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Adsorption of Toxic Indigo Carmen Dyestuff from Aqueous Solution by Chitosan and Chitosan Phthalate

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ABSTRACT

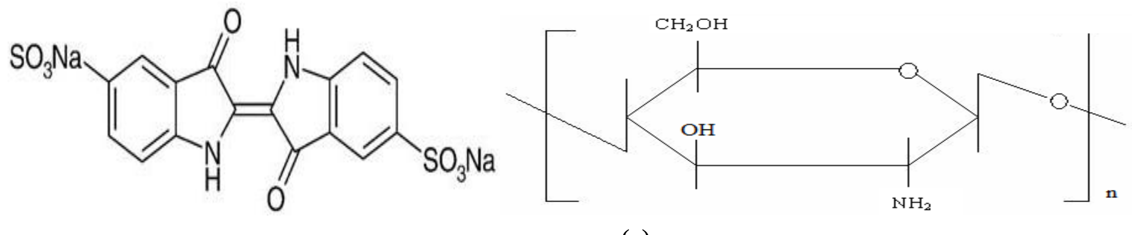
Toxic indigo carmen dyestuff was removed from the aqueous solution by adsorption. Adsorption was examined kinetically and thermodynamically based on temperature. Derivative of chitosan which is called chitosan phthalate was synthesized and used in removal of indigo carmen from aqueous solution. Some kinetic and thermodynamic parameters were calculated. Adsorption isotherms were drawn. Lastly, the adsorption of indigo carmen from the aqueous solution by chitosan and chitosan phthalate were compared.

Keywords: Adsorption; Indigo carmen; Dyestuff; Chitosan

1. Introduction

Dyestuffs are organic compounds that are used to color objects. Synthetic dyestuffs have a complex aromatic structure containing units such as benzene, toluene, xylene and anthracene. This complex aromatic structure allows the dyestuffs to be highly stable and resistant to biochemical degradation[1]. The use of synthetic dyes in textile, leather, rubber, food, paper, plastic, pharmaceutical and cosmetic industries is increasing day by day. Dyestuffs which are left in water after being used in industrial processes leave some deleterious effects on human and aquatic life. Many of these harmful dyestuffs are toxic and carcinogenic[2]. Many physical, chemical and biological decolorization methods have been developed to remove dyestuffs that are highly resistant to heat, light and oxidizing agents from waste water. These are chemical precipitation, reverse osmosis, membrane filtration, ozonation, oxidation, ion exchange, irradiation and adsorption. Among these methods, the process which gives the best result is the adsorption technique. Besides, it is known as a low-cost technique[3-6].

Chitosan is a deactylated derivative of chitin. It is the most commonly found polysaccharide in nature after cellulose. Chitosan can be obtained from the shell of shrimps, mushrooms, crabs and insects[7]. Chitosan which is a natural biosorbent, is a good adsorbent for removing harmful dyestuffs in industrial wastewater. It is non-toxic and low cost[8]. As it contains both amino and hydroxyl groups, chitosan can easily be modified[9,10]. This study analyzes kinetic and thermodynamic properties of the adsorption of toxic indigo carmen (IC) dyestuff from aqueous solution by chitosan and its synthesized derivative chitosan phthalate.



(a)

(b)

Figure 1. Molecular structure of chitosan and indigo carmine

2. Experimental Studies

2.1 Adsorption Kinetics

Adsorbate- adsorbent equilibrium contact time is found by understanding adsorption kinetics. For determining this

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contact time, 0,1 gram of chitosan/chitosan phthalate were added to 50 ml of indigo carmine (IC) solutions whose initial concentrations are 200 ppm. This mixture was shaken for 12 hours at 293 K. During this time, samples were taken from each solution at different time intervals and absorbance values were determined with UV- spectrophotometer. This process was repeated at 313 and 333 K.

The data obtained from kinetical experiments were applied to the following equations: The Lagergren (equ.1)[11], the Arrhenius (equ.2)[12] and the intrapartical diffusion (Equ. 3,4)[13] rate equations.

$$\log(q_e - q) = \log q_e - \frac{k_{ads,1}}{,303}.t \qquad (1)$$

$$\log k_{ads,1} = \log Z_e \quad \frac{E_a}{2,303RT} \, x \, \frac{}{T} \qquad (2)$$

$$q = k_p . t^{1/2} \qquad (3)$$

$$\frac{t}{q} = \frac{1}{k_{ads,2} \, q_e^2} + \frac{t}{q_e} \qquad (4)$$

2.2 Preparation of Chitosan Phthalate

1 g chitosan (6,2 mmol) was dissolved in the acetic acid solution (% 1, 100 ml). Then, a solution of the phthalic anhydride (6.25 mmol) in pyridine (5 mL) was added dropwise to the mixture with vigorous stirring. pH of reaction was calibrated at 7.0 by the dropwise addition of NaOH solution (1.0 M). After 40 minutes, the reaction was terminated by the addition of NaCl aqueous solution (%20, 200 mL). The resulting precipitate was filtered, washed with acetone and diethyl ether, and desiccated to give chitosan phthalate conjugates[14].

