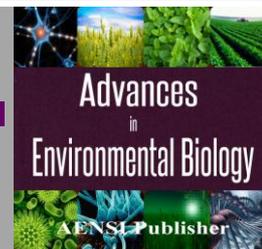




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Removal of Calcium and Magnesium by Activated Carbons Produced from Agricultural Wastes

¹Rokhsareh Rostamian, ¹Manouchehr Heidarpour, ²Sayed Farhad Mousavi and ³Majid Afyuni

¹Water Engineering Department, Isfahan University of Technology, Isfahan, Iran.

²Faculty of Civil Engineering, Semnan University, Semnan, Iran.

³Soil Science Department, Isfahan University of Technology, Isfahan, Iran.

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ABSTRACT

Use of carbon-based materials in different environmental aspects has increased in recent years. Rice husk (RH) and canola stalk (CS) were used for preparation of steam-activated carbons and their potential in removing calcium (Ca^{2+}) and magnesium (Mg^{2+}) as the major hardness cations was investigated. Results showed that type of precursor had significant effect on characteristics of the prepared activated carbons. Specific surface area of CS activated carbon (CSA) and RH activated carbon (RHA) was 564.4 and 317 m^2/g , respectively. Sorption data were analyzed using Langmuir and Freundlich isotherm models. Both models showed a good fit with experimental data. According to Langmuir model, maximum Ca^{2+} and Mg^{2+} sorption capacity for CSA was obtained as 51.8 and 15.1 mg/g , respectively. In general, CSA was more efficient in removing hardness cations than RHA because of more surface area and micropores. Both activated carbons had more potential for retention of Ca^{2+} than Mg^{2+} .

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INTRODUCTION

The scarcity of fresh water resources in arid and semiarid regions of the world has impelled humans to reuse poor-quality water such as brackish and drainage water. High concentration of ions causing hardness is an important limiting factor to reuse of these water resources. Hardness in water refers to existing multivalent ions such as Ca, Mg, iron (Fe) and manganese (Mn). Among these, Ca and Mg are known as the dominant species for water hardness. Water resources with total hardness higher than 200 mg/L can be tolerated by consumers as poor resources, while concentrations larger than 500 mg/L are not acceptable for most consumptions [1]. Although water hardness does not have serious health impacts, it is responsible for the formation of deposits in facilities.

Recently, various techniques have been used for the removal of different ionic species from water and wastewater. The sorption process is an economic method which can trace large amounts of solutes from aqueous solutions. Hence, finding inexpensive and efficient adsorbents for removing cations causing hardness from water resources is an important issue. Gasco et al. [2] introduced carbon-based adsorbents prepared from sewage sludge as inexpensive acceptable materials to remove Na^+ , K^+ , Ca^{2+} and Mg^{2+} cations from saline water. Aghakhani et al. [3] considered dual adsorbents (combinations of peat, activated carbon, zeolite, cationic resins and anionic resins) in removal of salinity ions from drainage water. This study confirmed that application of cationic resin with peat had higher ability to desalinate drainage water as compared to other adsorbents.

Activated carbons having high surface area, porosity and surface functional groups have been used extensively for removal of various pollutants including heavy metals, pesticides and organic compounds from gaseous and liquid phases [2, 4, 5]. Activation of carbon can be carried out by either physical or chemical methods. Physical activation involves activating the precursor with an oxidizing gas such as CO_2 , steam or their combination, at relatively high temperatures [6]. In chemical activation, the precursor is impregnated with a chemical agent such as KOH, NaOH, K_2CO_3 , ZnCl_2 or H_3PO_4 and then it is heated in an inert atmosphere at various temperatures [7]. Agricultural wastes are good precursor to make carbon-based materials. Unfortunately, most of these residues are burned, causing air pollution and human health problems. Therefore, it will be useful

Corresponding Author: Rokhsareh Rostamian, Water Engineering Department, Isfahan University of Technology, Isfahan, Iran.

to consider the use of these materials for producing applicable and suitable products, which provide positive effects on the environment.

Previous studies have shown that sorption behavior of the activated carbon varied widely based on precursor type and the nature of activation [8, 9]. Therefore, knowing the characteristics of carbon-based materials is an important issue for selecting a suitable adsorbent to remove specified compounds. The main objective of this research was to convert rice husk and canola stalk to activated carbon and also evaluation of their sorption capacity to remove Ca and Mg as main cations causing hardness.

