheapest agro residue consisting of rice husk are cellulose (55–60%), hemicelluloses (20–25%) and lignin (20–25%). The use of unmodified or modified rice husk as an adsorbent for the removal of pollutants has become considerable attention in recent years because of its abundance in nature [9]. In the present work, Rice husk was used as a precursor for the preparation of activated carbon. Surface modification was done by treating nitric acid on raw rice husk followed by carbonization and carbonized rice husk followed by nitric acid treatment. The comparison was made on adsorption performance of activated carbon from acid treated rice husk (ACARH) and activated carbon from rice husk followed by acid treatment (ACRHA). The experimental data obtained from better adsorbent was used to evaluate the adsorption isotherm, adsorption kinetics and thermodynamic parameter.

2. Material and methods

2.1. Materials

Raw rice husk was obtained from a local rice mill. Potassium dichromate ($K_2Cr_2O_7$) was used for the preparation of Cr (VI) stock solution. Hydrochloric acid—potassium chloride, acetic acid—sodium acetate and boric acid—sodium hydroxide were used to maintain the pH of the solutions in the range of 1–3, 4–6 and 7–10 respectively. All the chemicals used were of analytical grade. Double distilled water was used for preparing all the solutions.

2.2. Preparation of adsorbents

In this present study, adsorbent was prepared by the following two methods.

2.2.1. Preparation of activated carbon from acid treated rice husk (ACARH)

Rice husk was thoroughly washed with distilled water and dried in hot air oven at 100°C. The dried sample was treated with 70% concentrated nitric acid (1:1 wt. ratio) and stirred in a water bath at a temperature of 70°C for 1½ h. Then the nitric acid treated samples were subjected to carbonization under an inert atmosphere at 500°C with a constant heating rate of 5°C min^{-1} in a tubular furnace for 4 h.

2.2.2. Preparation of activated carbon from rice husk followed by acid treatment (ACRHA)

The washed and dried rice husk was initially subjected to carbonization under an inert atmosphere at 700°C in a tubular furnace for 4 h. The product obtained after carbonization was treated with 70% concentrated nitric acid (1:10 wt.% v^{-1} of carbonized rice husk and nitric acid) and stirred at 90°C in a water bath for about 2 h. Then, the mixture was cooled and washed thoroughly with distilled water until the pH of rinsed water was found to be neutral. Then the samples were dried in a hot air oven at 100°C.

2.3. Characterization of adsorbents

The specific surface area of the carbonized materials was measured by using GeminiV2.00 Micromeritics. The chemical characterization of adsorbents was performed using EDAX analysis. The morphological structure was observed by Hitachi S3000H scanning electron microscope (SEM). FTIR spectra were recorded using Perkin Elmer, spectrum RXI FTIR spectrophotometer to analyze the functional groups present in the adsorbent.

2.4. Batch adsorption studies

Adsorption studies were conducted to determine the equilibrium time and agitation speed for a known concentration of initial metal ion solution. Batch adsorption studies were carried out to investigate the effect of initial metal ion concentration, adsorption dosage and pH of the solution at equilibrium time and agitation speed in rotary shaker. The supernatant liquid was filtered and the concentration of Cr (VI) ions was determined using UV/Visible spectrophotometer at a wavelength of 540 nm. The adsorption capacity ($q_e$mg g^{-1}) and % removal were calculated using Eqs. (1) and (2) respectively:

$$q_\mathrm{e} = \left(C_0 - C_e\right) \times \left(\frac{V}{W}\right) \tag{1}$$

$$\%\ \text{Removal} = \frac{\left(C_0 - C_\mathrm{e}\right)}{C_0} \times 100 \tag{2}$$

where C_0 and C_e (both in mg l^{-1}) are the initial concentration of Cr (VI) ion and the concentration of Cr (VI) ion at any instant, V is the volume of the solution (l), W is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of adsorbents

The synthesized adsorbents were characterized by BET, FTIR, SEM and EDAX analysis which as follows.

