RESEARCH ARTICLE

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Equilibrium and Kinetic Studies on the Adsorption of Acid Yellow 36 Dye by Pinecone

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Background & Aims of the Study: Dyes have significant role in environmental problems, due to their toxic effects on the food chain and sources of water. The purpose of this research was to study the adsorption of acid yellow 36 dye onto pinecone using batch system.

Materials & Methods: This research was performed at laboratory scale and batch system. Equilibrium isotherms were modeled using Langmuir, Freundlich, and D-R models. Also kinetic studies were done by three models of pseudo first order, pseudo second order, and intra-particle diffusion.

Results: The maximum adsorption was achieved at pH 5.0, adsorbent dose 0.7 g/l and contact time 20 min. The equilibrium adsorption capacity (mg/g) increased with increasing initial dye concentration. The Langmuir model (R^2=0.99) provided the best fit for the experimental data. The adsorption kinetics were studied and best fit was achieved by pseudo- second order model (R^2= 0.96).

Conclusions: According to the results obtained of equilibrium and kinetic studies on the adsorption of acid yellow 36, pinecone can be a suitable and efficient adsorbent in the removal of yellow acid 36 dye from industrial wastewater.

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Background

The azo dyes are widely used in dyeing paper and pulp, textiles, plastics, leather, cosmetics and food industries and textile industrial. The azo dyes are potential pollutants that not only represent an important environmental problem, but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. These colored compounds effects on the environment and presence in surface waters and effluent of sewage treatment plants and usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (1). The dyes cause allergy, dermatitis, skin irritation, cancer and mutations in humans. They are released into the environment and surface water by different industries and because of their low biodegradability, a conventional biological treatment process is not very effective in treating a dye wastewater (2,3). Therefore, a pretreatment process is often required prior to discharge into the biological treatment process

(4). Figure 1 shows molecular structure of acid yellow 36 dye.

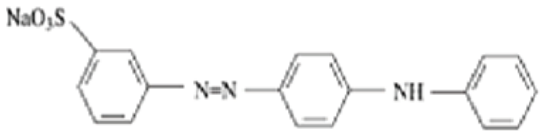


Figure 1) Structural formula of acid yellow 36

Conventional treatment techniques such as (chemical coagulation, activated sludge and carbon adsorption) are largely ineffective and costly for removing organic contaminants. Also biological treatment processes have no effect on the amount of the medicine (because of the toxicity of dye for microbes), and coagulation generates chemical sludge and doesn't remove acid and reactive dyes of low molecular weight, activated carbon cannot adsorb dispersed and pigmented dyes, and has the disadvantage of higher costs and regeneration problems. As a result, it is essential that processes be used that can reduce the amount of dye in the wastewater. One of the new technologies used in the treatment of water supplies and industrial sewage containing toxic material is sorption. Azo dyes are usually treated by physical, chemical and process that among the physico-chemical processes, adsorption technology is one of the methods useful in the removal of dyes, having potential application in both water and wastewater (5). The adsorption process is economical, easily available, highly effective and established to remove organic compounds from wastewater (6-8). Adsorbent of prepared from agricultural wastes has a porous structure consisting of a network of interconnected macropores, mesopores, and micropores that create a satisfactory capacity for the adsorption of organic compounds form aqueous solutions. Mechanisms responsible for the adsorption of organic compounds by adsorbent include electrostatic forces, ion change, dipole-dipole interactions, covalent bonding and water bridging. Pinecone is a suitable tree for decorative planting in park and is used usually as a decorative plant national park, therefore pinecone may be abundantly available and having a porous structure can be created a satisfactory capacity for the adsorption of organic compounds form aqueous solutions and can contribute to the amelioration of serious environmental problems. Mechanisms responsible for the adsorption of organic compounds by adsorbent include electrostatic forces, ion change, dipole-dipole interactions, covalent bonding and water bridging (9). The many researchers have been used pinecone adsorption for removal of dye from wastewater. Argun et al (2008) used to activation of pine cone using Fenton oxidation for Cd(II) and Pb(II) removal(10). Mahmoodi et al (2011) used to pinecone for adsorption of textile dyes from colored wastewater (11).

Aims of the study: In this work pretreated pinecone with sulfuric acid as a low-cost adsorbent was used to act as the adsorbent in the removal of acid yellow 36 from wastewater. The purpose of this research was to study the adsorption of acid yellow 36 dye onto pinecone adsorption using batch system.

