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CONFERENCE PAPER · JUNE 2013

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Digital Proceeding Of THE ICOEST'2013 - ,Cappadocia
C.Ozdemir, S. Şahinkaya, E. Kalıpcı, M.K. Oden (editors)
Nevsehir, Turkey, June 18 – 21, 2013

Adsorption of Telon Red FRL From Aqueous Solutions On Fish Scale

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ABSTRACT
The main purpose of this study was to investigate the adsorption of Acid Red 337 (AR337),Telon Red FRL, to fish scale, a waste, in a batch system relating to the initial pH, initial dye concentration, adsorbent concentration and temperature. For the adsorption of AR337to fish scale, the optimum initial pH, temperature and adsorbent concentration were determined to be 2.0, 30^{o}C and 1 g/L, respectively. The adsorbed AR 337 amounts by fish scale increased with increasing initial dye concentration from 25 mg/L to 1000 mg/L. The Langmuir and Freundlich adsorption models were applied to experimental equilibrium data and the isotherm constants were calculated. The monolayer coverage capacity of fish scale for AR337 adsorptionwas obtained as 1000 mg/g. 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, Acid Red 337

1. INTRODUCTION
Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing and also from food colouring, cosmetics, paper and carpet industries. Removal of dyes from such wastewaters is a major environmental problem. The uptake or accumulation of chemicals by adsorbent has been termed adsorption. Adsorption is more effective technique than the other conventional techniques with its efficiency, capacity and applicability on a large scale to remove dyes from aqueous streams [1]. In recent years, many methods including coagulation and flocculation, reverse osmosis, chemical oxidation, biological treatments, photodegradation, and adsorption, have been developed for treating dye containing wastewater [2]. Among various treatment technologies, adsorption technique is quite popular due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents. Now, there is a growing need to find locally available, low cost and effective materials for the removal of dyes. Many investigators are still searching for the use of cheap and efficient alternative materials such as bagasse pith, carbonized bark, peat, soil, tree and eucalyptus barks, chitin, rice husk, wood and fly ash [3]. In this study, using fish scale as adsorbent for textile dyes also offers a potential alternative.

2. MATERIAL AND METHODS
2.1.Fish scales
Fish scales were collected from the Fisherrmen'sMarket located in Mersin. Mature fish scales were washed repeatedly with water to remove adhering dust and soluble impurities form their surface. The fish scales were allowed to dry in in shade for 2 days. The scales were then kept in a drying-oven at 110 °C till the fish scales became crispy.The dried scales were then

converted into fine powder by grindingin a mechanical grinder.

2.2. Dye solutions

The stock solution of AR 337 dye was prepared in 1.0 g/L concentration. Necessary dilutions for the dye were made from the stock solution to prepare solutions in the range of concentrations 20–1000 mg/L. Dyestuff, Acid Red 337, was supplied by DyStar with commercial name Telon Red FRL.

3.3. Batch adsorption studies

1.0 gof the fish scale, except for adsorbent concentration experiments, was mixed with 100 ml dye bearing solution 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, 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 H_2SO_4 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 AR 337 dye concentration in supernatant liquid was analysed at 529 nm wavelenght with Chebios UV-VIS spectrophotometer.

3.RESULTS AND DISCUSSION

The effects of initial pH, temperature, initial dye concentration and adsorbent concentration on the adsorption of AR 337 on fish scale were studied in a batch system and results were presented in following sections:

3.1. Effect of initial pH

The AR 337 uptake amounts by fish scale decreased with increasing initial pH values and the optimum initial pH value was determined as 2.0. The adsorbed AR 337 amount and removal percentage values decreased from 102.06 to 38.14 mg/g and 91.67 to 42.22 %, respectively, with increasing the initial pH from 2.0 to 5.0. Low pH leads to an increase in H^+ ion concentration in the system and the surface of the fish scale acquires positive charge by absorbing H^+ ions. As the fish scale surface is positively charged at low pH, a significantly strong electrostatic attraction appears between the positively charged fish scale surface and anionic dye molecule leading to maximum adsorption of dye. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the fish scale does not favour the adsorption of anionic dye molecules due to the electrostatic repulsion [4].

