REMOVAL OF MANGANESE(II) IONS FROM AQUEOUS SOLUTIONS. I. KINETICS

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ABSTRACT

White rice husks ash (WRHA) was obtained via thermal degradation of rice husks, which was used for sorption of Mn(II) ions from aqueous solutions. Adsorption kinetics was studied under agitation at 288, 298 and 308 K and different solution concentrations. Pseudo-first-order kinetic equation was found as the most appropriate kinetic model. On it basis, the values of rate constants of the sorption process were calculated for the studied temperatures, which was found to be equal to $k_{288} = 8.75\times10^{-4}$ min^{-1}, $k_{298} = 2.51\times10^{-3}$ min^{-1} and $k_{308} = 6.69\times10^{-3}$ min^{-1}, respectively. They were fitted to the Arrhenius equation to determine the values of the activation energy (E_A = 75 kJ mol^{-1}) and the frequency factor ($A = 3.51\times10^{10}$ min^{-1}). The obtained results showed that white rice husks ash can be successfully used for adsorption of Mn(II) ions from aqueous solutions.

Keywords: *Adsorption, Manganese(II) ions, Rice husk ash, Batch study, Adsorption kinetics.*

INTRODUCTION

Manganese is the third most abundant transition metal on Earth. It is an essential trace element for the human body, which plays a role in a variety of enzyme systems. It has many applications, as the major is for making iron-manganese and non-ferrous alloys, but also is used in ceramics, dry battery cells, electrical coils, etc. Manganese is contained in the untreated wastewater from the above-mentioned industries, but also in coking and flue gas wastewater [1]. The removal of metal ions such as Mn(II) ions from aqueous solution is serious problem in many countries. Manganese is one of the elements which are very difficult to be removed from surface waters. It is established the blocking of toxic effects of hydrogen ion by manganese and that the manganese has low chronic toxicity [2]. For the maximum concentration of manganese admissible in drinking water by World Health Organization is stated 0.05 mg L^{-1}, the same as in Bulgaria, where by the ordinance on the quality of water for irrigation of agricultural crops is stated 0.2 mg L^{-1}

Many studies were conducted on Mn(II) ions removal in the past, including those designed to evaluate chemical dynamics, experiment with packed columns of limestone, and evaluate passive treatment systems [3-5]. As adsorbents usually are used activated carbon, silica and zeolites.

In the present water management study are prepared some adsorbing materials, obtained from pyrolysis of agricultural wastes, namely rice husks, and was made an attempt to remove water soluble Mn(II) ions by adsorption onto those silica adsorbents.

EXPERIMENTAL

Only analytical grade reagents were used in the experiments. An initial stock solution of Mn(II) ions (1000 mg L^{-1}) was prepared from manganese acetate $Mn(CH_3COO)_2{\cdot}4H_2O$ (Merck) by dissolving the necessary amount. A series of Mn(II) ions standard solutions were prepared by diluting different aliquots of the stock solution with double distilled water.

Adsorbents preparation

Batches of white rice husk ash (WRHA) and black rice husk ash (BRHA) have been produced via pyrolysis of raw rice husks in a pilot plant fluidized-bed reactor with a capacity of 100 kg h^{-1}. Nitrogen adsorption-desorption isotherms were obtained on a classical volumetric BET apparatus at 77 K. Comprehensive physicochemical characterization of the BRHA and WRHA has been presented elsewhere

[6]. The obtained products were used without any pretreatment in batch experiments for the removal of Mn(II) ions from model aqueous solutions.