Materials & Methods

Pinecone was collected from a local park and was washed several times with distilled water. To further remove any remaining impurities, pinecone was mixed with sulfuric acid heated in an oven for 24 h at 150°C. The heated material was washed with distilled water and dried in the air. To remove residual acid, materials were soaked in a 1% sodium bicarbonate solution and were dried in an oven (105°C for a period of 24h). Then ground to a fine powder and powder of -80 to +230 sizes was used for the study. The acid yellow 36 (Formula: $AY_{36}C_{18}H_{14}N_3NaO_3S$) was purchasedfrom the Alvan Sabet company. Sulfuric acid (96%) and NaOH (98%) (In order

To pH adjustment), were purchased from the Merck Company. To determine pH_{zpc} (zero point of charge), 50ml of potassium nitrate (0.01M) solution was added to Erlenmeyer flasks, and initial solution pH was adjusted (range 2 to 12). Then 0.2 g of the adsorbent was added and mixed for 24h and the final pH of solutions was measured. The intersection point of curves was recorded as pH_{zpc}. The experiments were carried out in the Jar test device containing a definite volume (100 ml of the solution was poured in each glass beaker) at 200 rpm. Stock solution (1000 mg/l) was produced by dissolving 0.1 g dye in 1000 ml distilled water and the desired concentrations of dye were obtained by diluting the stock solution. To determine the optimum pH of solution, the pH was changed within a range of 3-10 and the optimum pH was determined (The flasks were agitated by the shaker at 200 rpm for 72h (the time required for equilibrium). To evaluate the isotherm models, 0.1g pinecone was added to Erlenmeyer flasks and was stirred in 100 ml of different concentrations of the solution (20-200 mg/l) at a pH of 5 for 72 h. The kinetics of adsorption was investigated by shaking 0.1 g chestnut shell in different concentrations of dye at a pH of 3 and varying contact times (2-20min).The residual concentrations of dye were collected from Erlenmeyer flasks and were filtered to remove solid material. The residual concentrations of dye were determined via a colorimetric method according to standard method (12).The absorbance of the color was read at 435 nm.

Data analysis: One-way analysis of variance (ANOVA) test used for evaluate significant differences among mean values. In all tests, the selected significance level at which the differences between critical values were evaluated was 5%.

Results

In the adsorption process, the pH has a significant role in dye removal since the adsorption process occurs within a specific range of pH (due to its influence on the surface properties of the adsorbent, surface charge of the adsorbent and ionization/dissociation of the adsorbate molecule). To survey of effects of pH on dye removal, the solution pH was altered from 3-10 at an dye concentration of 10 mg l^{-1} and an adsorbent dosage of 0.1g of pinecone per 100 ml of solution. As shown in Fig. 2, the maximum dye removal rate was achieved at pH 5.0.

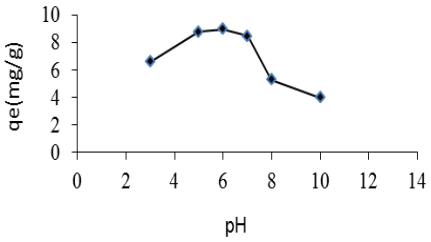


Figure 2) Effect of solution pH on the adsorption of dye onto the pinecone (C_0=10mg/l, adsorbent dose =1g/l, t= 72 hour and T=25±1)

Adsorption isotherm models such as the Langmuir, Freundlich and D-R, can describe distribution of adsorbate dye molecule between the liquid phase and the solid phase (13).The linear forms of the adsorption isotherms of Langmuir, Freundlich and D-R isotherm equations are stated as E_{qs}. 1-3:

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

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (2)$$

$$\ln q_{e=} \ln Q_{s-} B\varepsilon^2 \qquad (3)$$

In these equations, q_e is the amount of dye adsorbed per unit of adsorbent mass (mg g^{-1}) C_e is concentration of adsorbate at

Equilibrium in the solution (mgl^{-1}), q_m is the amount of maximum adsorption capacity ($mg\ g^{-1}$), and b is the Langmuir constant ($l\ mg^{-1}$) that is related to the energy of adsorption. K_f (indicative of the relative adsorption capacity of the adsorbent) and 1/n (for a favorable adsorption n should have values lying in the range of 1 to 10) are the Freundlich constants (Khorramfar et al., 2009). Q_S is the maximum of adsorption capacity of the adsorbent ($mol\ g^{-1}$) B is a constant related to the average free energy of adsorption ($mol^2\ kj^{-2}$) and ε is the Polanyi potential ($J\ mol^{-1}$).

Table 1 shows the values of the isotherm constants and maximum adsorption capacities. The maximum uptake capacity of penicillin G on the chestnut shell was achieved 100 $mg\ g^{-1}$. The Langmuir model (R^2=0.99) provided the best fit for the experimental data.