The variation of the adsorbed AR 337 amounts with time for the studied initial pH values was given in Figure 1and effect of initial pH on the equilibrium uptake capacity of fish scale was presented in Figure 2. According to Figures 1 and 2; the maximum AR 337 dye uptake capacity of fish scale was obtained at initial pH 2.0.

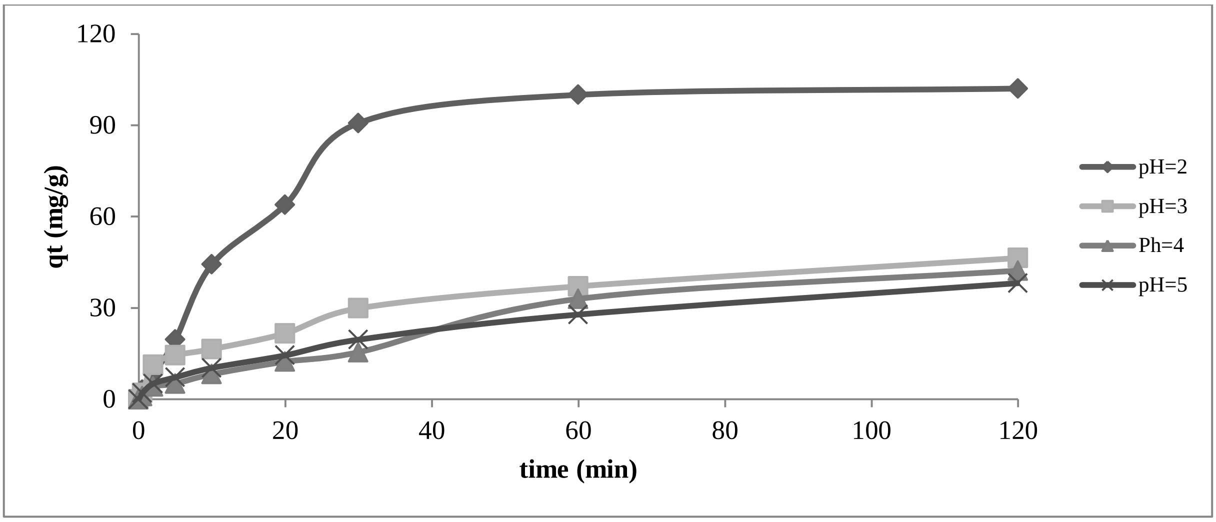

Figure 1: The variation of the adsorbed AR 337 amounts with time (X_0 = 1.0 g/L, initial pH 2.0, temperature 25ºC)