Analytical measurements

The concentrations of Mn(II) solutions were determined using a spectrophotometer JENWAY 6300 (UK) by measuring the absorbance at the characteristic wavelength of 525 nm after setting a standard curve. Manganese was oxidized into permanganate with acid-medium potassium periodate according to the following reaction:

$$2Mn^{2+} + 5IO_4^- + 3H_2O \leftrightarrow 2MnO_4^- + 5IO_3^- + 6H^+ \quad \text{(I)}$$

Batch experiment

For the kinetic study, six Mn(II) ions solutions were prepared with concentrations 10, 20, 40, 60, 80 and 100 mg L^{-1}. In each adsorption experiment, 0.25 g of WRHA was added to 100 mL of Mn(II) ions solution of known concentration in a 150 mL glass container equipped with a water jacket by which the solution temperature was maintained constant (288, 298 and 308 ± 0.5 K) with continuous agitation at 300 rpm by an electromagnetic stirrer. The initial Mn(II) ions concentration and temperature were varied in order to investigate their effect on the adsorption kinetics. For the determination of pH effect, 0.1 M HCl and 0.1 M NaOH were used to adjust the desired initial pH of the solutions.

The percent removal of Mn(II) ions by BRHA and WRHA, expressed in %, and the amount of ions adsorbed per unit weight of adsorbent at time t, mg g^{-1}, were calculated using the following equations:

$$\%\ \text{removal Mn(II) ions} = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

$$Q_t = \frac{C_0 - C_t}{m} \times V, \quad (2)$$

where: C_0 is the initial Mn(II) ions concentration and C_t is the concentration at any time t, respectively, mg L^{-1}, V is the solution volume, L, and m is the weight of the adsorbent, g.

RESULTS AND DISCUSSION

The main physicochemical characteristics of the rice husks (RH) and the products of their thermal degradation in different atmospheres are presented in Table 1, and for comparison, these of Aerosil A200 (AR), Degussa AG, Germany.

Table 1. Physicochemical characteristics of the RH, WRHA, BRHA and AR.

Parameter	RH	WRHA	BRHA	AR
SiO_2, mass%	20.2	94.2	54.0	100
Moisture, mass%	7.1	0.8	0.6	–
Mean particle size, μm	80	50	60	20
Surface area, $m^2\ g^{-1}$	<1	228	241	273
True density, g cm^{-3}	1.47	2.2	1.8	2.2

Fig. 1 shows the typical nitrogen adsorption-desorption isotherms of BRHA and WRHA and pore size distribution curves of both samples. As can be seen from Fig. 1, the adsorption isotherms of BRHA and WRHA were of type IV and each had hysteresis loop (associated with capillary condensation) from type H1 according to IUPAC classification [7]. Under these observations, both the samples were mainly microporous (mean radius 1.8–2.0 nm) with narrow pore size distribution. It can be seen that the adsorption isotherms and the curves of pore volume distribution of BRHA and WRHA are identical. The uniformity of the adsorption isotherms shows that the presence of certain amount of amorphous carbon did not result in substantial changes in the amorphous SiO_2 porous structure. The specific surface area of both samples was in the order of 230–240 $m^2\ g^{-1}$, and

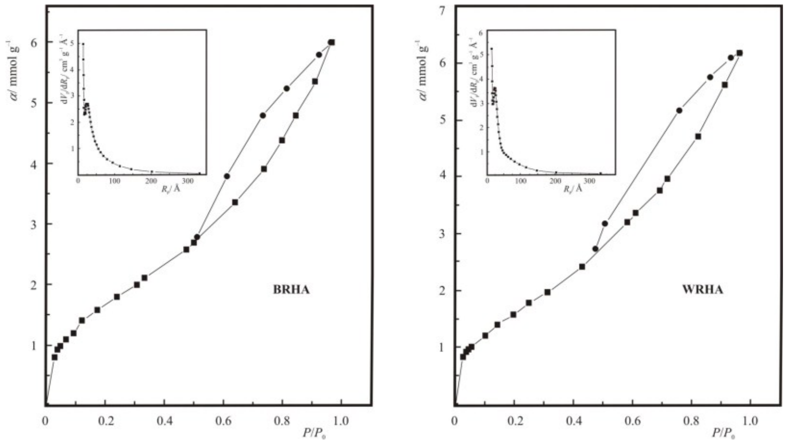

Fig. 1. Nitrogen adsorption isotherms of BRHA and WRHA and pore size distribution curves.

their pore volume – in the range of 0.22–0.25 cm^3 g^{-1}. These results were reason to be expected that both products could be used as adsorbents, as should be considered that hydrophilic WRHA would adsorb predominantly polar molecules whereas hydrophobic BRHA would adsorb principally non-polar molecules. Taking into account the differences and characteristics of BRHA and WRHA, study was carried out on the adsorption of Mn(II) ions from aqueous solutions only onto WRHA, obtained in a pilot plant fluidized bed reactor.