2.3 Adsorption Thermodynamics

After kinetical study, the equilibrium contact time of adsorption was determined. Then 50 ml of IC solutions at different initial concentrations were prepared and 0,1 g of chitosan/chitosan phthalate was added to each solutions. This mixture was shaken during the equilibrium contact time at 293, 313 and 333 K. After shaking, absorbance values of solutions remaining from adsorption (C_e) were measured and the amount of IC which is adsorbed (q_e) was calculated. Then, the adsorption isotherms were drawn. Adsorption isotherm of chitosan and IC was suitable with Langmuir İsotherm. The adsorption isotherm of chitosan phthalate and IC was suitable with H-type isotherm according to isotherm classification made by Giles. Langmuir constants C_m (connected with adsorption capacity) and b (connected with adsorption energy) were calculated for the adsorption of chitosan and IC. b constants values were applied to the following equations:

$$\log b = \log A \quad \frac{\Delta H}{2,303R} \frac{1}{T} \qquad (5)$$

$$\Delta G = -RT \ln b \qquad (6)$$

$$\Delta G = \Delta H - T.\Delta S \qquad (7)$$

3. Results

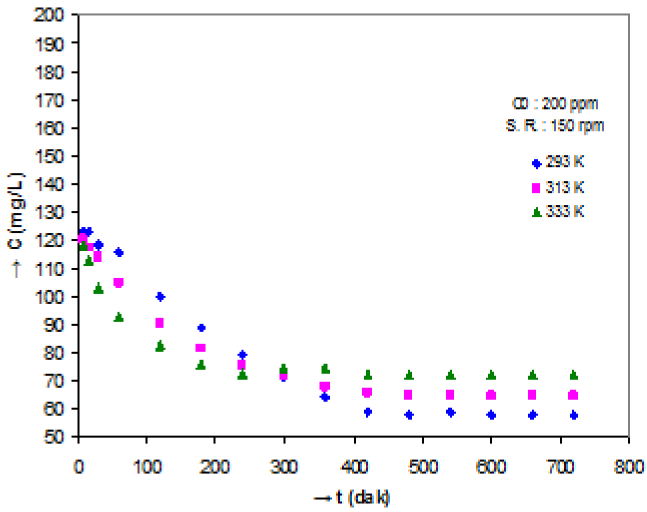
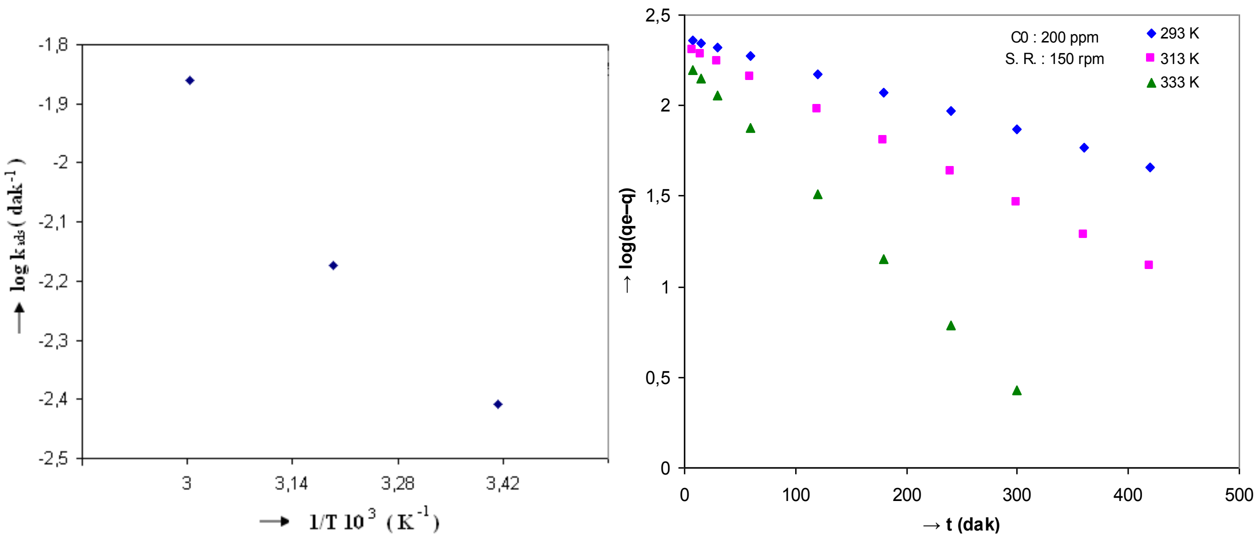


