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Kinetic, isotherm and thermodynamic investigations of phenol adsorption by a new adsorbent chitosan grafted with a mixture of IA-Mam

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ABSTRACT: In this research, after grafting chitosan (CTS) using a mixture of itaconic acid (IA) and methacrylamide (MAm) monomers in the presence of 4, 4-azobis-4-cyanovaleric acid (ACV) and ethylene glycol dimethacrylate (EGDMA), adsorption isotherm and kinetics were investigated. The obtained results are consistent with the Langmuir isotherm and pseudo-second-order kinetic models. Thermodynamic studies confirmed the endothermic and spontaneity of the adsorption process. On the other hand, due to the increase in entropy, the proper interaction of adsorbent and adsorbate was confirmed.

Keywords: *Chitosan, Isotherm, Kinetic, Itaconic acid , Methacrylamide, Thermodynamic.*

INTRODUCTION

Phenols are a wide and important group of priority water pollutants. They are discharged in the liquid effluents of various factories such as chemical, petrochemical, paper, wood, metallurgy and etc [1]. Phenolic compounds are also present in wastewater from agricultural industries, olive oil factories, and tomato processing [2, 3]. Chitosan is a material that has function as an adsorbent because of its biodegradable nature, means the ability to be decomposed by the environment (soil) after used [4]. Chitosan isolated from shrimp waste which potential to use as a material in the modification process because chitosan has -OH, $-NH_2$ and $-NHCOCH_3$ groups which can form kelat, which is considerably available in the environment and nontoxic [5]. Chemical modification of chitosan with monomers is one of the most important ways to increase its stability in different pH conditions and can increase its absorption capacity [6]. In my recent study, chitosan was grafted with a mixture of itaconic acid-methacrylamide-monomer and the optimum conditions for phenol adsorption in aqueous solutions were reported [7]. In this research, thermodynamic parameters, isotherm and kinetics of phenol adsorption have been investigated.

MATERIALS AND METHODS

All required materials including medium molecular weight chitosan (Sigma-Aldrich) and IA and MAm as monomers, EGDMA as crosslinker, ACV as radical ini-

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tiator, phenol and required solvents of the highest purity by (Merck. Germany) were prepared and doubly distilled water was used in all experiments. Adsorption studies were investigated by Uv- spectroscopy (Shimadzu-1208) and the morphology of the adsorbent before and after adsorption was investigated by Scanning electron microscopy (SEM) (Philips CM120).

Synthesis of Copolymer

According to the conditions mentioned in the previous article, 0.2 g of chitosan was dissolved in 35 ml of 5 wt% acetic acid. Then, ACV was dissolved in 5 ml of distilled water and added to the solution. Two monomers of itaconic acid (IA), methacrylamide (MAm) are also added. Finally, ethylene glycol dimethacrylate (EGDMA) is added to the solution as a cross-linker.The contents were placed in a water bath preset at 90ºC. Finally, the purification was performed with Whatman filter paper and washed with fresh methanol and dried at 50°C. The best conditions were recorded (EGDMA = 2 ml, ACV = 0.01 g, IA = 0.01g, MAm = 0.09 g, t = 45min, CTS = 0.2 g) [7, 8].

Adsorption Isotherms and Kinetics

Surface adsorption experiments were performed using 0.01 g of the grafted chitosan in a total volume of 20 mL, phenol concentration (50 mg/L) in a 250 mL Erlenmeyer flask at the constant shaker speed (150rpm) and constant temperature (298K). After the desired time, the solution was filtered by filter paper (Whatman No. 40) and then centrifuged at 3000 rpm for 10 minutes. Analysis of phenol in solution was performed using a Uv-spectrophotometer (Shimadzu 1208) at maximum absorption (275 nm). The amount of adsorbed phenol (mg/g) on grafted chitosan was calculated based on this equation.

$$q = (C_0 - C) \times V / m \qquad (1)$$

Where, q is the amount of adsorbed phenol (mg/g), C_0 and C are the initial and equilibrium phenol concentrations (mg/L), V is the volume (L) and m is the mass of adsorbent (g) [9]. Adsorption isotherms were done in the presence of 0.01g adsorbent at 298K, in a total volume of 20 mL, constant shaker speed (150 rpm), constant pH 3.0 and optimal time of 45 minutes. The results of the UV- spectroscopy were evaluated according to the isothermal models of Langmuir and Freundlich [10, 11]. Kinetics of adsorption were investigated at the fixed condition of the other variables (T = 298K, [phenol] = 50(mg/L), adsorbent = 0.01 g, pH= 3.0, solution volume = 20 mL, shaking rate = 0.0) at different times 5-30 minutes. Kinetics data were investigated by the using of Lagergren pseudo-first-order and Ho's pseudo-second-order [12, 13].