MATERIALS AND METHODS

Preparation of activated carbons:

Rice husk and canola stalk were used for preparation of activated carbons. Raw materials were rinsed with distilled water, oven-dried at 105 °C for 24 h, and then sieved to less than 0.5 mm. Properties of these materials are shown in Table 1.

The raw materials were pyrolysed under inert N₂ gas from room temperature to 600 °C at a heating rate of 10 °C/min and held at the peak temperature for 2 h before cooling to

Table 1: Properties of the studied raw materials.

Sample	Ultimate analysis (%)				Ash (%)	S _{BET} (m ² /g)	pH
	C	H	N	O*			
Rice husk	40.9	6.1	2.2	50.8	18.9	1.43	6.7
Canola Stalk	46.2	7.4	3.5	42.9	2.1	1.19	6.5

* by difference

Room temperature. For activation, steam water was used as a simple and environmentally friendly agent. The pyrolysed samples were reheated under N₂ gas from room temperature to 800 °C. Then, steam was replaced with N₂ gas at 800 °C for 1 h. After that, the samples were cooled down under N₂ gas. Activated carbons prepared from rice husk and canola stalk are denoted as RHA and CSA, respectively.

Characterization of activated carbons:

The prepared activated carbons were characterized by several techniques. The product yield was calculated as the weight ratio of final activated carbon to the initial-dried raw material. Ash content of the samples was obtained by burning a sub-sample at 800 °C for 4 h and weighing the remained mass. Electrical conductivity (EC) and pH were measured by adding each sample to deionized water in a mass ratio of 1:100. The solution was shaken for 2 h and then filtered before measuring the pH and EC. The pH at which the solid surface charge is zero is referred to as zero point of charge (pH_{ZPC}) and was determined utilizing the batch equilibrium and KNO₃ solution [10].

Physical characteristics of the samples were determined by N₂ adsorption-desorption

isotherm at -196 °C using Belsorp mini II instrument. The BET surface area (S_{BET}) was calculated by the Brunauer–Emmet–Teller (BET) method. The total pore volume (V_t) was obtained by N₂ adsorption at a relative pressure of 0.98. Micropore volume (V_{mic}) was derived from the t-plot method. Pore-size distribution and mesopore volume (V_{mes}) were determined by Barret–Joyner–Hanlenda (BJH) method. The surface functional groups were recorded by Fourier Transform Infra-red (FTIR) spectra using JASCO FTIR-680 spectrophotometer, within the range of wave number of 400 to 4000 cm⁻¹.

Batch experiment:

Ca and Mg sorption capacity was determined to compare hardness removal capacity of the prepared activated carbons. MgCl₂·6H₂O and CaCl₂·H₂O salts were used for the preparation of stock solutions containing Ca²⁺ or Mg²⁺ cations at the concentration range of 30-500 mg/l. The salts used in this experiment were of analytical grade. Equilibrium isotherm studies were performed by adding 0.2 g of each activated carbon to 25 ml of prepared stock solution. The mixture was shaken for 6 h. The solution was filtered using Whatman 42 filter paper and Ca and Mg concentration in the equilibrium solution was measured using titration method [11]. The amount of adsorbed target cation was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg/g) is the amount of adsorbed target cation at equilibrium, C₀ (mg/l) is initial concentration of target cation, C_e (mg/l) is the equilibrium concentration of target cation, V (L) is the volume of solution and m (g) is mass of the sample.

The adsorption data were analyzed using Langmuir and Freundlich models. Langmuir isotherm model is defined as follows:

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (2)$$

where q_e (mg/g) is the amount of adsorbed cation, C_e (mg/l) is the equilibrium concentration of cation, q_m (mg/g) and b (l/mg) are constants related to maximum sorption and energy of sorption.

The important feature of the Langmuir model can be described based on the separation factor (R_L) expressed by:

$$R_L = \frac{1}{1 + b C_0} \quad (3)$$

If $R_L > 1$, the adsorption is unfavorable; when $R_L = 0$, the adsorption is irreversible; when $R_L = 1$, the adsorption is linear; if $0 < R_L < 1$, then the adsorption is favorable.

Freundlich isotherm model is expressed as:

$$q_e = k C_e^{1/n} \quad (4)$$

where q_e (mg/g) is the amount of adsorbed cation, C_e (mg/l) is the equilibrium concentration of cation, K and $1/n$ are Freundlich adsorption constants.