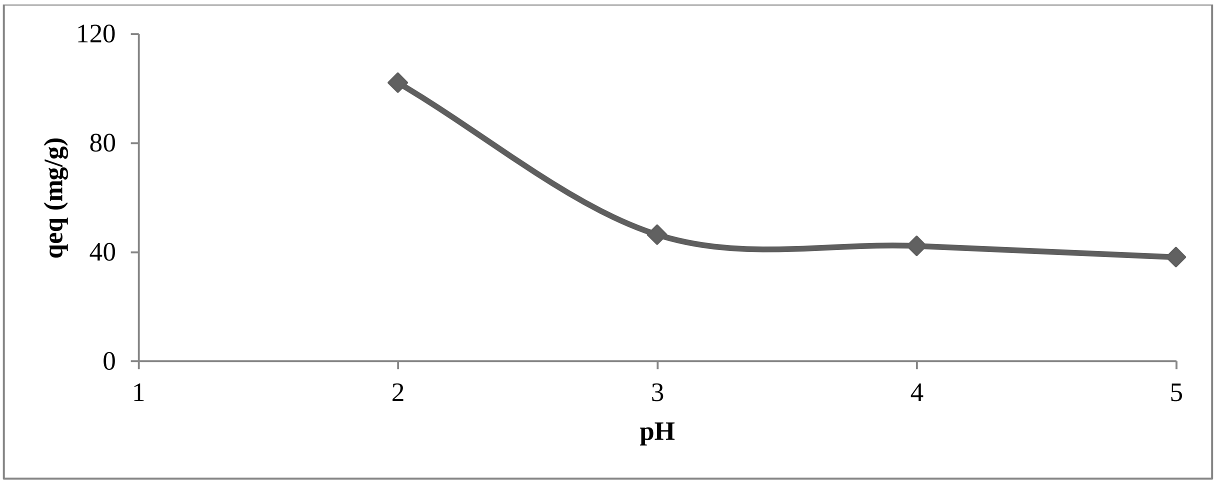

Figure 2: Effect of initial pH on the equilibrium uptake capacity of fish scale (X_o = 1.0 g/L, initial pH 2.0, temperature 25ºC)

3.2. Effect of initial dye concentration

The AR 337 uptake amounts of fish scale increased with increasing the initial dye concentration from 25 mg/L to 1000 mg/L. Especially, the uptake amounts of fish scale increased up to 800 mg/L of initial dye concentration and then did not changed by further increase in initial dye concentration suggesting that available sites on the adsorbent are the limiting factor for dye adsorption. At lower dye concentrations, solute concentrations to adsorbent sites ratio is higher, which cause an increase in colour removal [4]. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

The variation of the adsorbed AR 337 amounts with time for the studied initial dye concentrations was given in Figure 3 and effect of initial dye concentration on the equilibrium uptake capacity of fish scale was presented in Figure 4.

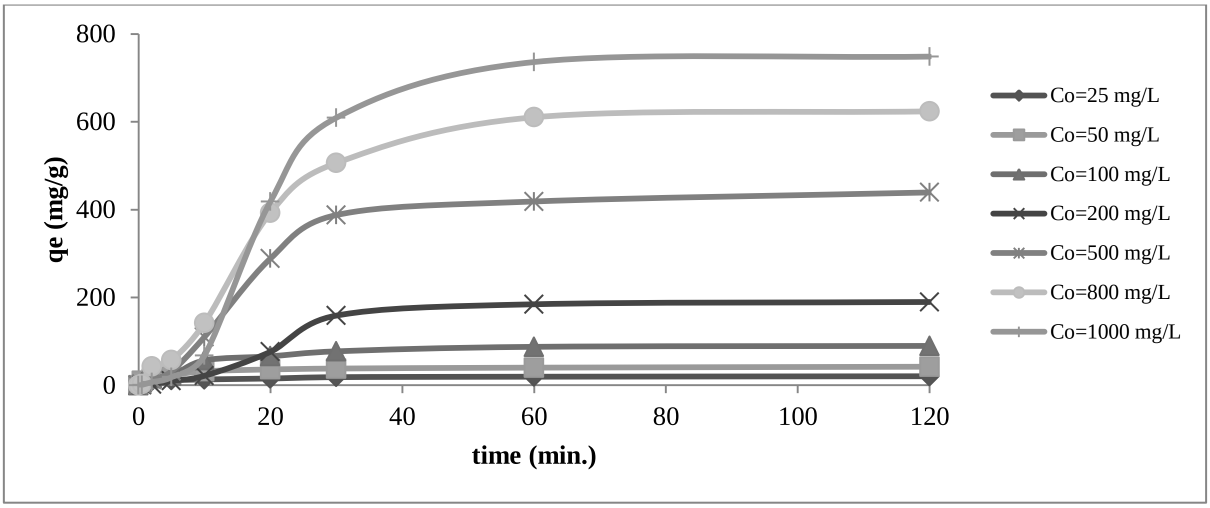

Figure 3: The variation of the adsorbed AR 337 amounts with timeat different initial dye concentrations (X_o = 1.0 g/L, initial pH 2.0, temperature 25ºC)