Adsorption kinetics is an important characteristic regarding the determination of the adsorption process efficacy. The adsorption of a solute by a solid in aqueous solutions is a phenomenon that typically has complicated kinetics. The rate of adsorption is strongly influenced by several parameters related to the physicochemical conditions under which adsorption is carried out, and the state of the adsorbent, which has usually heterogeneous surface. The adsorption kinetic data were analyzed employing pseudo-first-order equation and pseudo-second-order equation.

Pseudo-first-order kinetic model

The differential form of the pseudo-first-order kinetic equation can be expressed as [8,9]:

$$\frac{\mathrm{d}Q_\mathrm{t}}{\mathrm{d}t} = k_\mathrm{f}\left(Q_\mathrm{eq} - Q_\mathrm{t}\right), \qquad (3)$$

where Q_{eq} and Q_t are the amounts of Mn(II) ions adsorbed at equilibrium and at time t, respectively, mg g^{-1}; k_f is the pseudo-first-order rate constant, min^{-1}; and t is the contact time between the adsorbent and adsorbate, min. The integration of Eq. (3) when, using the following boundary conditions: $t = 0$ to $t = t$ and $Q_t = 0$ to $Q_t = Q_t$, resulted in the next linear form, known as Lagergren's first-order rate equation:

$$\ln\left(Q_\mathrm{eq} - Q_\mathrm{t}\right) = \ln Q_\mathrm{eq} - k_\mathrm{f}t \qquad (4)$$

Plotting the linear dependence of $\ln(Q_{eq} - Q_t)$ versus t, the fitness of this kinetic model was found. From the slope and intercept values, the pseudo-first-order rate constant k_f and the amount of ions adsorbed at equilibrium $Q_{eq,\ calc}$ can be calculated, respectively.

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is given by the expression [10-12]:

$$\frac{\mathrm{d}Q_\mathrm{t}}{\mathrm{d}t} = k_\mathrm{s}\left(Q_\mathrm{eq} - Q_\mathrm{t}\right)^2 \qquad (5)$$

where k_s is the rate constant of the pseudo-second-order adsorption, g mg^{-1} min^{-1}, and the other symbols are the same as these in Eq. (3). The integrated linear form of Eq. (5) becomes:

$$\frac{t}{Q_\mathrm{t}} = \frac{1}{k_\mathrm{s}Q_\mathrm{eq}^2} + \frac{t}{Q_\mathrm{eq}} \qquad (6)$$

A linear fit of t/Q_t versus t gives a straight line with a slope of $1/Q_{eq}$ and an intercept of $1/k_sQ_{eq}^2$, and shows the applicability of that kinetic model.

Figure 2 shows the decrease of manganese concentration and the increase of the quantity adsorbed on a gram of WRHA in relation to time at 298 K at initial Mn(II) ions concentration of 100 mg L^{-1}

