Journal of Chemical Health Risks 2(1); 7-14 2012

Removal of Blue 56 by Orange Peel from the Waste Water

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Abstract: The use of orange peel as low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. This paper concerns with the removal of Blue 56 from aqueous solutions by orange peel. The effects of pH, initial concentration, adsorbent dosage, and particle size of adsorbent, temperature and also isotherm data analysis and adsorption kinetics were investigated. A maximum removal of 96.76% was obtained at pH 2.5 for an adsorbent dose of 0.2 mg. Rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation (R^2=0.99). The maximum adsorption capacity obtained from Langmuir equation was 9.69 (mgg^{-1}).

Keywords: Orange peel; Adsorption; Low-cost adsorbent; Dye; Blue 56

INTRODUCTION

Dyes are used in order to color products in many industries such as food, paper, carpet, rubber, plastics, cosmetics, and textile (Robinson *et al.* 2002; Ramakrishna *et al.* 1997; Nigam *et al.* 2000). The discharge of colored wastewater from these industries into natural streams has caused many significant problems, such as increasing the COD (chemical oxygen demand) of the effluent, and also reducing the light penetration which has a derogatory effect on photosynthetic phenomenon. From the aesthetic point of view, the presence of dyes, in particular carcinogenic compounds, in surface and underground waters is not safe, pleasant, or welcomed. So the removal of color from waste effluents is environmentally important (Sanghi *et al.* 2002, Malik 2003)The USEPA (Environmental Protection Agency) has classified textile wastes into four groups, dispersible, hard-to-treat, high-volume, and hazardous and toxic wastes (Tsui *et al.* 2003). Many physicochemical methods have been tested but only that of adsorption is considered to be superior to other techniques. This contributed to low cost, easy availability, simplicity of design, high efficiency, ease of operation, biodegradable of natural adsorbents [Sanghi *et al.* 2002, Meshko *et al.* 2001, McKay and Chem, 1982) many researchers have investigated low-cost, biodegradable substitutes made from natural resources to remove organic contaminants such as dyes from wastewater. Adsorbents used include agricultural solid wastes such as coir pith (Namasivayam and Kadirvelu 1994), banana pith (Namasivayam *et al.* 1997), coconuthusk (Low 1990), sawdust (Asfour *et al.* 1985), biogas residual slurry(Namasivayam and Yamuna 1994), peatmoss and rice hulls (Nawar and Doma 1989), bagasse and paddy straw (Deo and Ali 1993), and industrial solid wastes such as fly ash and coal (Gupta *et al.* 1990), red mud (Namasivayam.,1997) and Fe/Cr (III) hydroxide Namasivayam *et al.*1994). In this study, orange peel was used as an adsorbent to remove blue 56 from aqueous solution.

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MATERIALS AND METHODS

Chemicals and materials

Waste orange peel was obtained from a fruit stall, and changed into small pieces. The peels were first washed to remove the adhering dirt and then were dried, crushed, and sieved. They were dried at room temperature (25°C) for 36 h. After drying sieved and powdered, the powdered orange peel was sieved for particles of 40, 60 and 100 mesh sizes and used as an adsorbent. The dye which was used in this study was Blue56 .The dyes with Molecular nFormola$C_{40}H_{35}N_3O_3S$, Molecular weight 637.7892 [g/mol], and λmax=603(nm) were purchased from Isfahan loom company. Chemical structures of these dyes were showed in Fig. 2. Other chemicals were Analar grade from Merck. The pH of the solutions was adjusted by adding proper amounts of 0.1 M HCL and 0.1M NaOH. UV–VIS spectrophotometer model-160A SHIMADZU was used to measurement of absorption aqueous solutions.

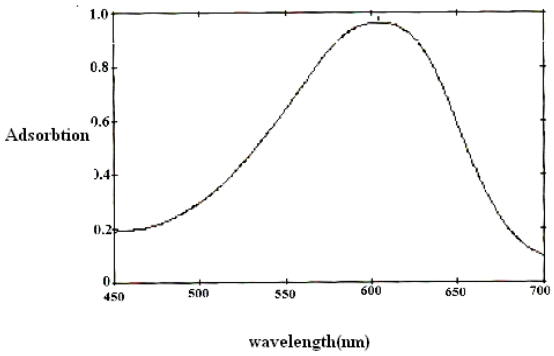

Fig.1: spectrum of BLUE 56

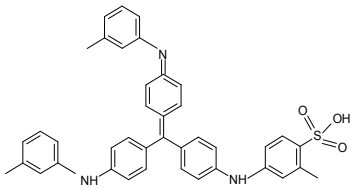

Fig. 2. Chemical structure of Blue 56. Chemical name of BLUE 56dye:2-Methyl-4-((4-((4-((3-tolyl) amino) phenyl)(4-(3-tolylimino)2,5-cyclohexadien-1-ylidene) methyl) phenyl) amino) benzenesulphonic acid.

