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Single Stage Adsorption of Procion Red MX-5B On Fish Scale

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Abstract

The main purpose of this study was to investigate the adsorption of Reactive Red 2 (RR2) on a fish scale in a batch system. The optimum adsorption conditions were determined as initial pH 2.0, temperature 25 °C and adsorbent concentration 1 g/L. It was observed that the adsorbed RR 2 amounts on fish scale increased with increasing initial dye concentration from. The isotherm models were applied to adsorption data and the Langmuir isotherm model was the best suitable adsorption model. The monolayer coverage capacity of fish scale for RR2 was found as 1000 mg/g. The adsorption kinetic of this acidic dye on fish scale was described by the pseudo-second-order kinetic model. The intraparticle diffusion model was applied to the experimental data in order to describe the removal mechanism of the studied dye by fish scale.

Keywords: Adsorption, fish scale, pseudo second order kinetic model, Procion Red MX-5B.

1. Introduction

Dyes have been extensively used in many industries, such as textile, leather tanning, paper production, food technology, hair colorings, etc. Today more than 100.000 commercially available dyes with over 7×10^5 tonnes of dye-stuff produced annually. Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical or chemical processes. However these processes are costly and can not effectively be used to treat the wide range of dye wastewaters. Adsorption of heavy metal ions, radioactive elements and dyes from industrial effluents are of great significant in connection with environmental and human health safety. Among these process adsorption has been shown to be an effective technique with its efficiency, capacity and applicability on a large scale to remove non-biodegradable dyes from aqueous streams [1]. Adsorption on activated carbon has been found to be an effective process for dye removal, but it is too expensive. Consequently numerous low cost alternatives have been proposed including mango leaves, banana peel, crabshell, grapes talk, seaweed, neem leaf, palm kernel fibre, sour soup seed [2]. New economical, easily available and highly effective adsorbents are still needed.

The main objective of the present work is to study the adsorption of RR2, reactive azo dye, from aqueous solution on fish scale, as a new alternative adsorbent. Effects of initial pH, temperature, contact time, initial dye and adsorbent concentrations

on RR2 adsorption were discussed, the equilibrium and kinetic model studies were done.

2. Material And Methods

2.1. Fish scales

Fish scales were collected from the Fishermen's Market located in Mersin. Mature fish scales were washed repeatedly with tap water to remove adhering dust and soluble impurities from their surface. The fish scales were allowed to dry in shade for 2 days. The scales were then kept in a drying-oven at 110 °C till the fish scales became constant weight.

2.2. Dye solutions

RR2, reactive azo dye, was chosen for this study, because it is widely used for dyeing cellulosic fibres. Only 60–70% of the reactive dye reacts with the fibre during the dyeing process, the remainder is hydrolyzed and is released in to the environment [3].

The stock solution of RR2 dye was prepared in 1.0 g/L concentration. Necessary dilutions were made from the stock solution to prepare solutions in the range of concentrations 20–500 mg/L for the dye. Dyestuff, Reactive Red 2, was supplied by DyStar with commercial name Procion Red MX-5B.

3.3. Batch adsorption studies

1.0 g of the fish scale, except for adsorbent concentration experiments, was mixed with 100 ml of the desired initial dye concentration and initial pH in Erlenmayer flasks. The flasks were agitated on a shaker at constant temperature for 2 h ample time for adsorption equilibrium. Samples (5 ml) of adsorption medium were taken before mixing the adsorbent suspension and dye bearing solution, then at pre-determined time intervals (0.5, 2, 5, 10, 20, 30, 60 and 120 min) for the residual dye concentration in the solution. Samples were centrifuged at 3500 rev/min for 5 min and the supernatant liquid was analysed. Initial pH of each solution was adjusted to the required value with concentrated and diluted H₂SO₄ and NaOH solutions before mixing the adsorbent solution. Experiments were repeated for different initial pH, initial dye concentration, temperature and adsorbent concentration values.

3.4. Analysis

The unadsorbed RR 2 dye concentration in supernatant was analysed at 538 nm wavelength with Chebios UV-VIS spectrophotometer.

3. Results And Discussion

In this study; the effects of initial pH, initial dye concentration and temperature to adsorption of RR2 on fish scale were investigated in a batch mode.

3.1. Effect of initial pH

The effect of initial pH to the adsorption of RR2 on fish scale was studied in the range of initial pH 2.0-4.0. It was observed that the equilibrium uptake amounts decreased with increasing initial pH values and the optimum initial pH was determined as 2.0. The adsorbed RR 2 amount and removal percentage values decreased from 97.08 to 27.50 mg/g and 98.68 to 28.15 %, respectively, with increasing the initial pH from 2.0 to 4.0. Solution pH also influences both the cell surface for dye binding sites and the dye chemistry in water. Higher uptakes obtained at lower pH values may be due to the electrostatic attractions between negatively charged dye anions and positively charged cell surface [4].