3.1.1. BET analysis

From BET analysis, the surface areas of ACARH and ACRHA were found to be 16 and 10 $m^2\ g^{-1}$ respectively.

3.1.2. FTIR analysis

Fig. 1 shows the FTIR spectra of ACARH and ACRHA adsorbents. The functional groups in the adsorbents are presented in Table 1.

The functional groups like O–H stretching at 3496.8 and 3425.13 cm^{-1}, C–N stretching at 1089.99 and 1094.48 cm^{-1}, NH_2 and NH wagging at 798.27 and 796.79 cm^{-1}, C–H groups at 462.10 and 464.33 cm^{-1} are common in both the adsorbents. The functional group like N–H stretching peaks at 3396.04 and 3291.76 cm^{-1} and N–H bending at 1619.51 cm^{-1} are present in ACARH which is responsible for the enhancement in removal of Cr (VI) ions.

3.1.3. SEM analysis

Figs. 2(a) and (b) show the SEM images of ACARH and ACRHA. These images indicate the surface texture and porosity of the adsorbent samples. From the images, it can be inferred that both the adsorbents have an irregular and porous surface, which leads to better % removal of metal ions.

Table 1
A comparison of functional groups present in ACARH and ACRHA

Functional groups	ACARH	ACRHA
O–H stretching	3496.8 cm^{-1}	3425.13 cm^{-1} (H bonded)
N–H stretching	3396.04 cm^{-1}	–
	3291.76 cm^{-1}	–
N–H (1° amide)	–	1622.58 cm^{-1}
N–H bending	1619.51 cm^{-1}	–
C–N stretching	1089.99 cm^{-1}	1094.48 cm^{-1}
O–H bending	–	1382.68 cm^{-1}
NH_2 and NH wagging	798.27 cm^{-1}	796.79 cm^{-1}
C–H groups	Out of plane deformation 462.10 cm^{-1}	575.49 cm^{-1} 464.33 cm^{-1}

3.1.4. EDAX analysis

The elemental analysis of ACARH and ACRHA was done by using EDAX analysis and the results are presented in Tables 2 and 3 respectively. From the tables, the major component present in both the samples is carbon. However the carbon content in ACRHA was found to be low compared to ACARH. This may be due to the reduction of silica content when treatment of nitric acid on rice husk.

3.2. Effect of contact time

The preliminary experiments were conducted to determine the equilibrium time of contact for the removal of Cr (VI) ions using ACARH and ACRHA.

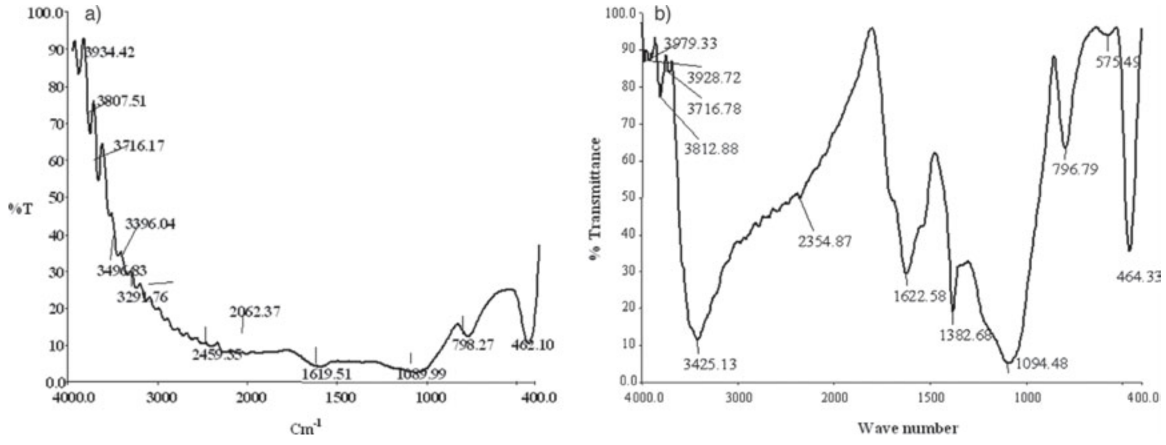

Fig. 1. FTIR spectrum of (a) ACARH and (b) ACRHA.

