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REMOVAL OF HUMIC ACID FROM AQUEOUS SOLUTION USING MgO NANOPARTICLES

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The main purpose of this work was to investigate the removal of humic acid (HA) from aqueous solutions using MgO nanoparticles as a novel adsorbent. The effect of contact time, competing anions in the aqueous solutions, for the removal of HA in batch system was studied. The nanoparticle was characterized by scanning electron microscope method. Experimental results show that MgO nanoparticles can remove more than 90% of HA under optimum conditions. The results showed that the examined interfering anions influenced the HA removal. The adsorption kinetics and isotherm were also studied. The adsorption kinetics was well described by the pseudo-second-order equation, and the adsorption isotherms were better fitted by the Langmuir model.

Key words: aqueous solution, removal, humic Acid, MgO nanoparticles.

1. Introduction

One of the most important contaminants being present in water supplies is natural organic matter (NOM). NOM is a set of few complex organic materials produced from dead or living animals, plants and microorganisms [1].

Naturally humic substances are known as humic, humic acid (HA) and fulvic acids (FA). These organic substances based on their solubility and with regard to acidic or alkaline characteristics in aqueous solutions are classified [2]. Humic substance comprises the greatest proportion of NOM. Recent studies indicate some concentration of NOM in surface waters in Tehran [3]. Humic substances can react with chlorine during water treatment and produce disinfection byproducts. These disinfection byproducts include a group of chemicals known as Trihalomethanes (THMS) [4 – 6].

Removal of Humic acid substance from water is very important, because they have a harmful effect on the water quality human health. Some of these hazardous materials are known as mutagenic compounds and are consumed

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as food for bacterial growth and also are capable of accumulating heavy metals and pesticides in living organisms, therefore increases their concentrations in aqueous solutions [1, 7, 8]. Several methods have been investigated for removals of organic materials and humic substances from water include: adsorption, ultrafiltration membrane, advanced oxidation and photocatalytic oxidation [9 – 18]. Recently, ultrasonic technology and nano/microcrystals have attracted significant attention for their advancements in science and technology [18 – 21].

Among these, MgO nano particles represent a highly efficient application in a variety of area for environmental remediation due to their high surface area, higher reactivity and sorption ability [22, 23]. HA have negative charged molecules due to carboxylic and phenolic functionalities [24]. The pH of zero point charge (pH_{zpc}) of MgO is 12,4; therefore, it is a proper adsorbent for the adsorption of anions, as a matter of favorable electrostatic attraction mechanism [25]. However, there are no reports available in literature dealing with the application of MgO nano crystalline for the removal of HA from water solution. In this study the removal capacity of HA by MgO nanoparticles was studied at different condition, including: effect of time, effect of interfering ions normally being present in surface water, adsorption isotherm and kinetic study.

2. Experimental

HA sodium salt was purchased from "Aldrich Co". A 1000 mg/L stock solution of HA was prepared by using distilled water.

2.1. Preparation of MgO nanoparticles. In this study MgO nanoparticle synthesized by sol-gel method according to the procedure described in literature [26]. 0,1 M of $\text{Mg}(\text{NO}_3)_2$ was stirred with 0,2 M aqueous solution of NaOH. The stirring was carried out at 25°C for 4 h. The suspension was centrifuged at 6000 rpm for 20 min to obtain $\text{Mg}(\text{OH})_2$ gel. The precipitate magnesium hydroxide was filtered and repeatedly washed with deionized water to remove residual chloride ions. The samples were dried overnight at 110°C and calcined at 400 for 4 h in air to obtain MgO nanoparticles. The surface morphology of MgO was examined by using a scanning electron microscope XL30 (SEM), "Philips Company" (Fig. 1). The SEM image of MgO nanoparticle is shown.