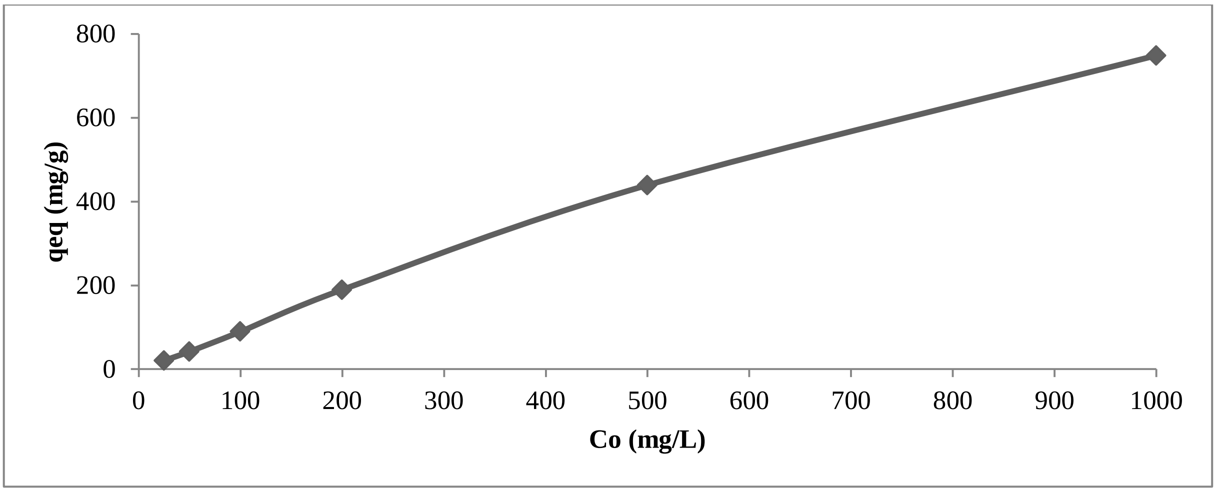

Figure 4: Effect of initial dye concentration on the equilibrium uptake capacity of fish scale (X_o = 1.0 g/L, initial pH 2.0, temperature 25ºC)

3.1. Effect of temperature

The variation of the adsorbed AR 337 amounts with time for different temperatures and the uptake amounts with temperature were given in Figure5 and Figure 6, respectively.As can be seen from Figures 5 and 6, the optimum temperature for AR 337 adsorption by fish scale was determined as 20-30 ºC and adsorption decreased with further increase in temperature. A decrease in equilibrium uptake value of fish scale by increasing the temperature from 30 to 50 ºC indicated that this adsorption process is exothermic in nature. This decrease at higher temperatures may be due to the damage of active binding sites in the adsorbent [5].

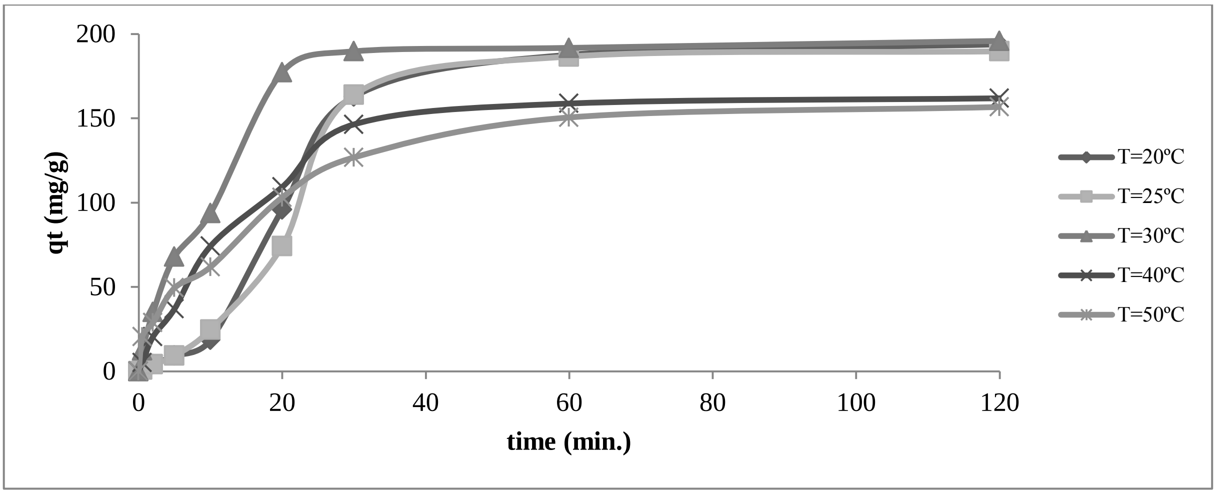

Figure 5: The variation of the adsorbed AR 337 amounts with timeat different temperatures (X_0 = 1.0 g/L, initial pH 2.0, initial dye concentration 200 mg/L)