Figure 2. The effect of contact time on the adsorption of chitosan and IC.

According to **Figure 2**, chitosan adsorbed more IC at 293 K. and, as the equilibrium contact time of adsorption is shorter, we can say that IC was adsorbed faster at 333 K. by chitosan. Therefore, a chemical adsorption occurs between chitosan and IC at high temperatures.

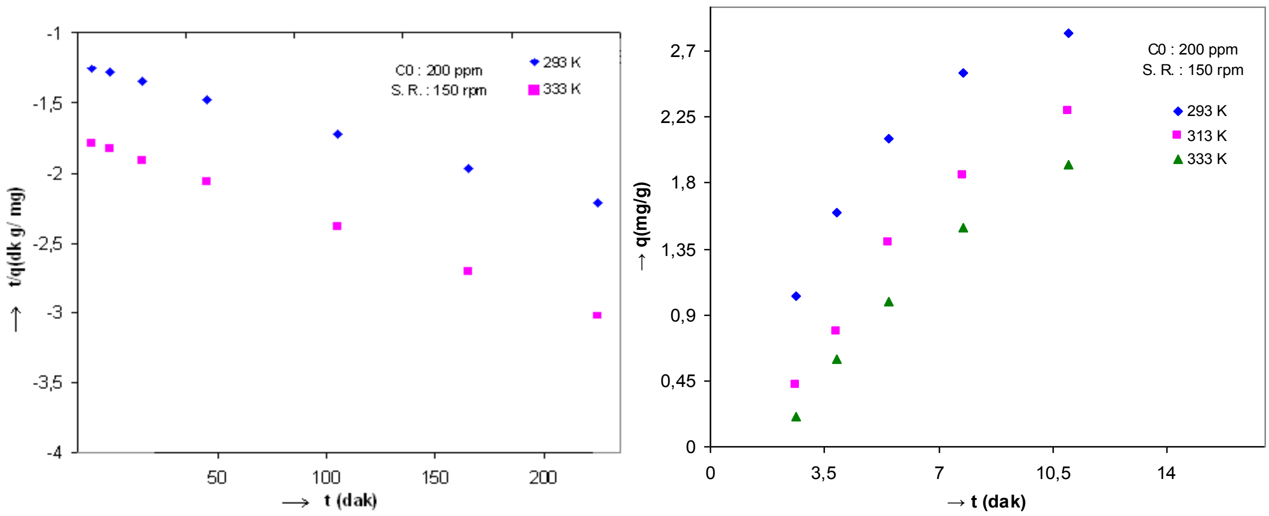


(a)

(b)

Figure 3. Lagergren (a) and Arrhenius (b) drawings of adsorption of chitosan and IC.

Adsorption rate constants k_{ads} were calculated from Lagergren drawings. q_e (mmol/L); is the amount of adsorbate adsorbed at equilibrium time and q (mmol/L); is the amount of adsorbate adsorbed at any time. k_{ads} values were determined as 0,0037; 0,0063 and 0,0135 (min^{-1}) at 293, 313 and 333 K respectively. This k_{ads} values were evaluated at Arrhenius equation and activation energy of adsorption was calculated as 25, 628 kJ/mol. k_{ads} values also show chitosan adsorbed more IC at high temperature.



(a)

(b)

Figure 4. Weber-Morris (a) and Ho-Mckay (b) drawings of adsorption of chitosan and IC.

The data obtained from experiments were also applied to the Weber- Morris and Ho-Mckay equations and intraparticle rate constants (k_p) were calculated. k_p values are 3,93; 4,02; 4,54 ($min^{-1/2}$) at 293, 313 and 333 K respectively.