RESULTS AND DISCUSSION

Properties of the prepared activated carbons:

Selected properties of the two prepared activated carbons are shown in Table 2. Results indicate that characteristics of the samples depend on precursor type. The ash content of

Table 2: Selected properties of the prepared activated carbons.

Sample	Yield (%)	Ash (%)	pH	EC (dS/m)	pH _{ZPC}
RHA	32.6	46.8	10.1	0.21	7.8
CSA	16.1	14	9.4	0.17	6.9

RHA was very high because rice husk consists mainly of silica [12]. Both carbon samples had alkaline pH values. The pH_{ZPC} is a very useful parameter that expresses surface charge of the adsorbent and its interactions with adsorbates. Net charge of the adsorbent under and above pH_{ZPC} is positive and negative, respectively. The results indicated that CSA had more acidic surface sites than basic sites, compared to RHA.

Physical characteristics:

It is well known that surface area, porosity and pore size distribution are the most important parameters for evaluating the sorption capacity of porous carbon materials. Textural characteristics of the prepared activated carbons are shown in Table 3. Raw materials had very low surface area and activation increased it significantly. Removal of volatiles resulting from decomposition of major compounds of raw material during the carbonization process and reaction of steam with carbonized material during the activation process improved development of pores and enhanced surface area of the porous carbon material. The surface area and pore volume of RHA was less than CSA. High ash content of rice husk (Table 1) decreased the conversion of organic carbon to volatile compounds; therefore, RHA had less surface area and pore volume than CSA. Shackley *et al.* [12] reported similar results. Micropores volume contained about 78% and 45% of total pore

Table 3: Textural characteristics of the activated carbons

Sample	*S _{BET} (m ² /g)	V _t (cm ³ /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)	D _p (nm)
RHA	317	0.175	0.136	0.039	2.21
CSA	564.4	0.621	0.281	0.340	4.40

*S_{BET}: BET surface area; V_t: total pore volume; V_{mic}: micropore volume, V_{mes}: mesopore volume; D_p: mean pore diameter.

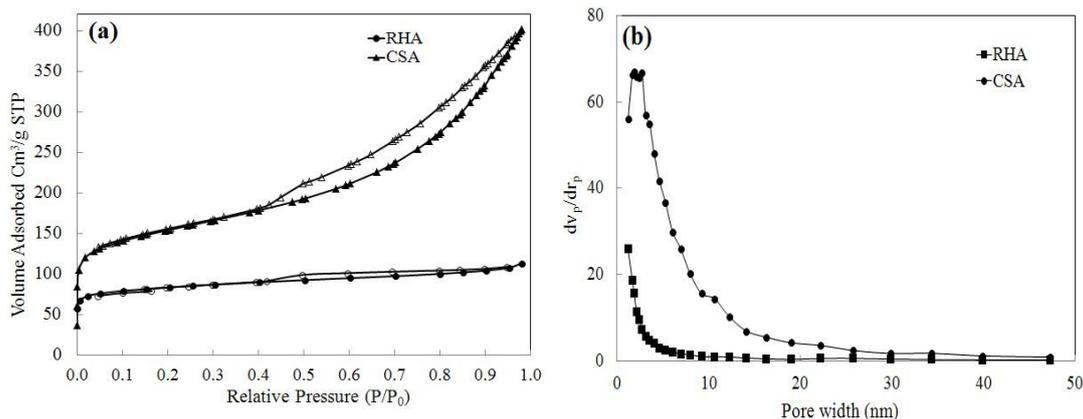


Fig. 1: a) Adsorption-desorption isotherm of nitrogen at $-196\text{ }^{\circ}\text{C}$ and b) pore size distribution for RHA and CSA

Volume of RHA and CSA, respectively.

In order to investigate the structure of prepared samples, the N_2 adsorption-desorption isotherms and their pore size distributions are shown in Fig. 1. According to IUPAC classification [13], the isotherm of RHA is type I and that of CSA is combination of type I and II. Type I mostly indicates a microporous and type II indicates a mesoporous structure. Sharp positive slope of adsorption in the relative pressure of $P/P_0 > 0.4$ in CSA isotherm shows a mesopore development in its structure. The hysteresis loop indicates presence of mesopore within the structure of the samples. Pore size distribution of the samples (Fig. 1(b)) indicates that precursor type influenced pore size distribution of the activated carbon.