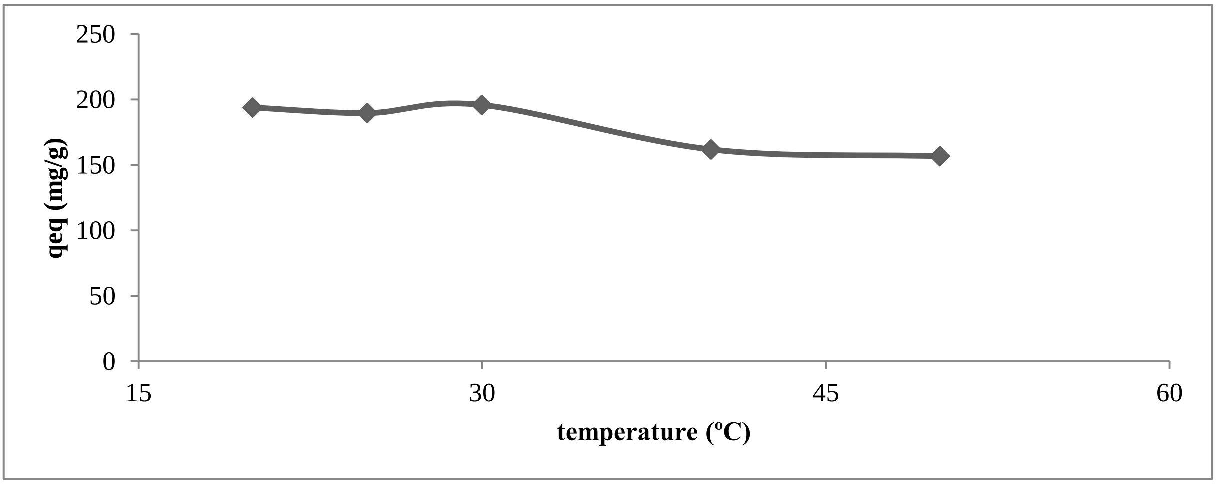

Figure 6: Effect of temperature on the equilibrium uptake capacity of fish scale (X_o = 1.0 g/L, initial pH 2.0, initial dye concentration 200 mg/L)

3.4. Effect of adsorbent concentration

The variation of the adsorbed AR 337 amounts with time for the studied adsorbent concentrations and the uptake amounts with adsorbent concentrations were given in Figure7 and Figure 8, respectively.As can be seen from Figures 7 and 8,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 381.44 mg/g to 49.82 mg/g. The decrease in the adsorption capacity with increasing adsorbent concentration may be due to the particle interaction, such as aggregation which would lead to a decrease in total surface area of the adsorbent and an increase in the diffusional path length [4].