3.2. Effect of initial dye concentration

The initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process, thus increases the uptake. The effect of initial dye concentration was studied in the initial concentration range of 25-500 mg/L. The uptake amounts of RR 2 increased with increasing up to 300 mg/L of the initial dye concentration, and then didn't change with further increase in initial dye concentration. The adsorbed RR 2 amount and removal percentage values increased from 23.62 to 339.80 mg/g and 98.61 to 74.13 %, respectively, with increasing the initial dye concentration from 25 to 500 mg/L. The uptake amounts increased with increasing initial dye concentration as a result of the increase in the driving force and then did not change with further increase in initial dye concentration, suggesting that available sites on the adsorbent are limiting factor for dye adsorption [4].

3.3. Effect of temperature

One of the parameters affecting the adsorption is temperature. The effect of temperature to the adsorption was studied in the temperature range of 20-50 °C and the optimum temperature was determined as 25°C. The adsorption capacity of fish scale increased up to 25°C and then decreased with increasing temperature, from 287.05 mg/g at 25°C to 260.52 mg/g at 50°C. The increase in dye adsorption up to 25°C can be explained as follows; the enhancement in adsorption with temperature may be attributed to increase in the number of active surface sites available for adsorption, increase in the porosity and in the total pore volume of the adsorbent. The enhancement in adsorption could be also due to the decrease in the thickness of the boundary layer surrounding the sorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. This may also be a result of an increase in the mobility of the dye molecule with an increase in their kinetic energy, and the enhanced rate of intraparticle diffusion of sorbate with the rise of temperature [5]. At higher temperature values, surface activity reduces by increasing temperature and so the amount of dye adsorbed in equilibrium decreases [4]. The reason of decrease in surface activity is decay of active regions on surface of the adsorbent at higher temperature or bond breaking.

3.4. Effect of adsorbent concentration

Adsorption of RR2 on fish scale was investigated at 0.5-3.0 g/L of adsorbent concentration range. With increasing adsorbent concentration from 0.5 g/L to 3.0 g/L the adsorbed dye amount per unit mass fish scale decreased from 268.60 mg/g to 55.56 mg/g. Because adsorption sites remain unsaturated during the adsorption. This is due to the fact that as the dosage of adsorbent is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent [6].

3.5. Equilibrium modelling

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [1]. The linear form of Langmuir isotherm equation is given as:

$$(1/q_{eq}) = (1/Q^0 b C_{eq}) + (1/Q^0) \quad (1)$$

where q_{eq} (mg/g) and C_{eq} (mg/L) are the adsorbed dye amount per unit mass of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q^0 and b are Langmuir constants related to monolayer coverage capacity of adsorbent and bonding energy of adsorption, respectively [7]. Q^0 and b can be determined from the linear plot of $1/q_{eq}$ versus $1/C_{eq}$.

The well-known Freundlich isotherm used for adsorption is a special case for heterogeneous surface energy in which the energy term in the Langmuir equation varies as a function of surface coverage strictly due to variation of the adsorption. The Freundlich equation is given as [6]:

$$q_{eq} = K_f \cdot C_{eq}^{1/n} \quad (2)$$

where K_f is roughly an indicator of the adsorption capacity and $1/n$ is an indication of adsorption intensity. K_f and $1/n$ can be determined from the linear plot of $\ln(q_{eq})$ versus $\ln(C_{eq})$.

The Langmuir and Freundlich isotherm models were applied to the experimental equilibrium data and the isotherm constants were presented in Table 1. As can be seen from Table 1, the maximum monolayer coverage capacity of fish scale for RR2 was determined as 1000 mg/g at 25°C which is the optimum temperature for adsorption of RR2 to fish scale. The R^2 value of 0.99 indicated that the adsorption data of RR2 onto fish scale at the five temperatures studied were best fitted to the Langmuir isotherm model.

Table 1: The Langmuir and Freundlich isotherm constants at different temperatures

Temperature (°C)	Langmuir isotherm			Freundlich isotherm		
	Q^0 (mg/g)	b (L/mg)	R^2	K_f (mg/g) (L/mg) ^{1/n}	n	R^2
20	200.00	0.02857	0.999	1.8423	0.4629	0.859
25	1000.0	0.00640	0.998	2.5244	0.5015	0.971
30	500.00	0.00390	0.997	0.3444	0.5770	0.928
40	333.33	0.02857	0.996	1.6686	0.3426	0.908
50	250.00	0.03149	0.991	1.8645	0.5905	0.984

According to Table 1; n values were very close to each other. So, the adsorption intensity was not affected by changing the temperature of adsorption solution. The highest K_f was found as 2.5244 at optimum temperature, but data did not fit in good agreement as was the case for the Langmuir isotherm model due to the low R^2 values.