Table 1) Isotherm parameters for dye adsorption onto the pinecone

Langmuir isotherm				Freundlich isotherm			D-R isotherm			
q_m ($mg\ g^{-1}$)	B ($L\ mg^{-1}$)	R_L	R^2	K_F $(mg/l)^{-n}$	n	R^2	Q_S ($mg\ g^{-1}$)	B ($mg^2\ Kj^{-1}$)	E ($Kj\ mg^{-1}$)	R^2
100	0.19	0.34	0.99	36.3	5.29	0.94	62.73	1×10^{-8}	7.09	0.77

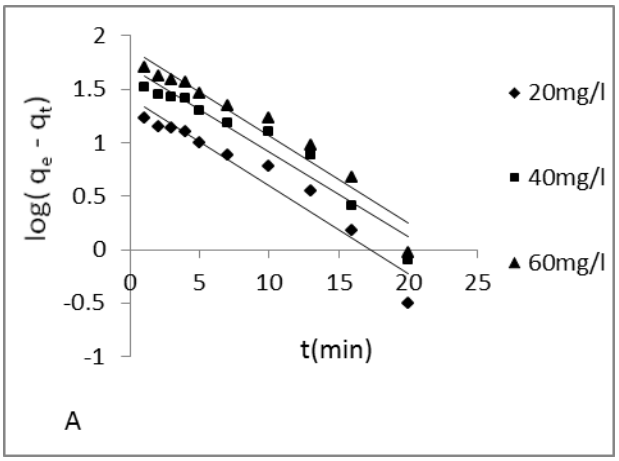
Also, the kinetics of adsorption was investigated using kinetic models such as the Pseudo-first order, Pseudo-second order and Elovich (14). The linear plots of the adsorption kinetics are shown in Fig. 3 (a-c). The values k_1, k_2, q_e, α and β can be calculated from the slopes and intercepts (Fig. 3 a-c). The constants and correlation coefficients of kinetic models are presented in Table 2. The adsorption kinetics were studied and best fit was achieved by pseudo- second order model (R^2= 0.96). The pseudo – first order, pseudo – second order, Elovich and kinetic are expressed as E_{qs}. (4-6).

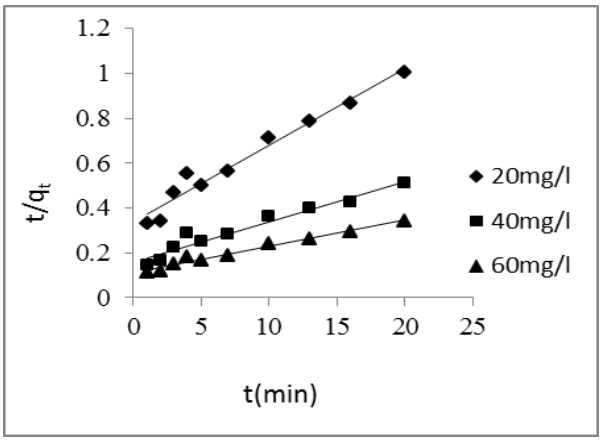
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \quad (6)$$

Where q_e (mg g-1) and q_t are the amounts of dye adsorbed at equilibrium and t (min), respectively. k_1 (min^{-1}) and K_2 ($g\ mg^{-1}\ min^{-1}$) are the rates constant in the pseudo – first order adsorption and the pseudo – second order adsorption respectively. The parameters of α (mg/ g.min) and β (g/ mg) are the rate of chemisorptions at zero coverage and the surface coverage and activation energy of chemisorptions respectively





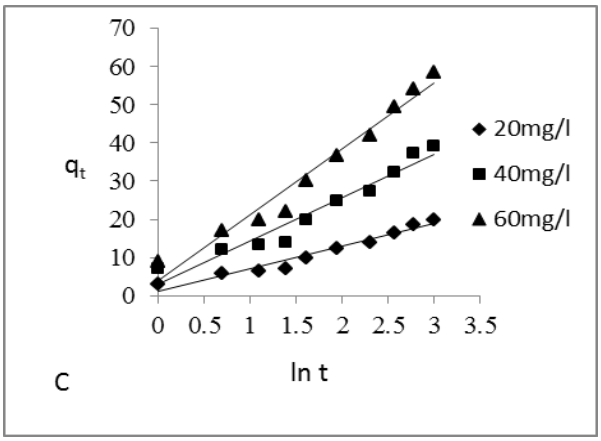


Figure 3) Pseudo-first order (A), Pseudo-second order (B), Elovich (C) kinetic models for the adsorption of PEN G onto chestnut shell