2.2. Adsorption experiments. Adsorption Experiment was carried out using a batch equilibrium technique on a shaker operated at 120 rpm. Experimental solution of desired concentrations of HA was prepared by dilution of stock solution of HA and then shaken at room temperature with a known weight of

MgO. After shaking for a defined equilibrium time, the sample was filtered and then its residual concentration was determined. In each of experiment the solution was filtered and the HA concentration was determined in filtrates and the amount of adsorbed HA was calculated from the following equation

$$q_e = V(C_0 - C_e) / W, \quad (1)$$

where q_e is the adsorption capacity (mg/g) at equilibrium; C_0 and C_e are the initial and equilibrium HA concentrations (mg/L), respectively; V is the volume (l) of solution and W is the mass (g) of adsorbent used. Similar procedures were followed to study the effect of contact time, interfering ions, sorption isotherm and kinetic study.

2.3. Analytical procedures. The concentration of HA in the solution was determined using a UV-Vis spectrophotometer at $\lambda_{\max} = 465$ nm (PU 8700 "Philips").

3. Results and discussion

3.1. Characteristics of MgO nanoparticle. The morphology, structure and size of the sample were investigated by SEM that shown in Fig. 1. The average crystallite size of the MgO nanocrystals was 80 nm which is set in nano size.

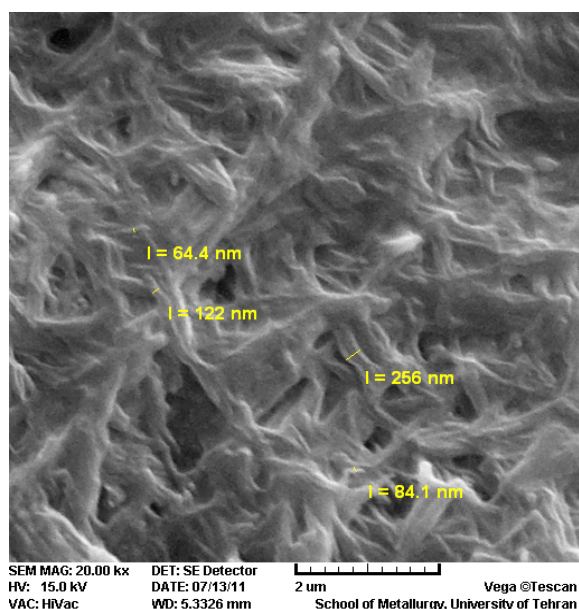


Fig. 1. SEM image of MgO.

3.2. *Effect of contact time.* The effect of contact time was investigated in the range of 5 – 60 min with the initial HA concentration of 25 mg/L at room temperature. The solution pH and MgO dosage were fixed at the optimum values. As shown in Fig. 2, the HA removal efficiency was increased with increasing the contact time and reached equilibrium after 20 min. At this time, the maximum removal efficiency of HA is about 91%, so 20 min is fixed as a proper contact time for further studies. These results indicate that the high efficiency removal of HA MgO may be due to the large surface site initially available for HA removal [27].

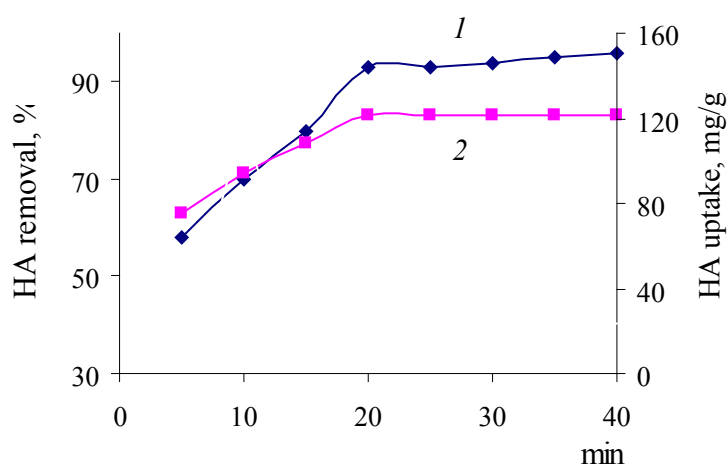


Fig. 2. *Effect of contact time on HA removal by MgO (initial pH 3, sorbent dose – 0,1 g, initial HA concentration – 25 mg/L)*