3.6. The pseudo second-order kinetic model

The pseudo second-order kinetic model is based on the sorption capacity of the solid phase. Contrary to the other model, it predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step [7]. In order to quantify the extent of uptake in adsorption kinetics, a pseudo second order kinetic model can be used. The linear form of the pseudo second order equation can be represented as [8]:

$$t/q_t = 1/k_2q_{eq}^2 + t/q_{eq} \quad (3)$$

Where k_2 is the rate constant of pseudo second order kinetic (g/mg min), q_{eq} and q_t are the adsorbed dye amount per unit mass of adsorbent at equilibrium and any time, t , respectively. If the pseudo second order kinetic model is applicable, the plot of t/q_t against t of Equation 3 should give a linear relationship, from which calculated $q_{eq,cal}$ and k_2 can be determined from the slope and intercept of the plot.

The pseudo second order kinetic model was applied to adsorption data of RR2 on fish scale for different initial dye concentrations and the experimental ($q_{eq,exp}$) and calculated ($q_{eq,cal}$) uptake amounts and k_2 values for different initial dye concentrations was given in Table 2. As can be seen from Table 2, the pseudo-second order rate constant values decreased with increasing initial dye concentration, the experimental data ($q_{eq,exp}$) and the calculated values ($q_{eq,cal}$) were very close to each other and the correlation coefficients of all concentrations studied were also found very high. These results showed that the adsorption of RR2 onto fish scale was well described by pseudo-second order kinetic model.

Table 2: The pseudo second-order kinetic model constants and regression coefficients for different initial dye concentrations

C_o (mg/L)	$q_{eq,exp}$	$q_{eq,cal}$	k_2 (g/mg min)	R^2
25	23.6246	24.1546	0.0153000	0.9988
50	44.6602	45.8716	0.0064100	0.9980
75	70.8738	74.0741	0.0027000	0.9953
100	93.8511	97.0874	0.0025100	0.9970
200	194.4984	208.3334	0.0005097	0.9832
300	287.0549	312.5000	0.0002586	0.9803
400	331.7152	357.1428	0.0002334	0.9767
500	339.8057	357.1428	0.0002587	0.9697

Figure 1 shows the variation of the experimental and calculated from the pseudo second order kinetic model uptakes with contact time for initial dye concentrations. From Figure 1, a contact time of 60 min for RR2 adsorption on fish scale was sufficient to achieve equilibrium and the adsorbed dye amounts did not change with further increase in contact time for all of the studied concentrations.