Adsorption procedure

An aliquot of dye solution was passed through a mini column containing powdered orange peel (mesh=100). The absorbance of Blue 56 was measured spectrophotometrically at λmax (603 nm) before and after passing of Blue 56 through the column. The used column was a funnel with following dimensions; inside diameter=7mm, height =5-6cm. Finally, per cent removal of Blue 56 (R%) was calculated using the equation (2.1)

$$(R\%) = \frac{(A_0 - A)\times 100}{A_0} \qquad 2.1$$

Where, A_o is the initial absorbance and A is the final absorbance.

RESULTS AND DISCUSSIONS

The effect of pH

The effect of pH was studied by varying the initial pH of dye solution and keeping the other process parameters as constant. Experiments were carried out at different pH (PH 2-10) for different dye concentration (60,70,80 mg/l) and constant orange peel dosage of 0.2 g. The effect of pH on the adsorption of Blue 56 dye by orange peel is shown in Fig. 3. The maximum dye adsorption obtained 96.76% at pH 2.5 orange peel is composed of various functional groups, such as amino and carboxyl, which could also be affected by the pH of solutions. Therefore, the electrostatic attraction, as well as the organic properties and structure of dye molecules and orange peel, could play a very important role in dye adsorption on orange peel. Electrostatic attraction exists between the positively charged surface of the adsorbent and the anionic dye.

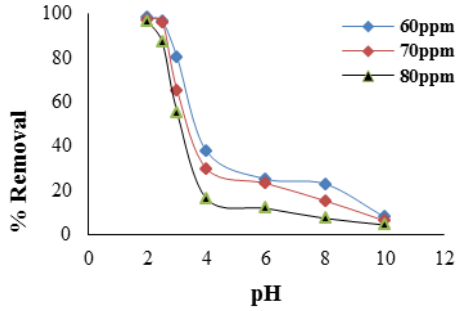

Fig. 3. Effect of pH dye concentration (60, 70, 80) mg/l, mesh=60, adsorbent dosage=0.2gr

The effect of initial concentration of dye

The effect of dye concentration was studied by keeping the adsorbent dose constant at 0.2 g and the concentration of dye was in the range of 30-90 ppm. R% was decreased with increasing initial concentration of dye (Fig. 4) and this could be due to lack of available active sites required for high initial concentration of the dye, as maximum dye adsorption obtained 99.25% at 30mg/l initial concentration.

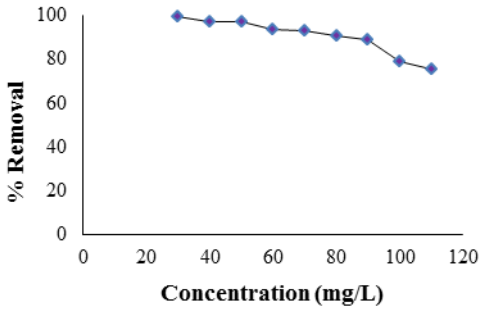

Fig. 4: Effect of dye concentration Dye concentration (30-90) mg/l, pH=2.5, mesh=100, adsorbent dosage=0.2g

The effect of adsorbent dosage

To investigate the effect of adsorbent dosage, the adsorption of blue 56 onto orange peel was measured at three dye concentrations (60, 70, and 80) mg/l for different adsorbent dosages (0.05g-0.2g). When the adsorbent dosage was increased from 0.05g to 0.2g, R% was increased from 53 to 98. It is clear from Fig. 5 that the increased R% with increasing adsorbent dose was due to the availability of larger surface area with more active adsorbent sites.

The effect of particle size

Particle size has an important effect on adsorption. The effect of particle size (mesh size) was studied with 40, 60 and 100 mesh sizes at three dye concentrations (60, 70, and 80) mg/l (Fig. 6). It was observed that the R% with smaller adsorbent size (mesh 100) was higher than R% with bigger adsorbent size (mesh 40) due to availability of more adsorption sites.