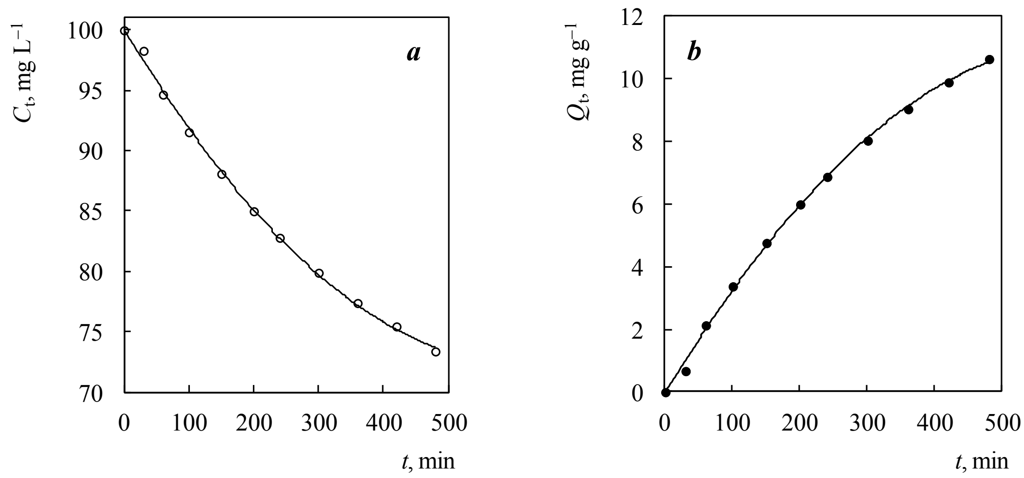

Fig. 2. Dependence of the concentration of Mn(II) ions in the solution (a) and the quantity of adsorbed Mn(II) ions (b) onto WRHA in relation to time.

The fast kinetics in the beginning of the adsorption was interpreted by the significant number of active sites available on the adsorbent surface. After the occupation of these sites by Mn(II) ions, the reaction rate decreased. On the basis of the obtained experimental data, using the Eqs. (4) and (6), the corresponding kinetic curves were plotted. The pseudo-second-order kinetic model did not correlate well with the results obtained because the value of R^2 was far from unity. At the same time Eq. (4) for the pseudo-first-order kinetic model gave straight line with higher coefficient of correlation of linear regression. In Fig. 3 is presented the corresponding kinetic curve.

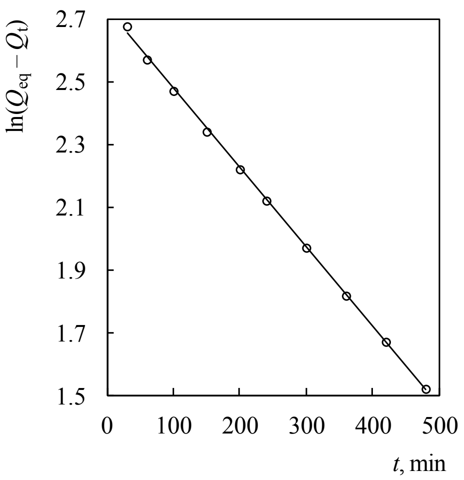

Fig. 3. Dependence of $\ln(Q_{eq}–Q_t)$ versus t for adsorption of Mn(II) ions on WRHA.

The value of the rate constant of the adsorption process was calculated at 298 K, k_{298}, which was found to be equal to 2.51×10^{-3} min^{-1}. On the same manner were calculated the values of the rate constants at 288 and 308 K ($k_{288} = 8.75\times10^{-4}$ min^{-1} and $k_{308} = 6.69\times10^{-3}$ min^{-1}). The value of the activation energy E_A of the sorption process and frequency factor A was found by the well-known Arrhenius equation:

$$\ln k = \ln A - \frac{E_A}{RT} \quad (7)$$

From the slope of the straight line was calculated the value of E_A, equal to 75 kJ mol^{-1}, and from the ordinate intercept – the value of the frequency factor A, equal to 3.51×10^{10} min^{-1}. The value of the activation energy could provide information on type of adsorption – either physical or chemical. As the observed value was above 42 kJ mol^{-1}, the adsorption mechanism was chemical adsorption.

CONCLUSIONS

On the basis of the experiments carried out the values of rate constant of adsorption of Mn(II) ions at 288, 298 and 308 K were calculated, as well as the values of the activation energy and frequency factor in the Arrhenius equation. The obtained results showed that white rice husks ash obtained via thermal degradation of rice husks can be successfully used for adsorption of Mn(II) ions from aqueous solutions.

Acknowledgments

The work was financially supported by the project “Young scientists – 2011” from National Science Fund, Ministry of Education, Youth and Science – Bulgaria.

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