FTIR analysis:

FTIR is perhaps the most powerful tool for identifying type of the functional groups. They are one of the most effective parameters in sorption capacity of the adsorbents. Figure 2 shows FTIR spectra of the prepared samples. The spectra of RHA were characterized by several major peaks. Broad peak at $3400\text{--}3500\text{ cm}^{-1}$ is typically attributed to hydroxyl groups. The strong peaks located at 471 cm^{-1} , 794 cm^{-1} and 1096 cm^{-1} are ascribed to bending vibration, symmetric stretching and asymmetric stretching of Si-O bonds [14, 15]. The presence of these peaks was due to the existence of silica compounds. The peak at 1383 cm^{-1} can be assigned to C-O stretching vibration. The peak appeared at 2354 cm^{-1} can be associated with $=\text{C}=\text{O}$ in ketene group [16].

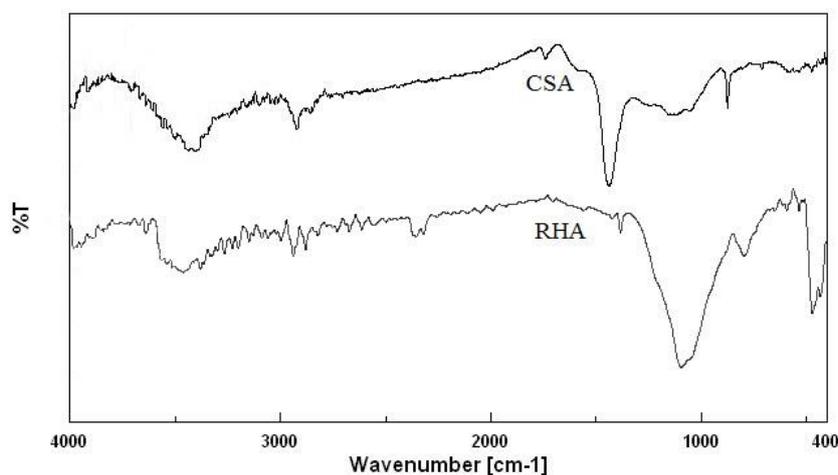


Fig. 2: FTIR of the activated carbons.

The FTIR of CSA shows a broad peak around 3440 cm^{-1} which can be attributed to hydroxyl groups. The stretching vibration of C-H bond in aromatic structures is visible as a peak at around 2920 cm^{-1} . The peak at 1742 cm^{-1} can be ascribed to C=O of carboxyl groups. The peak at 1437 cm^{-1} can be assigned to $-\text{COO}$ symmetric stretching vibration of carboxyl group. The peak at 880 cm^{-1} represents aromatic C-H bending.

Hardness removal capacity of activated carbons:

Figure 3 shows the amount of adsorbed Ca and Mg versus equilibrium concentration. The equilibrium data were analyzed by fitting them to Langmuir and Freundlich isotherm models (Table 4). Coefficient of determination (R^2) and Standard Estimation Error (SEE) were used for evaluation of the models. The results shown in Table 4 demonstrate that equilibrium data were well fitted to both isotherm models. R_L value is Langmuir constant used for evaluation of the sorption process. According to R_L values (Table 4), the sorption of hardness cations onto the prepared activated carbons is favorable. Freundlich constant ($1/n$) was found to be in the range of 0.665-0.722. This range ($1/n < 1$) confirms that both prepared activated carbons are favorable for separation of Ca and Mg cations under the conditions used in this study. Ca sorption capacity of CSA and RHA was estimated as 51.8 and 15.1 mg/g, respectively. Mg sorption capacity of 11.1 and 6.9 mg/g was obtained for CSA and RHA. CSA had higher sorption capacity than RHA. Overall, CSA had higher sorption capacity than RHA and both adsorbents had more tendency for Ca sorption, compared to Mg sorption.