RESULTS AND DISCUSSION

Adsorption Isotherms and Kinetics

Experimental data were processed according to adsorption isotherms such as Langmuir and Freundlich. The Langmuir isotherm is based on the assumption that it exists on the surface of the adsorbent and each of these places has the validity and probability of the presence of one molecule. The Langmuir and Freundlich equations are given below:

$$C_e/q_e = C_e/q_m + 1/K_a.q_m \qquad (2)$$

In this equation, C_e (mg / L) is the equilibrium concentration, q_e (mg / g) is the amount adsorbed in equilibrium, q_m and K_a are the constants of Langmuir equations and determine the efficiency of the process.

$$\ln q_e = \ln K_f + 1/n . \ln C \qquad (3)$$

In the mentioned equation, K_f indicates the adsorption capacity and n determines the absorption intensity. As can be seen from Figs 1, 2 and Table -1, the

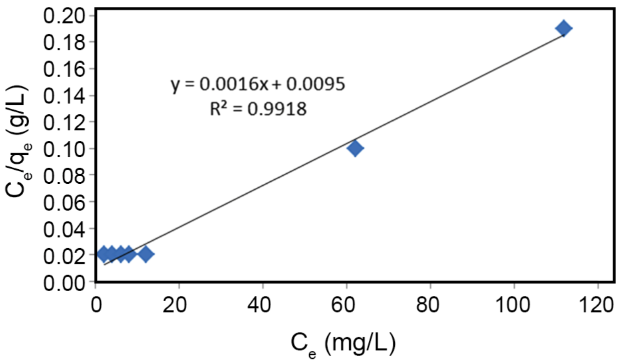


Fig. 1. Langmuir isotherm (T = 298 K)

Table 1. Adsorption Isotherm Constants

Langmuir constants	K_a (L / mg)	q_m (mg / g)	R^2
Phenol (298K)	0.637	712.285	0.9989
Freundlich constants	K_f (mg / g)	n (L / mg)	R^2
Phenol (298K)	129.606	2.247	0.9520

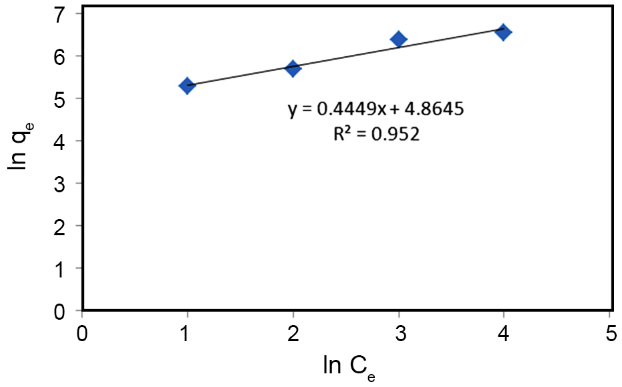


Fig. 2. Freundlich isotherm (T = 298 K).

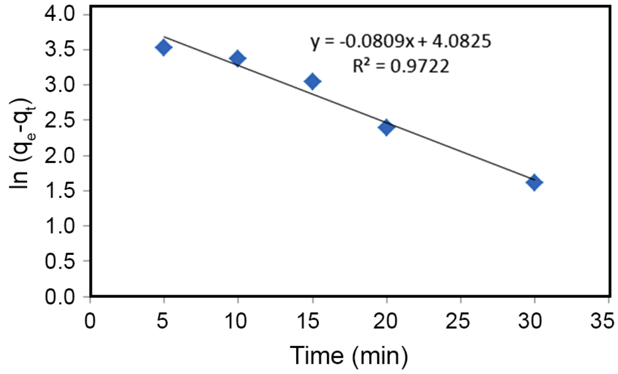


Fig. 3. Pseudo-first order kinetics.

best isotherm to justify the adsorption of adsorbate is the Langmuir isotherm. The correlation coefficient is higher than $R^2 = 0.99$. This fact indicates the homogeneity of the adsorption process on the adsorbent surface [8].