3.3. *Effect of various anions.* In general, natural water contains anions such as SO_4^{2-} , NO_3^- , Cl^- , HCO_3^- , I^- and H_2PO_4^- . The effect of these anions was studied at optimal experimental conditions. Experiments carried out in the presence of 50 mg/L of anions. With regard to Table 1, it was found that the effect of various anions on the efficiency removal of HA is as the following order: $\text{Cl}^- > \text{I}^- > \text{HCO}_3^- > \text{H}_2\text{PO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-}$. By this, it can be concluded that Cl^- had less impact on HA adsorption; sulphate had more effect on HA adsorption. The effect of these anions on UA reduction is shown in Fig. 3. This was partly as a matter of higher negative charges of sulphate compared to chloride or nitrate ions, since; sulphate needs two close surface groups, which decreases its effect [24]. It seems that the presence of anions in aqueous solution would enhance the coulombic repulsion forces being present between the anions and HA molecules. The development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions, ions

of opposite charge to that of the particle, close to the surface. Thus an electrical double layer exists round each particle and change of double electric layer (DEL) MgO particles by adding an electrolyte.

Table 1. Effect of competing ion on HA removal by MgO

HA	Cl ⁻	I ⁻	HCO ₃ ⁻	H ₂ PO ₄ ⁻	NO ₃ ⁻	SO ₄ ²⁻
	77	71	66	63	61	52

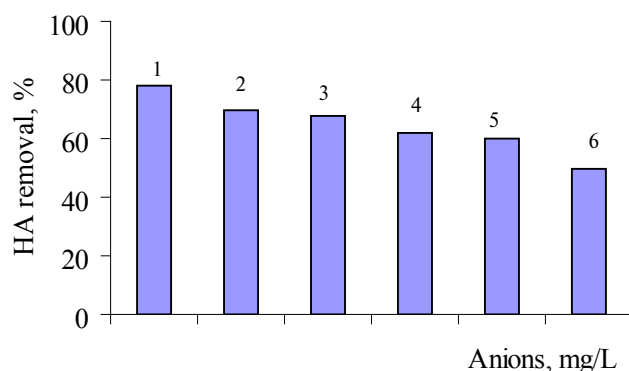


Fig. 3. Effect of competing ion on HA removal by MgO: 1 – Cl⁻; 2 – I⁻; 3 – HCO₃⁻; 4 – H₂PO₄⁻; 5 – NO₃⁻; 6 – SO₄²⁻.

3.4. Sorption isotherm. Adsorption isotherms describe the relationship between the amount of adsorbate adsorbed on the adsorbent surface and the concentration of dissolved adsorbate in the liquid at equilibrium condition. The Langmuir and Freundlich isotherms are the most commonly used isotherms to describe the adsorption characteristics of adsorbent used in water and wastewater [27]. The Langmuir model assumes that the adsorption occurs in surface sites. The Freundlich equation is based on sorption on a heterogeneous surface [28]. HA sorption capacity by MgO was evaluated using two isotherms namely Langmuir and Freundlich, as represented by the following equations:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}, \quad (2)$$

$$q_e = K_F C_e^{1/n}. \quad (3)$$

Where, sorption capacity (Q^0) is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent. b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption. Q^0 and b were determined, respectively, from the slope and intercept of the straight line plot of C_e/q_e versus C_e , which are presented in Fig.4.