Table 2) Kinetic parameters for PEN G adsorption onto chestnut shell at different initial concentration

C_0mg/l)	Pseudo-first- order			Pseudo- second- order			Elovich		
	q_e(mg g^{-1})	k_1(min^{-1})	R^2	q_e(mg g^{-1})	k_2(g $mg^{-1}min^{-1}$)	R^2	α(mg g^{-1} min^{-1})	β(g mg^{-1})	R^2
20	25.7	0.18	0.934	29.41	0.0035	0.965	7.1	0.17	0.965
40	48.9	0.18	0.939	58.1	0.0017	0.948	16.1	0.08	0.944
60	74.1	0.18	0.938	90.1	0.0011	0.979	21.8	0.058	0.964

Discussion

The pH solution is an important parameter for removal of pollutants from water solutions. The optimum pH is related to pH_{zpc}.The pH_{zpc} has the significant effect on surface charge of adsorbent (at pH_{zpc}, surface charge is neutral at pH levels lower than pH_{zpc} surface charge is positive, while at pH levels higher than pH_{zpc} surface charge is negative). Optimum pH and pH_{zpc} of solution were 5 and 6.9 respectively. Therefore surface of the adsorbent having a positive surface charge is favorable to the adsorption of dye anions; because, in pH levels below 6.9, the anions of dye will be attracted to adsorbent surface and interact electrostatically with the positively charged surface of the adsorbent and can increase the process efficiency (7). In a previous on biosorption of

PEN G on Rhizopus arrhizus, the optimum pH level for biosorption was determined to be 6 (15).

The adsorption isotherms are very important to design the reaction systems and describe how the adsorbate molecules distribute between the liquid phase and the solid phase and this is an important step in finding a suitable model that can be used in the design of adsorption systems. They describe interaction between adsorbent and pollutant and are therefore critical in optimizing the use of sorbent material (16).For the Langmuir isotherm a dimensionless separation factor (R_L) can be presente according to Eq. (7)

$$R_L = \frac{1}{(1 + bC_o)} \quad (7)$$

The amount of R_L was determined 0.34, therefore according to Table 3; adsorption of dye on pinecone is favorable.

Table3) Langmuir isotherm dimensionless separation factor parameter (R_L)

Type of isotherm	R_L value
Unfavorable	$R_L>1$
Linear	$R_L=1$
Irreversible	$R_L=0$
Favorable	$0<R_L<1$

The average free energy of adsorption (E) can be written as:

$$E = \frac{1}{\sqrt{-2b}} \quad (8)$$

The amount of E is used to determine the mechanism of the adsorption process (if amount of E(k_J mol^{-1}) be less than 8, adsorption mechanism is physical and if E be 8 and 16 mechanism is chemical). The value of E was determined 7.09 k_J mol^{-1}, therefore the adsorption of dye onto the pinecone occurs through a physical mechanism. The maximum uptake capacity of dye on the pinecone was found to be 100 mg g^{-1}. Aksu and Tunc (2005) obtained a maximum uptake capacity of 330 mg PEN G per gram of activated sludge. The Langmuir model (R^2=0.99) provided the best fit for the experimental data (15).This may be due to saturated monolayer of solute molecules on the adsorbent surface and that the energy of adsorption is constant (16).The adsorption kinetics were studied and the pseudo-second order model best described the sorption of dye on pinecone (R^2 = 0.96). The pseudo-second order model considers a chemical adsorption involving sharing or exchange of electrons between the sorbent and the sorbate (17,18). Mullai and Vishali (2007), showed that in biodegradation of PEN G wastewater using Phanerochate chrysosporium, experimental kinetic data followed the first order rate expression (19).The obtained results observed, favorable adsorption site for Acid yellow 36 dye on the surface of pinecone adsorption. Also results improve the knowledge of Acid yellow 36 dye removal by pinecone and demonstrate that pinecone can be a suitable, low cost and efficient adsorbent in the removal of yellow acid 36 dye from industrial wastewater. Table 4 shows comparison between different dyes removal by pinecone adsorption.

Table 4) the sorption of different dyes by pinecone adsorbent

Dye	q_m (mg/g)	pH	Time (min)	adsorbent	Ref.
Direct blue 2B	327.9	2	120	Pinecone	(12)
Methylen blue	19.41	10	60	Pinecone	(16)
Acid blue 25	76.9	2.5-4.2	60	Pinecone	(9)
Acid yellow 36	100	5	20	Pinecone	This study

Footnotes

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Conflict of Interest:

The authors declare no conflict of interest

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