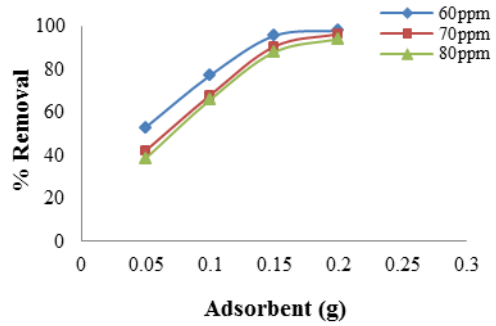

Fig. 5. Effect of adsorbent dosage pH=2.5, adsorbent dosage (0.05-0.20) g, dye concentration (60, 70, 80) mg/l.

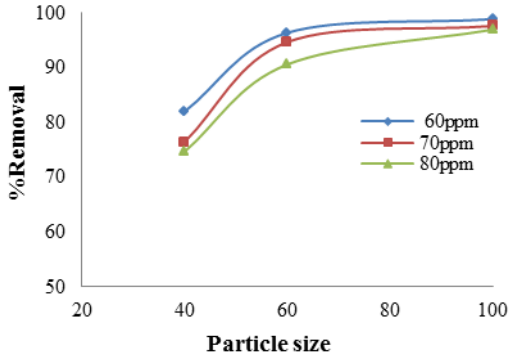

Fig. 6: Effect of particle size (mesh size) pH =2.5, mesh size (40, 60, 100), dye concentration (60, 70, 80) mg/l

The effect of temperature

Temperature is a highly significant parameter in adsorption process. The effect of temperature was studied at three concentrations (60, 70, 80) mg/l at pH=2.5 and mesh size =40. The experiments were carried out at four different temperatures 15, 25, 35, and 45°C. From the results in Fig.7 was understood that the removal of BLUE 56 was increased from 60% to 95.5% by orange peel with increasing temperature from 15 to 45°C. The increase in uptake of orange peel, with temperature may be due to dissolve of the

adsorbing species, the change in pore size and enhanced rate of intra- particle diffusion of adsorbate. Thus, the adsorption process is an endothermic process.

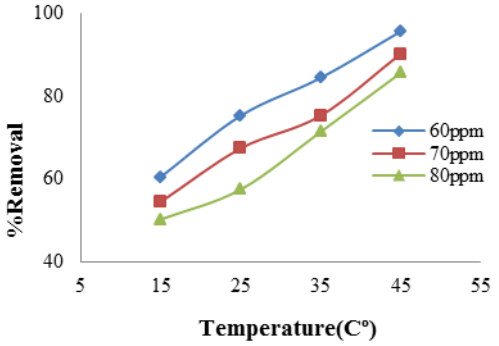

Fig. 7. Effect of temperature pH=2.5, siz mesh=40, temperature (15, 25, 35, 45 °C)

Isotherm data analysis

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental sorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the sorbent. The most widely accepted surface adsorption models for single solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid-phase concentration was tested with the Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D–R) isotherm equations. The Linear regression is frequently used to determine the best isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients. Langmuir and Freundlich isotherm equations were tested in this work.

Langmuir isotherm

The theoretical Langmuir isotherm (Langmuir, 1916) is valid for sorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption on to the surface without transmigration of adsorbate in the plane of the surface (Dogan *et al.* 2000).Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the sorbent surface. The Langmuir non-linear equation is commonly expressed as followed:

$$C_e/q_e = 1/(Kq_m) + C_e/q_m \qquad 3.1$$

In Eq. (3.1), qe is the amount of dye adsorbed on the orange peel at equilibrium, Ce is the equilibrium concentration of dye solution, q_m is the maximum adsorption capacity and K is adsorption equilibrium constant (l/mg) that is related to the apparent energy of sorption. (Kinniburgh. 1986, Longhinott *et al.* 1998)The equilibrium isotherm for the adsorption of dye BLUE 56 on orange peel was determined with 0.2 gr orange peel and 25 ml of dye solution (50-90 mg/ l), (200 rpm) in a constant temperature at pH 2.5. Fig. 8 shows the langmuir isotherm of dye BLUE 56 using orange peel (qe versus Ce). A plot of Ce/qe versus Ce should indicate a straight line of slope $1/q_m$ and an intercept of $1/(Kq_m)$. The values of q_m and k were determined slop and intercepts of the plots q_m, K, r^2 (correlation coefficient for Langmuirisotherm), are given in Table 2.