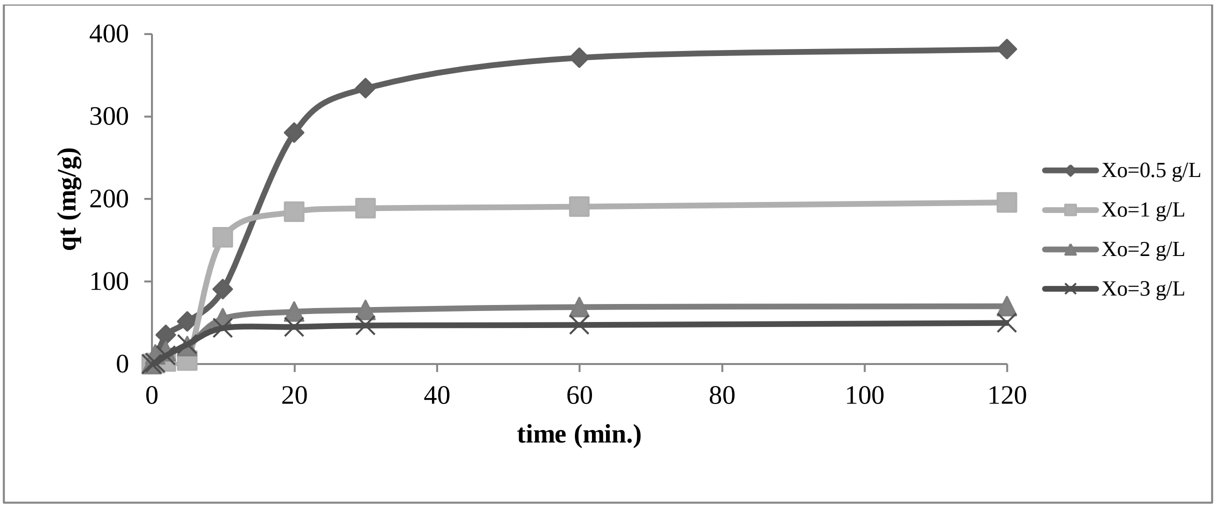

Figure 7: The variation of the adsorbed AR 337 amounts with timeat different adsorbent concentrations (temperature 30ºC, initial pH 2.0, initial dye concentration 200 mg/L)

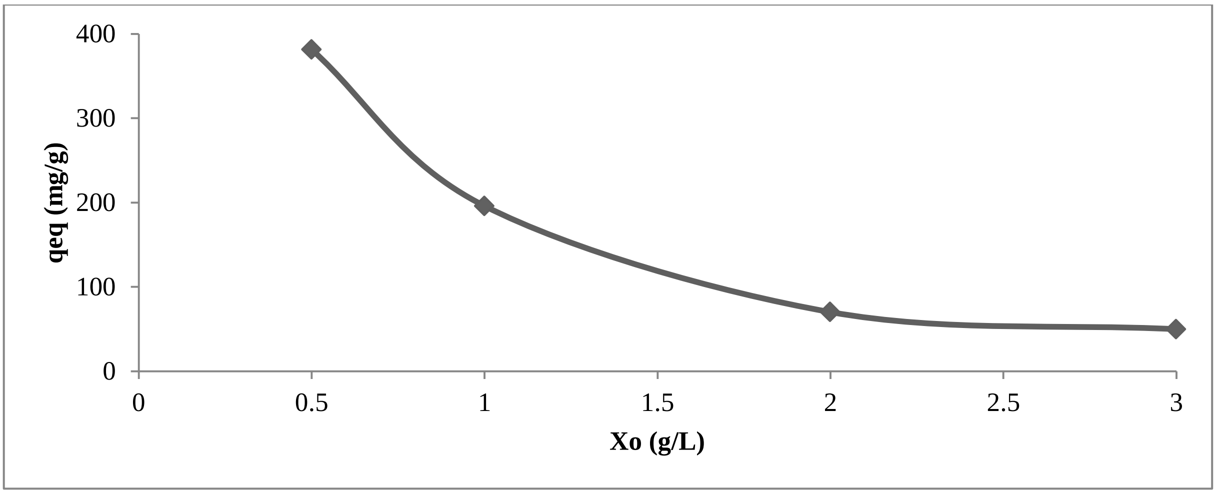

Figure 8: Effect of adsorbent concentration on the equilibrium uptake capacity of fish scale (temperature 30ºC, initial pH 2.0, initial dye concentration 200 mg/L)

3.5.Equilibrium modelling

The Langmuir model is valid for monolayer adsorptiononto a surface with a finite number of identical sites. The well-known expression of the Langmuir model is given by Eq. (1)

$$q_{eq} = [Q^o bC_{eq}]/[1 + bC_{eq}] \qquad (1)$$

Eq. (1) can be rearranged to the following linear form:

$$1/q_{eq} = 1/Q^o + [1/(bQ^o)] \cdot 1/C_{eq} \qquad (2)$$

where q_{eq} (mg/g) and C_{eq} (mg/L) are the amount of adsorbed dye per unit mass of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q^o is the maximum adsorbed dye amount per unit mass of adsorbent to form a complete monolayer on the surface bound at high C_{eq} (mg/L) and b is a constant related to the energy of adsorption (L/mg). Q^o represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and it assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments.