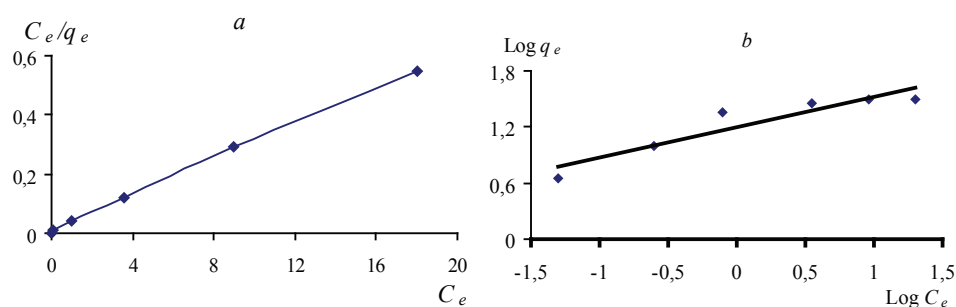


Fig. 4. Isotherm plots of HA removal on MgO, Langmuir isotherm (a) and Freundlich isotherm (b). MgO dosage – 0,1 g, HA concentration – 5 – 50 mg/L, pH 3.

In the linear form of Freundlich isotherm, q_e is the amount of HA adsorbed per unit weight of the sorbent at equilibrium (mg/g), C_e is the equilibrium concentration of HA in the solution (mg/L), K_F is a measure of adsorption capacity and $1/n$ is adsorption intensity. The Freundlich isotherm constants, K_F and n , were calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$. The values of $n = 1 - 10$ confirm the favorable conditions for adsorption. In experiments of equilibrium adsorption isotherm, a fixed amount of 0,1 g adsorbents were contacted with 100 mL of aqueous solutions HA with different concentrations (5 – 50 mg/L). From Table 2, it can be found that the linear equation of Langmuir model shows higher correlation ($R^2 = 0,99$) than Freundlich model ($R^2 = 0,94$). Therefore Langmuir model is selected as the best-fit model for the adsorption of HA on MgO. Result shows that the isotherm data has been fitted to the Langmuir model ($R = 0,99$).

Table 2. Adsorption isotherm parameters of HA on MgO

HA	Langmuir isotherm			Freundlich isotherm		
	R^2	b	q_{\max}	R^2	n	K_F
	0,99	1,42	50	0,94	3,12	15,48

In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [29]. Where, b is the Langmuir isotherm constant and C_0 is the initial concentration of HA (mg/g). The value of R_L indicates the types of isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$):

$$R_L = 1 + b C_0. \quad (4)$$

The calculated R_L value between 0 and 1 is indicating favorable adsorption of HA by MgO nanoparticle.

3.5. Kinetic study. In order to investigate the mechanism of adsorption process, the pseudo first-order and the pseudo second-order adsorption model were used to study experimental data [30]. The pseudo-first-order equation can be expressed:

$$\ln(q_e - q_t) = \ln q_e - k_1 t. \quad (5)$$

The pseudo-second-order model is based on the assumption of chemisorption of the adsorbate on the adsorbents. This model is given a next equaliation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}, \quad (6)$$

where q_e and q_t are the amount of HA adsorbed (mg/g) by MgO at equilibrium at time t (min), k_1 (1/min) and k_2 are pseudo-first-order and pseudo-second-order rate constants, respectively. k_1 and q_e values determined from the intercept and slope of the plots of $\ln(q_e - q_t)$ versus t and t/q_t (Fig. 5). The adsorption kinetics were studied for constant temperature condition and the quantity of HA adsorbed with time was recorded. The rate constants and the correlation coefficients of the two kinetic models are shown in Table 3. These results showed that the adsorption process followed the pseudo-second-order kinetic.