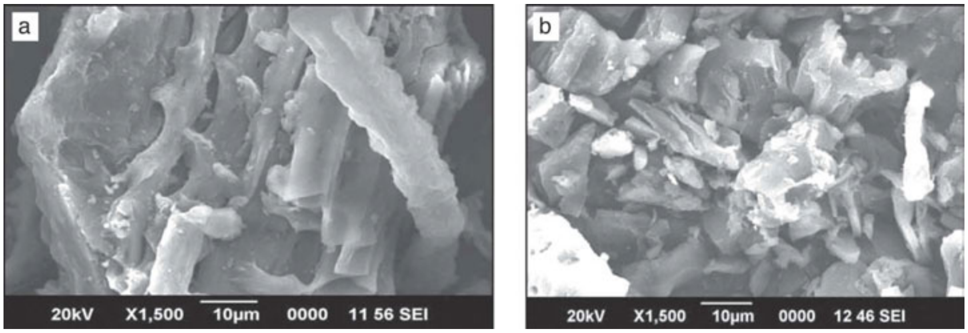

Fig. 2. SEM Analysis of (a) ACARH and (b) ACRHA.

Table 2
EDAX analysis of ACARH

Element	(keV)	Mass%	Atom%	K
C K	0.277	95.77	97.24	1
O K	0.525	2.81	2.14	0.3805
Si K	1.739	1.42	0.62	0.292
Total		100	100	

Table 3
EDAX analysis of ACRHA

Element	(keV)	Mass%	Atom%	K
C K	0.277	70.11	76.67	65.3949
O K	0.525	26.46	21.72	18.5018
Si K	1.739	3.43	1.61	5.3213
Total		100	100	

The results showed that the adsorption of Cr (VI) ions by ACARH and ACRHA was reached equilibrium in nearer to 3.5 h.

Fig. 3 shows that the adsorption rate was very fast initially and then gradually tailed off. The results indicate that the rate of percentage removal was progressively decreased with time. At the beginning of the process, the adsorption occurred on the adsorbent surface, hence a fast adsorption rate and gradually the rate became slower due to pore diffusion. Hence equilibrium time was fixed at 200 min.

3.3. Effect of pH

Fig. 4 represents the comparative effect of pH on percentage removal of Cr (VI) ions using ACARH and ACRHA. The maximum percentage removal was obtained at pH 2. It may be due to that the Cr (VI) ion undergoes redox reactions in certain conditions as given in Eqs. (3) and (4). The reduction reactions require H^+ ions to drive the reaction.

$$Cr_2O_7^{2-} + 14H^{++}6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad (3)$$

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \qquad (4)$$

The dominant Cr (VI) species at total chromium concentrations below 500 ppm are the oxyanions such as $HCrO_4^-$ and CrO_4^{2-}.The equilibrium reaction as given in Eq. (5) between the two species is highly dependent on pH [11]:

$$HCrO_4^- \rightarrow H^+ + CrO_4^{-2} \qquad (5)$$

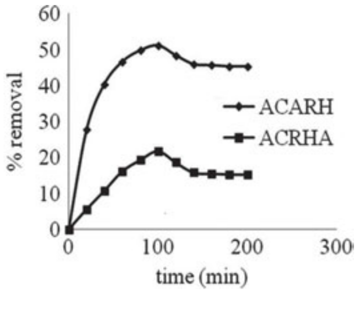

Fig. 3. Effect of contact time on percentage removal of Cr (VI) ions using ACARH and ACRHA (C_0 = 100 mg l^{-1}, m = 0.2 g, speed = 350 rpm, pH 2).