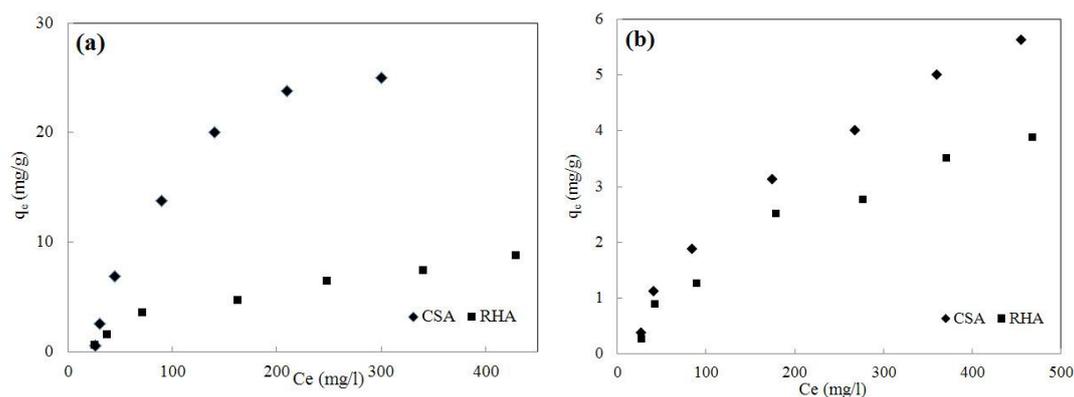


Fig. 3: Adsorption isotherm of a) Ca and b) Mg for activated carbons.

Table 4: Coefficients of Langmuir and Freundlich adsorption models.

Model	Parameter	CSA		RHA	
		Ca	Mg	Ca	Mg
Langmuir	q_m (mg/g)	51.79	11.09	15.14	6.90
	b (L/mg)	0.004	0.002	0.003	0.002
	R_L	0.36-0.90	0.47-0.94	0.4-0.92	0.43-0.93
	R^2	0.976	0.997	0.988	0.991
Freundlich	SEE	2.44	0.168	0.504	0.197
	K	0.456	0.081	0.156	0.067
	$1/n$	0.722	0.698	0.666	0.665
	R^2	0.961	0.995	0.985	0.986
	SEE	3.12	0.225	0.56	0.252

In general, sorption capacity of the porous carbon materials is influenced by such characteristics as surface functional groups, surface area, pore volume and pore size distribution. There was not any special surface group at FTIR spectra of activated carbons (Fig. 2), which indicates probability of involvement between Ca and Mg cations and surface groups in the sorption process. Therefore, sorption of hardness cations with prepared activated carbons is not based on chemisorption process.

The first step in ion removal is migration of ions from the bulk solution to the surface of the adsorbent. Surface area of CSA was about 1.8 times more than RHA. Higher surface area increases probability of ions migration to the surface of the adsorbent. The pH_{ZPC} of CSA (6.9) was lower than RHA (7.8); therefore, negative charge on the adsorbent surface in the pH range of the experiment was higher for CSA than RHA, causing greater electrostatic attraction between cations and CSA adsorbent. This could cause an increase in cation adsorption capacity of CSA as compared to RHA.

Sorption capacity of carbon porous materials is not related in a simple form to their surface area and porosity [17]. It depends on the accessibility of molecules to inner surfaces of the adsorbent, which depends on their size and pore size distribution. Pore diameter, which is larger than the size of adsorbate, improves accessibility to internal surface of the adsorbent materials. Rambabu *et al.* [8] introduced micropores with diameter < 0.7 nm as favorable pores for physical sorption of H_2S with size of 0.14 nm. Gundogdu *et al.* [18] reported that iodine element with a size of 0.56 nm is greatly adsorbed into micropores. Hydrated ionic radius of Ca and Mg is about 0.253 and 0.30 nm, respectively [19]. According to the size of Ca and Mg cations, micropores seem to be suitable pores for retention of these cations. Micropore volume of CSA is about 2 times more than RHA; hence, larger sorption capacity of CSA than RHA is expected.

Both adsorbents had more tendency for Ca, compared to Mg, probably due to smaller hydrated ionic radius of Ca, which can be adsorbed more easily. Noori Sepehr *et al.* [1] also reported more sorption capacity of Ca as compared to Mg by natural and alkaline-modified pumice stones.

Conclusions:

Potential of rice husk (RH) and canola stalk (CS) for preparation of steam- activated carbon to remove hardness cations was studied. Type of raw material affected physiochemical characteristics of the activated carbons. Surface area and pore volume of CSA were 1.8 and 3.5 times more than RHA. The high ash content of rice husk caused to lower development of textural of RHA. CSA had more sorption capacity for hardness cations. Both activated carbons had more potential in removing Ca^{2+} compared to Mg^{2+} . The conversion of agricultural wastes to activated carbon offers a solution for minimizing waste volume and producing valuable adsorbents to improve water quality.

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