The Freundlich expression (Eq. (3)) is an exponentialequation and therefore, assumes that as the adsorbate concentrationincreases, the concentration of adsorbate on theadsorbent surface also increases. Theoretically using this expression, an infinite amount of adsorption can ocur [6]:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (3)$$

or, in its linear form:

$$\ln q_{eq} = \ln K_F + 1/n \ln C_{eq} \quad (4)$$

In this equation, K_F and 1/n are the Freundlich constantsindicating adsorption capacity and intensity, respectively.

The Langmuir and Freundlich isoterm 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 AR 337 was determined as 1000 mg/g at 25°C which is the optimum temperature for adsorption of AR 337 to fish scale. The R^2 value of 0.99 indicated that the adsorption data of AR 337 onto fish scale at the studied temperatures were best fitted to the Langmuir isotherm model.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.

Table 1: The Langmuir and Freundlich isotherm constants

	Langmuir isotherm			**Freundlich isotherm**		
Temperature (^{o}C)	**Q^0 (mg/g)**	**b (L/mg)**	**R^2**	**K_F**	**n**	**R^2**
20	142.857	0.02287	0.997	3.6147	1.1919	0.985
25	1000.000	0.00735	0.994	5.6745	0.9852	0.978
30	83.330	0.10900	0.994	14.1116	2.5707	0.976
40	125.000	0.09756	0.997	14.3392	1.6694	0.981

3.6.Pseudo second order kinetic model

In this study, the pseudo second order kinetic model was used to describe the kinetic data. The linear form of the pseudo second order kinetic model equation can be represented as:

$$t / q_t = 1 / [k_2 q_{eq}^2] + t / q_{eq} \quad (5)$$

If the pseudo second order kinetic model is applicable, the plot of t/q_t against t according to Equation 5 should give a linear relationship, from which calculated q_{eq} and $k_2$can be determined from the slope and intercept of the plot. The experimental ($q_{eq, exp}$) and calculated ($q_{eq, cal}$) uptake amounts and k_2 values for different initial dye concentrations were given in Table 2.

Table 2: The constants from the pseudo second-order kinetic model

C_o(mg/L)	**$q_{eq,exp}$**	**$q_{eq,cal}$**	**k_2 (g/mg min)**	**R^2**
25	20.6185	20.1295	0.009584	0.9937
50	41.2371	40.5858	0.007510	0.9969
75	67.0103	66.7668	0.003669	0.9975
100	93.8144	94.2877	0.002891	0.9969
500	475.2578	467.8363	0.000980	0.9985

As can be seen from Table 2, the pseudo-second order rate constant values decreased with increasing initial dye concentration. The adequate fitting of calculated ($q_{eq,\ cal}$) and experimental ($q_{eq,\ exp}$) values for the whole studied range of initial dye concentration suggest the applicability of the pseudo-second order kinetic model to this adsorption system [7].

The graphically comparison of the experimental and calculated the pseudo second order kinetic model for different initial dye concentrations was given in Figure 9. The data obtained from the adsorption of AR 337 on fish scale showed that a contact time of 30 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time. Therefore, the uptake and unadsorbed AR 337 concentrations at the end of 30 min are given as the equilibrium values (q_{eq}, mg/g; C_{eq}, g/L), respectively.