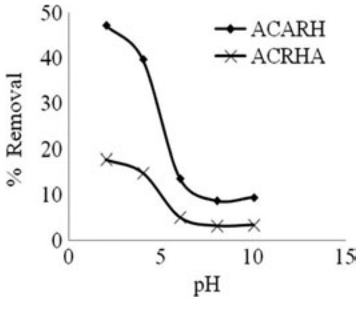

Fig. 4. Effect of pH on % removal of Cr (VI) ions using ACARH and ACRHA (m = 0.2 g, conc. = 100 ppm, t = 3.5 h, speed = 350 rpm).

At low pH, $HCrO_4^-$ is the dominant species, while CrO_4^{-2} predominates in a higher pH level. At low pH, the functional group on the surface of the sorbent carry positive charge, results in binding of negatively charged species ($HCrO_4^-$) due to electrostatic force of attraction. The decrease in adsorption with increase in pH may be due to the accumulation of negative charge on the carbon surface, resulting in decrease in the electrostatic force of attraction between the sorbent surface and the sorbate ions. Thus the pH was optimized at 2 for the removal of Cr (VI) ions.

3.4. *Effect of initial metal ion concentration*

The effect of initial concentration was studied by varying the concentration from 10 to 300 mg l^{-1} with the adsorbent dosage of 4 g l^{-1} at pH 2 and 30°C and the results are presented in Fig. 5. The percentage removal was decreased with increased initial concentration for both the adsorbents. The decrease in percentage removal with increase in initial concentration of Cr (VI) ions may be due to the increase in number of chromium ions for fixed amount of adsorbent [10]. The results observed that the percentage removal was found to be doubled while using ACARH than ACRHA.

3.5. *Effect of adsorbent dosage*

The effect of adsorbent dosage on the adsorption of Cr (VI) ions using ACARH and ACRHA was studied by varying the adsorbent dosage from 0.2 to 1.0 g at pH 2 for 100 ppm concentration of the solutions and the results obtained are shown in Fig. 6. It is observed that the percentage removal was increased with increased adsorbent dosage and this may be due to the availability of more number of active sites for fixed number of Cr (VI) ions [10]. When compared to ACRHA, the percentage removal was found to be more in ACARH, which may be due to the reduction in silica content and pore cleavage, occur during acid treatment in rice husk. Hence the experimental data obtained from the adsorption studies using ACARH were used to evaluate the adsorption isotherms and adsorption kinetic parameters.

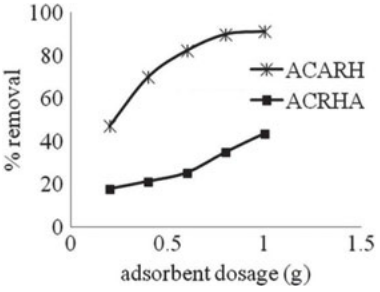

Fig. 6. Effect of adsorbent dosage on percentage removal of Cr (VI) ions using ACARH and ACRHA (C_0 = 100 mg l^{-1}, pH = 2, t = 3.5 h, speed = 350 rpm).

3.6. *Effect of temperature*

The effect of temperature on percentage removal of Cr (VI) ions was studied using ACARH and the results are shown in Fig. 7. The percentage removal of Cr (VI) ions was found to be decreased with decreased in temperature. This may be due to the kinetic energy of $Cr_2O_7^{2-}$ anion is low at lower temperature which results in poor contact between the $Cr_2O_7^{2-}$ and active sites of ACARH.

3.7. *Adsorption isotherms*

Various isotherm models such as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) were fitted with the experimental data obtained from ACARH adsorbent to determine the distribution of metal ions between the liquid phase and solid phase [11–14]. The various isotherm constants were calculated and presented in Table 4. It is found that the Freundlich isotherm model fitted satisfactorily with the experimental data, which reveals the multilayer adsorption of Cr (VI) ions on ACARH due to the presence of N–H stretching and bending functional groups and it is shown in Fig. 8.