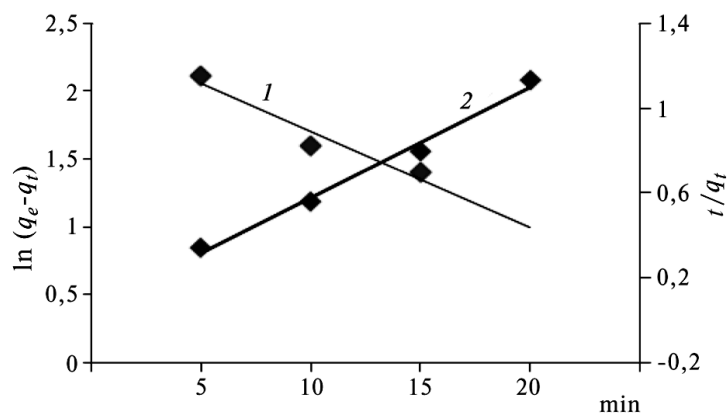


Fig. 5. Kinetic plot of HA removal by MgO pseudo-first-order model (1) and pseudo-second-order model (2).

Table 3. Pseudo-first and pseudo-second-order kinetic parameters, particle and intraparticle pore diffusion model parameter of HA on MgO

HA	Pseudo-first-order model			Pseudo-second-order model			Particle diffusion model		Intraparticle pore diffusion model	
	k_1	q_e	R^2	k_2	q_e	R^2	$k_1(\text{min}^{-1})$	R^2	$k_1(\text{mg/g} \times \text{min}^{0.5})$	R^2
	0,07	11,13	0,94	0.05	20	0,99	14,28	0,94	19,23	0,99

Sorption of a liquid adsorbate on porous solid adsorbent can be modeled by pore diffusion models, can be either particle diffusion or pore diffusion model [31]. The intraparticle pore diffusion model was proposed by Weber and Morris is also used to characterize the sorption data:

$$q_t = k_p t^{0.5}, \quad (7)$$

where k_p is the intraparticle diffusion coefficient ($\text{mg/g} \cdot \text{min}^{0.5}$), which can be obtained from slope of q_t versus $t^{0.5}$.

The particle diffusion model can be written as:

$$\ln \frac{C_t}{C_e} = k_p t. \quad (8)$$

According to this model the plots of linear forms of particle diffusion and intraparticle pore diffusion models are given in Fig. 6, *a*, *b*, respectively and the values of different parameters are given in Table 3.

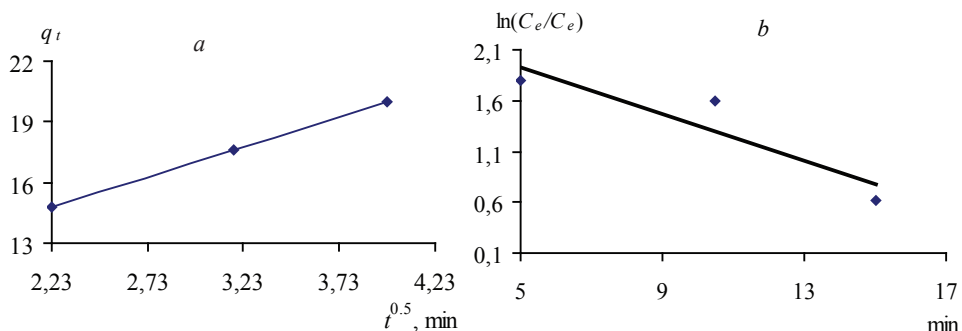


Fig. 6. Particle diffusion model (*a*) and Weber-Horris plot (*b*) of HA removal by MgO.

In this study, the linear portion of the curves do not pass through the origin (see Fig. 6) indicating that mechanism of Humic removal on MgO is complex and both the surface adsorption and intraparticle diffusion contribute to the rate determining step.

4. Conclusions

The following conclusion can be achieved from the experimental results: MgO nanoparticles are very capable in removal of HA with high efficiency; the optimum contact time was obtained to be 20 min; anions significantly affected the HA removal; equilibrium data are best fitted by Langmuir isotherm; the adsorption kinetic was better fitted by pseudo-second-order equation; the sorption of HA on MgO occurs through both the surface adsorption and intraparticle diffusion.

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