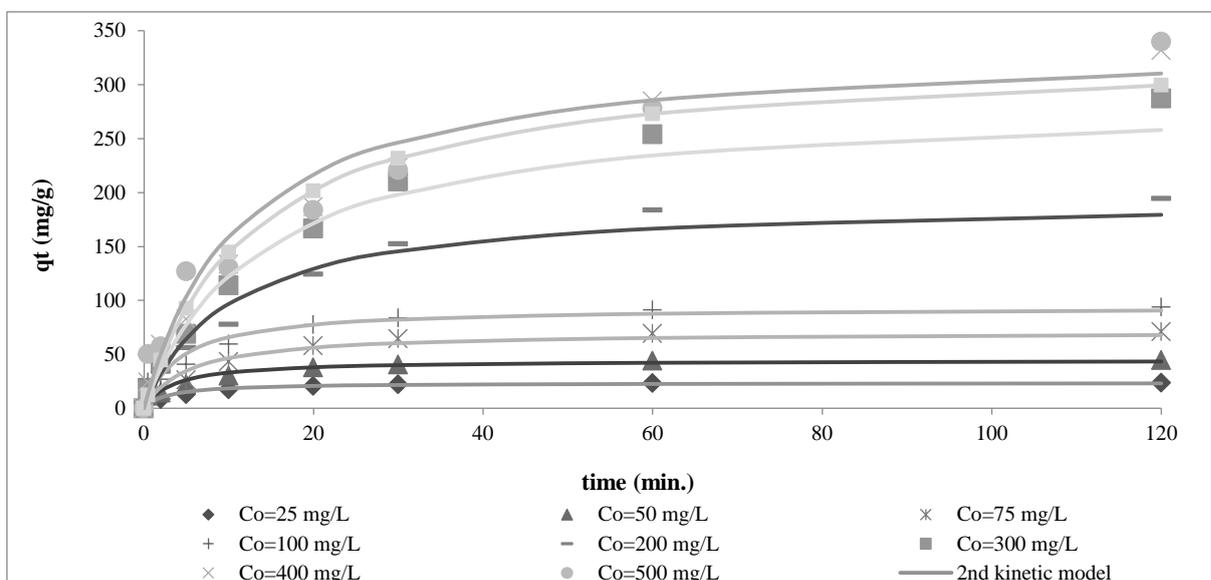


Figure 1. The graphically comparison of the experimental and calculated the pseudo second order kinetic model for different initial dye concentrations (experimental conditions: temperature 25 °C, initial pH 2.0, agitation rate 200 rev/min)

3.7. Intraparticle diffusion model

The importance of external mass transfer greatly reduces for the process at very well-stirred batch system or system that the effect of stirring rate on equilibrium is insignificant. In a diffusion controlled adsorption process, the adsorbed amount of the solute varies almost proportionately with a function of retention time, $t^{1/2}$ as early mentioned by Weber and Morris[9]:

$$q_t = K_i \cdot t^{1/2} \quad (4)$$

According to the Weber-Morris model equation; a plot of q_t versus $t^{1/2}$ should be a straight line with a slope and intercept when adsorption mechanism follows the intraparticle diffusion process. Such a deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial and final stage of sorption.

On the other hand, the intercept of the plot reflects the boundary layer effect.

Weber-Morris model was applied to the adsorption of RR2 on fish scale as a function of initial dye and adsorbent concentrations. Weber-Morris model constants, intercept values and regression coefficients were given in Table 3. As can be seen from Table 3, the linear line did not pass through the origin and this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [1].

Table 3: Weber-Morris model constants

C_0 (mg/L)	K_i (mg/g min ^{1/2})	Intercept	R^2	X_0 (g/L)	K_i (mg/g min ^{1/2})	R^2
25	3.8570	3.6219	0.9919	0.5	37.48	0.978
50	7.3750	5.4835	0.9911	1	37.06	0.984
100	16.7230	3.9539	0.9930	2	29.65	0.999
200	32.1600	10.785	0.9829	3	16.58	0.922
500	40.3890	1.3871	0.9995			

The observed increase in K_i values with increasing initial dye concentration can be explained by the growing effect of driving force, the concentration gradient. As can be seen from Table 3, the intraparticle diffusion rate constants (K_i) increased with initial dye concentration and decreased with adsorbent concentration. It was observed that the external mass transfer coefficients decreased with increasing the initial dye concentration and increased with increasing the adsorbent concentration [10].

4. Conclusion

Batch adsorption studies were done to test the feasibility of employing fish scales as a low-cost adsorbent for removal of RR2 dye from aqueous solutions. Results show that a pH value of 2.0 is favorable for the adsorption of reactive azo dye for fish scales. RR2 dye removal is also temperature-dependent and found to be maximum at 25 °C. It was seen that adsorption can be accomplished with a high uptake capacity by increasing the initial dye concentration up to 300 mg/L. At optimum adsorption conditions, the uptake amount and removal percentage of fish scale for RR2 dye molecules were found as 287.06 mg/g and 97.26 %, respectively. Equilibrium data fitted to Langmuir, with maximum monolayer adsorption capacity of 1000 mg/g at 25°C. The adsorption kinetic of RR2 on fish scale was defined the pseudo-second-order kinetic model. Weber–Morris model equation was applied to the experimental data for initial dye and adsorbent concentrations. As a result, fish scales can be effectively utilized as a

cheap, nonconventional adsorbent in wastewater treatment.

Nomenclature

C_{eq}	residual dye concentration at equilibrium (mg/L)
k_2	pseudo second order rate constant
K_f	adsorption capacity [(mg/g)(mg/L) ^{-1/n}]
K_i	intraparticle rate constant (mg/g min ^{1/2})
q_{eq}	the amount of adsorbed dye per unit mass of adsorbent at equilibrium (mg/g)
$q_{eq,cal}$	calculated amount of adsorbed dye per unit mass of adsorbent at equilibrium (mg/g)
$q_{eq,exp}$	experimental amount of adsorbed dye per unit mass of adsorbent at equilibrium (mg/g)
q_t	the amount of adsorbed dye per unit mass of adsorbent at any time (mg/g)
Q^0	maximum adsorbed amount of dye per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/g)
R^2	correlation coefficient
1/n	adsorption intensity

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