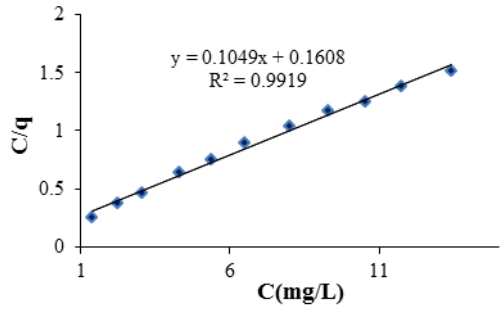

Fig. 8. Langmuir isotherm plot of effect of initial dye concentration on adsorption of orange peel (adsorbent dosage=0.2gr, s=200 rpm)

The Freundlich isotherm

The Freundlich isotherm model (Freundlich, 1906) is the earliest known equation describing the adsorption process. It is an empirical equation can be used for non-ideal sorption that involves heterogeneous sorption. The Freundlich isotherm can be derived assuming a log- arithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is commonly given by the following

$$\log q_e = \log K_F + (1/n) \log C_e \quad 3.2$$

Where K_f is a constant for the system related to the bonding energy. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is indicating the adsorption intensity of dye on to the sorbent or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/n below 1 indicates a normal Langmuir isotherm while 1/n above 1 is indicative of cooperative adsorption.

Table 2: Comparison of the coefficients isotherm parameters for B56 adsorption on to orange peel

Isotherm model			
Langmuir		Freundlich	
Q_m (mgg^{-1})	9.69	1/n	0.203
K_2(lmg^{-1})	0.641	K_f	2.02
R^2	0.991	R^2	0.981

The applicability of the Freundlich sorption isotherm was also analyzed using the same set of experimental data, by plotting log(q_e) versus log(C).The data obtained from linear Freundlich isotherm plot for the adsorption of the B56on to orange peel are presented in Table 2.

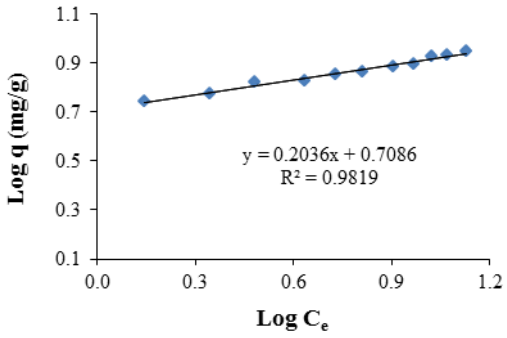

Fig. 9: Freundlich isotherm plot of effect of initial dye concentration on adsorption of orange peel. (Adsorbent dosage=0.2g, s=200rpm

Adsorption kinetics

Several steps can be used to examine the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer; kinetic models are used to test experimental data from the adsorption of B56 on to orange peel. The kinetics of B56 adsorption onto orange peel is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of B56 adsorption onto orange peel were analyzed using pseudo-first-order] (Lagergren, 1898), pseudo-second-order (Ho *et al.* 2000) kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). The relatively higher value is the more applicable model to the kinetics of B56 adsorption onto orange peel.

Pseudo-first-order equation

The adsorption kinetic data were described by the Lager- gren pseudo-first-order model (Lagergren, 1898), which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed a follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad 3.3$$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mgg^{-1}), k_1 is

the rate constant of Pseudo-first-orde adsorption ($Lmin^{-1}$). In order to obtain the rate constants, the values of log (q_e- q_t) were linearly correlated by plot of log (q- q_t) versus (t) to give a linear relationship from which k_1 and predicted (q) can be determined from the slope and intercept of the plot, respectively (Fig.10). The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Furthermore, the experimental q_e values do not agree with the calculated ones, obtained from the linear plots and the correlation coefficient R^2 are relatively low for most adsorption data (Table 3). This shows that the adsorption of B56 on to orange peel cannot be applied and the reaction mechanism is not a first-order reaction.