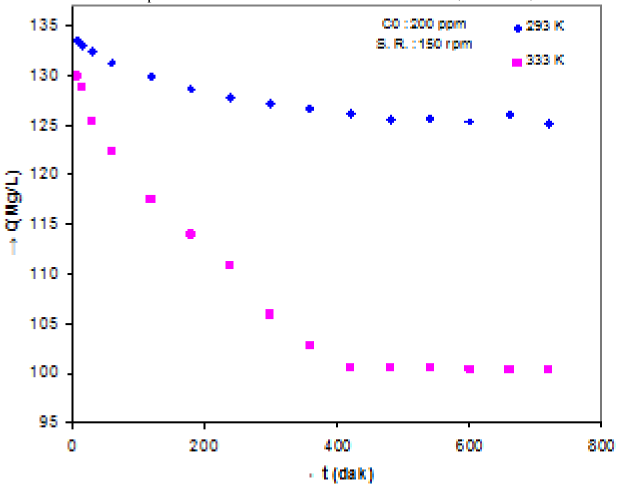
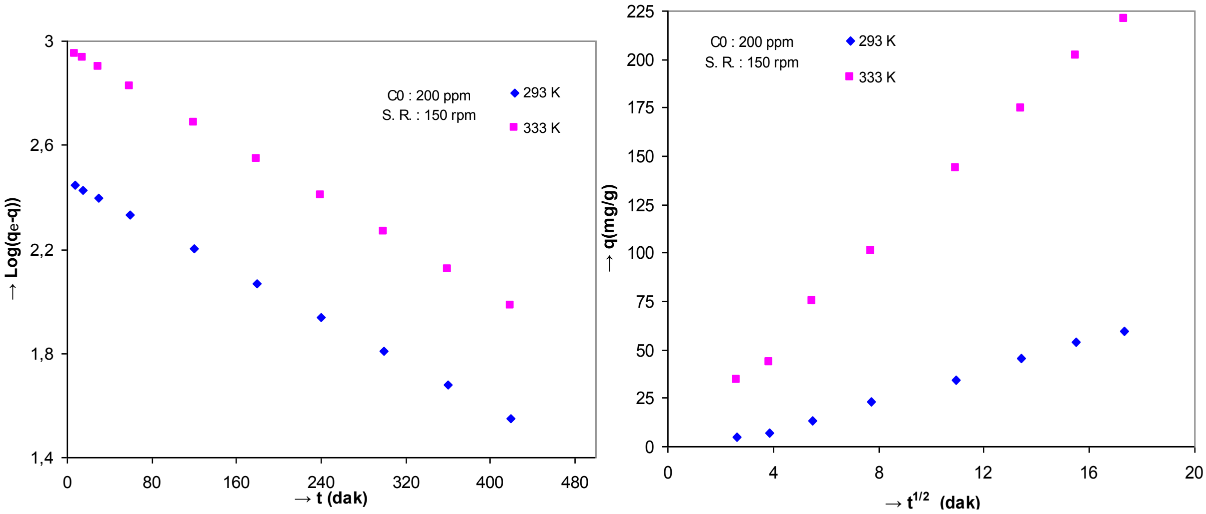


Figure 5. The effect of contact time on the adsorption of chitosan phthalate and IC.

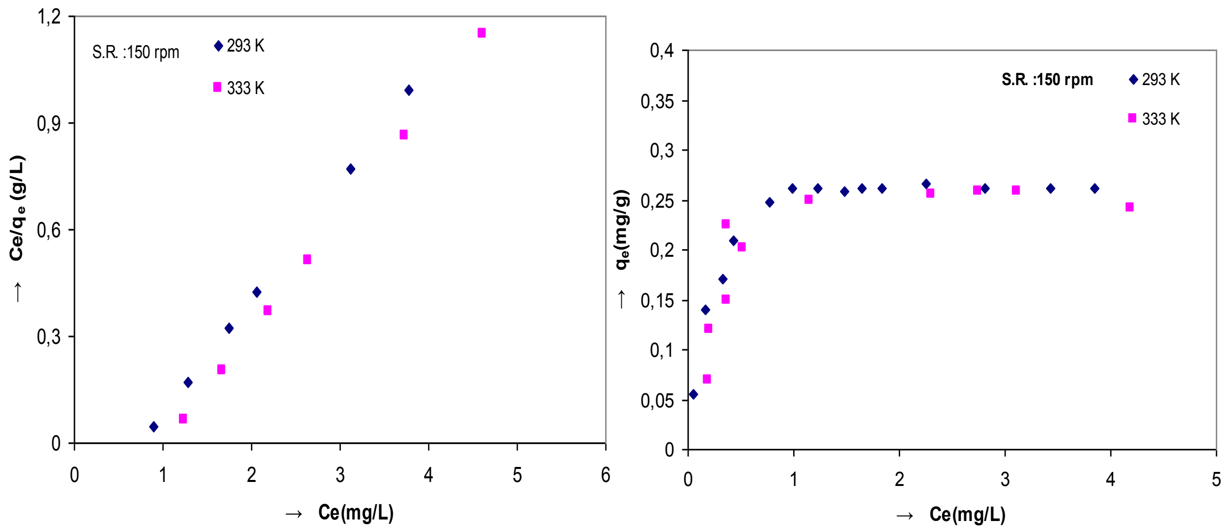
Figure 5 shows that chitosan phthalate adsorbed more IC at 333 K. Chitosan phthalate has amino groups and IC has $–SO_3$ groups. Amino groups have a positive charge in the IC solution. There is strong chemical adsorption between these amino groups and $–SO_3$ groups. So, we can say that the adsorption between chitosan phthalate and IC is chemical adsorption. For this reason, chitosan phthalate adsorbed more IC at higher temperature.