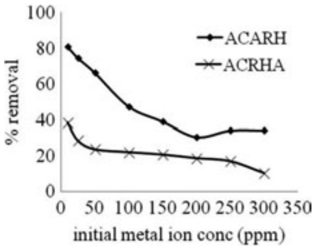

Fig. 5. Effect of concentration on % removal of Cr (VI) ions using ACARH and ACRHA (m = 0.2 g, pH = 2, t = 3.5 h, speed = 350 rpm).

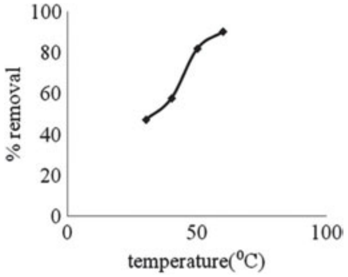

Fig. 7. Effect of temperature on percentage removal of Cr (VI) ions using ACARH (C_0 = 100 mg l^{-1}, pH = 2, t = 3.5 h, speed = 350 rpm, m = 0.2 g).

Table 4
Isotherms constants

Isotherms	Constants	Values
Langmuir	θ (mg g^{-1})	25.64
	b	0.0228
	R^2	0.849
Freundlich	n	2.045
	K (mg g^{-1})	1.69
	R^2	0.968
Temkin	a (1 g^{-1})	0.497
	b	4.387
	R^2	0.844
Dubinin–Radushkevich	q_D	15.879
	B_{D}	–1.0735
	R^2	0.845

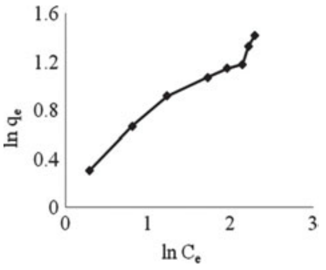

Fig. 8. Freundlich isotherm for ACARH.

3.8. Adsorption kinetics

In order to investigate the rate and order of adsorption process of Cr (VI) ions by ACARH, different kinetic models such as first order, second order, pseudo first order and pseudo second order kinetic models were used [15,16]. The adsorption kinetic constants of various models were presented in Table 5.

Table 5
Adsorption kinetic constants

Kinetic models	Parameters	Value
First order	K_{f} (min^{-1})	0.004
	R^2	0.494
Second order	K_{s} (g mg^{-1} min)	6×10^{-5}
	R^2	0.512
Pseudo first order	K_{lad} (min^{-1})	0.014
	R^2	0.263
Pseudo second order	K_{2ad} (g mg^{-1} min)	0.022
	q_{e} (mg g^{-1})	6.329
	R^2	0.968

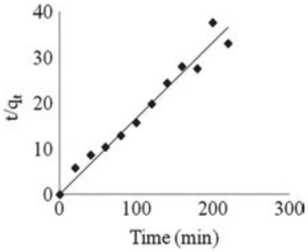

Fig. 9. Pseudo second order kinetics for ACARH.

It is observed that the pseudo second order kinetic model was fitted satisfactorily with the experimental data and it is given in Fig. 9. The pseudo second order kinetic model indicates that the adsorption of Cr (VI) ion on the surface of ACARH is chemisorption.

4. Conclusions

A comparative study was done with ACARH and ACRHA to find out the better adsorbent. The carbon content in ACRHA was found to be low compared to ACARH is due to the reduction of silica content during treatment of nitric acid on rice husk. Based on the experimental results, it was found that the activated carbon from acid treated rice husk (ACARH) is an effective adsorbent for the removal of Cr (VI) ions from aqueous solutions. Equilibrium adsorption data for Cr (VI) ion removal using ACARH was best represented by Freundlich isotherm. Adsorption kinetics of Cr (VI) ion removal using ACARH was found to fit suitably in a pseudo second order kinetic model.

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