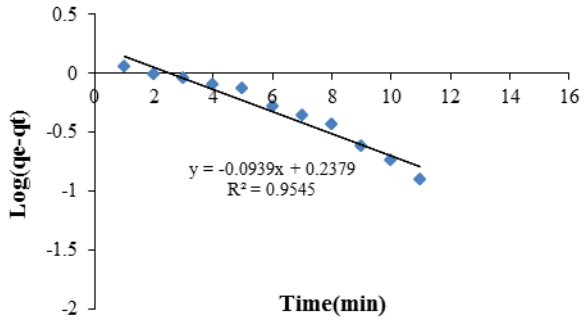

Fig. 10: Pseudo-first-order kinetics for B56 adsorption on to orange peel .Conditions: adsorbent dosage 0.3(g/L)

Table 3: Parameters of the first –order adsorption kinetics

dye	First-order kinetic model		
	q_e	K_1	R_1^2
Blue56	1.72	0.216	0.954

Pseudo-second-order equation

The adsorption kinetic may be described by the pseudo-second- order model (Ho *et al.* 2000). The differential equation is generally given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \qquad 3.4$$

Where, K_2 (g (mg min $^{-1}$)) is the second-order rate constant of adsorption. If the second-order kinetics is applicable, then the plot of (t/q) versus (t) should show a linear relationship. Values of (k_2) and equilibrium adsorption capacity (q) were calculated from the intercept and slope of the plots of (t/q) versus(t) (Fig.11) The correlation coefficients for the second-order kinetic model are greater than 0.993, which led to believe that the pseudo-second-order kinetic model provided good correlation for the biosorption of different initial of B56 on to orange peel.

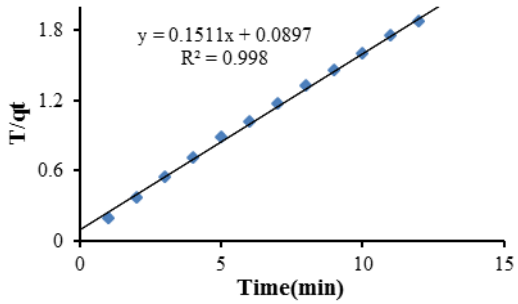

Fig. 11. Plot of the pseudo-second - order model at 80 ppm B56, orange peel 0.3(g/L)

Table 4: Parameters of the second –order adsorption kinetics

dye	Second-order kinetic model		
Blue56	q_e	K_2	R_2^2
	6.618	.254	.999

The effect of solution volume

The effect of solution volume was studied by keeping the concentration dye constant at 70 mg/l and the volume solution was in the range of 25-1000 ml. Fig. 8 shows that R% decreased with increasing volume solution.

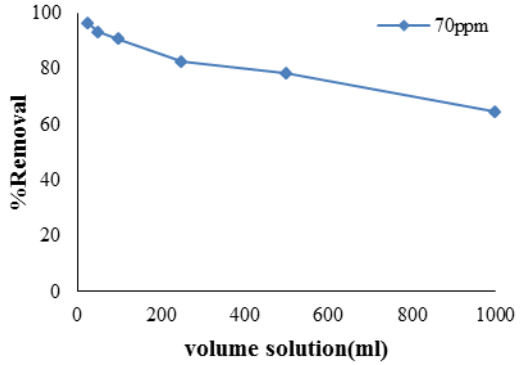

Fig. 11. Effect of solution volume

CONCLUSION

The experimental results include:

1. The effect of pH was studied at different pH (2-10) for different dye concentrations (60,70,80mg/l) and constant orange peel dosage of 150 mg. The maximum dye adsorption was obtained 96.76% at pH 2.5.

2. The effect of dye concentration was studied by keeping the adsorbent dose constant at 200 mg and the concentration of dye was in the range of(30-90ppm)maximum dye adsorption was obtained 99.25% at (30 mg/l) initial concentration.

3. To investigate the effect of adsorbent dosage, the adsorption of BLUE 56 onto orange peel was measured at three dye concentrations (60,70,80) mg/l for different adsorbent dosage(0.05-0.2) g. More dye adsorption was obtained by more adsorbent dosage.

4.The effect of particle size (mesh size) was measured at three dye concentrations (60,70,80) mg/l for different mesh sizes (40,60,100). More dye adsorption was obtained by smaller adsorbent size.

5. The effect of temperature was studied with three concentrations (60, 70, 80) mg/l at pH=2.5 and size mesh=40. More dye adsorption was obtained at higher temperature.

6. The effect of solution volume was studied by keeping the concentration dye constant at 70 mg/l and different solution volumes of 25-1000ml. The results indicate that R% was decreased with increasing solution volume of dye.

7. Langmuir isotherm was plotted. Maximum adsorption capacity (q_m) was obtained 9.69 mg/g, R^2=0.988, K=0.641.

8. The kinetic data indicate that the adsorption kinetics followed the pseudo- second-order rate with intra-particle diffusion as one of the rate determining steps.

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