(a)
(b)

Figure 6. Lagergren (a) and Weber- Morris (b) drawings of adsorption of chitosan phthalate and IC.

Adsorption rate constants k_{ads} were calculated from Lagergren drawings and intraparticle diffusion rate constants were calculated according to Weber- Morris drawings. k_{ads} values are 0, 0049 and 0, 0053 min^{-1} at 293 and 333 K respectively. k_p values are 3, 9824 and 13, 1233 $min^{-1/2}$ at 293 and 333 K respectively.



(a)
(b)

Figure 7. The Langmuir isotherm (a) and the Langmuir linear isotherm (b) of adsorption of chitosan and IC.

Experimental data which are related with the adsorption of chitosan and IC were applied to the following Langmuir linear isotherm equation:

$$C_a = {}_m\frac{bC_e}{1+bC_e}, \quad \frac{C_e}{C_a} = \frac{1}{C_m.b} \quad \frac{}{C_m} \qquad (8)$$

and the Langmuir constants (C_m and b) were calculated.

293 K		333 K	
C_m(mgg^{-})	b(L.mg^{-})	C_m(mgg^{-})	b(L.mg^{-})
0,3295	3,9620	0,3215	2,9942

Table 1. The Langmuir constants of the adsorption of chitosan and IC.

293 K			333 K		
ΔH (J.mol^{-1})	ΔG (J.mol^{-1})	ΔS (J.mol^{-1}K^{-1})	ΔH (J.mol^{-1})	ΔG (J.mol^{-1})	ΔS (J.mol^{-1}K^{-1})
-5680,8	-3353,8	-7,9421	-5680,8	-3036,2	-7,9417

Table 2. Thermodynamic parameters of the adsorption of chitosan and IC.

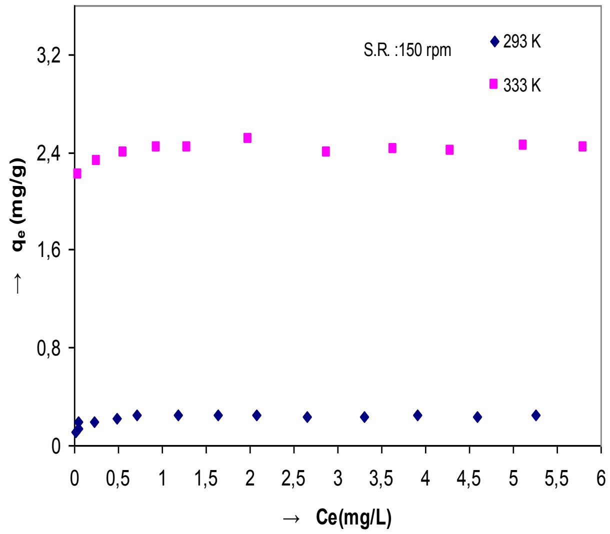


Figure 8. The isotherm of the adsorption of chitosan phthalate and IC.

According to **Figure 8**, the initial points of isotherms at both temperatures are on the ordinate. This situation is the indicator of strong chemical adsorption between IC and chitosan phthalate. As it is known, this kind of isotherm is called H-type isotherm according to isotherm classification made by Giles[15].

4. Conclusions

Chitosan adsorbed more IC at low temperature but chitosan phthalate adsorbed more IC at high temperature because of chemical adsorption. Chitosan phthalate removes IC more than chitosan. So, modifying chitosan with phthalate is advantageous.

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