Investigation of the adsorption kinetics based on two famous and important pseudo-first-order kinetics and pseudo-second-order kinetics models were accomplished. Constant conditions in the experiments: 0.01 g of adsorbent, total volume 20 mL, concentration of adsorbate 50 mg/L, shaker speed zero, pH 3.0 were carried out from 5 to 30 min.

$$\text{pseudo}-\text{first}-\text{order} \qquad \ln(q_e - q_t) = \ln q_e - K_1.t \qquad (4)$$

$$\text{pseudo}-\text{sec ond}-\text{order} \qquad t/q_t = 1/k_2.q_e^2 + t/q_e \qquad (5)$$

Where q_e and q_t denote the amounts of metal adsorbed (mg/g) at equilibrium and at time t(min), K_1(1/min) and K_2(g/mg.min) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively. As shown in Figs. 3, 4 and Table-2, due to the compatibility of the results with the pseudo-second-order kinetic model, in addition to physical adsorption, chemical adsorption was also performed [8].

Thermodynamic parameters

To determine the nature of the adsorption reaction, thermodynamic parameters such as Gibbs free energy

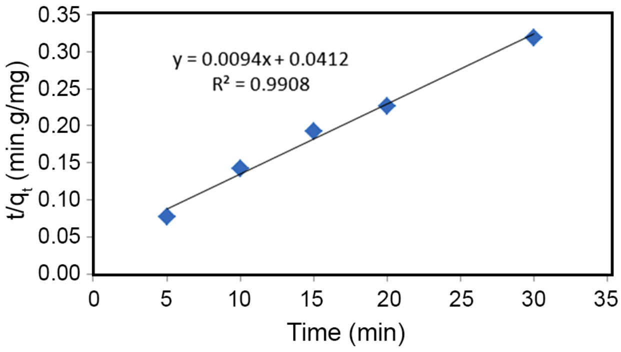


Fig. 4. Pseudo-second order kinetics.

Table 2. Adsorption Kinetic Parameters

Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
q_e(mg/g)	K_1(1/min)	R^2	q_e(mg/g)	K_2(g/mg.min)	R^2
59.293	0.081	0.9722	106.383	0.002	0.9908

Table 3. Thermodynamic Parameters at Different Temperatures

T (K)	ΔH° (kJ / mol)	ΔS° (kJ/mol .K)	ΔG° (kJ/mol)
298	3.661	15.289	-9.590
303			-10.127
308			-11.170

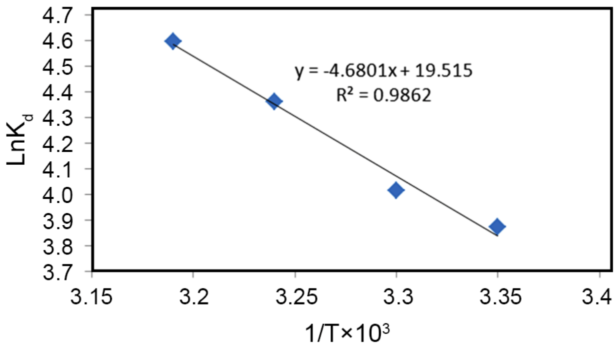


Fig. 5. The Van't Hoff plot for thermodynamic parameters.

change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated. These parameters were investigated with the following equations:

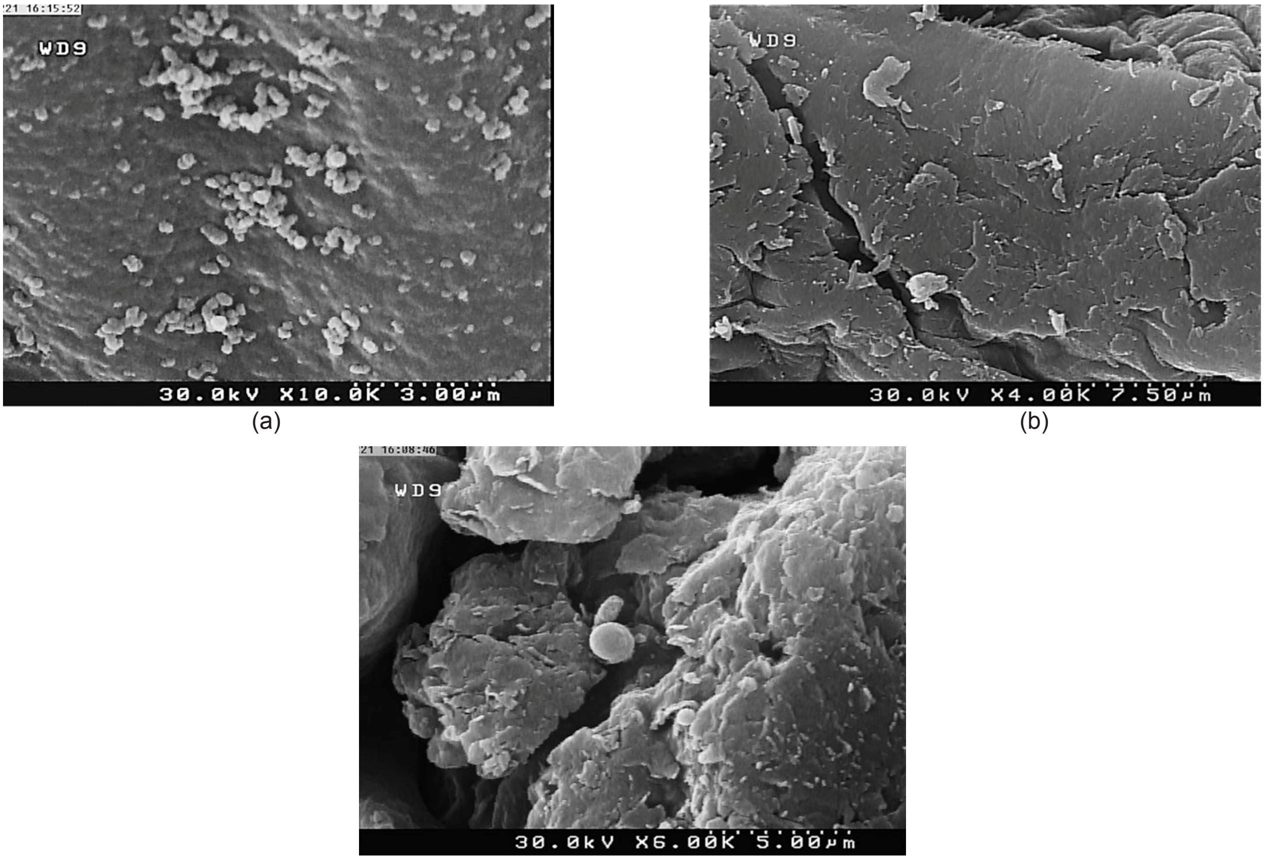
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

$$\Delta G^\circ = -RT\ln K_d \tag{7}$$

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \tag{8}$$

$$K_d = q_e / C_e \tag{9}$$

In these equations, K_d is the equilibrium constant, T is the temperature (K), R is the gas constant. ΔH° and ΔS° are the change of enthalpy and entropy and by the help of Van't Hoff plots were determined. Results presented in Fig. 5 and Table-3. According to the obtained results, the adsorption process is endothermic



(a)

(b)

(c)

Fig. 6a, b, c. SEM micrograph of (a) chitosan (b) grafted chitosan (c) grafted chitosan after adsorption.

and spontaneous and due to the positive entropy, confirms the appropriate interaction of adsorbent and adsorbate. SEM images clearly confirm the grafting and the adsorption of phenol. As can be seen, the chitosan surface is smooth and dense. But the surface of grafted chitosan is uneven and porous, and after adsorbing phenol, the unevenness and porosity have increased (Fig. 6 a, b, c).

CONCLUSION

In this research, chitosan copolymer with MAm-IA was successfully synthesized. Consistency with the Langmuir isotherm model and the pseudo-second-order kinetic model showed that the adsorption process of adsorbate is homogeneous, monolayer and chemical. The results of enthalpy and Gibbs free energy confirmed the endothermic and spontaneity of the adsorption process. In addition, in order to increase the entropy, the proper interaction between the adsorbent and the adsorbate was confirmed. SEM images confirmed the grafting and adsorption process.

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