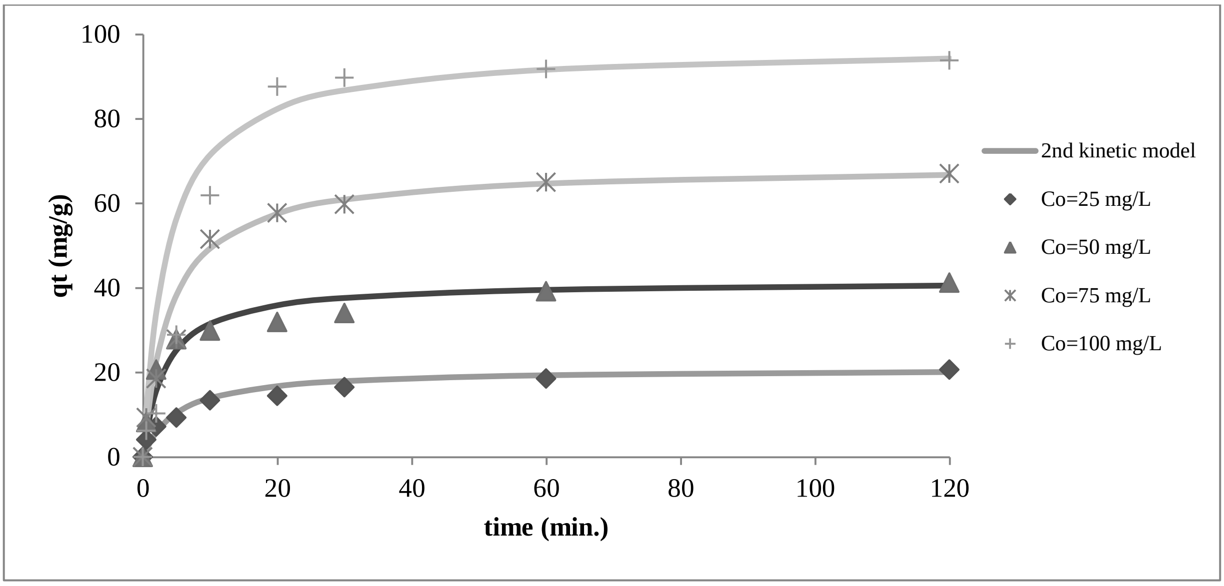

Figure 9: The graphically comparison of the experimental and calculated the pseudo second order kinetic model for different initial dye concentrations (X_o=1 g/L, temperature 30 °C, initial pH 2.0)

3.7.Weber-Morris model

In order to investigate the contribution of intraparticle diffusion, which is accepted to be rate controlling step, on theadsorption of AR 337 on fish scale, the equation described by Weber and Morris can be used to assess this opinion [8]:

$$q_t = K_i . t^{1/2} \qquad (5)$$

Where q_t is the adsorbed dye amount at any time t,K_i is the intraparticle rate constant. According to this model, the plot of uptake (q_t) versus the square root of time should be linear if intraparticular diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. In many cases, an initial steep-sloped portion indicating external mass transfer is followed by a linear portion to the intraparticle diffusion and plateu to the equilibrium.

Weber-Morris model was applied to the adsorption of AR 337 on fish scale as a function of initial dye concentrations and Weber-Morris model constants and regression coefficients were given in Table 3. As can be seen from Table 3, K_i values increased with initial dye concentrations.

Table 3: Weber-Morris modelconstants

C_o(mg/L)	K_i (mg/g min$^{1/2}$)	R^2
25	3.654	0.988
50	12.700	0.962
75	12.110	0.961
100	33.880	0.986
200	93.320	0.997

4. CONCLUSION

The adsorption of AR 337 on fish scale was investigated in a batch system. The adsorption is highly dependent on initial pH, temperature, initial dye concentration and adsorbent concentration. The optimum environmental conditions were determined as initial pH 2.0, temperature 30°C and adsorbent concentration 1g/L. The uptake amount and removal percentage values at optimum adsorption conditions were found as 475.25 mg/g and 95.25 %, respectively. Equilibrium data fitted to Langmuir, with maximum monolayer adsorption capacity of 1000 mg/g at 25ºC. 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 concentrations. As a result, toxic dye such as AR 337 can be removed by using a biological waste such as fish scale which is abundant and cheaply available in nature.

NOMENCLATURE

C_{eq} residual dye concentration at equilibrium (mg/L)
k_2 the pseudo second order rate constant (g/mg.min)
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^o the monolayer coverage capacity of adsorbent (mg/g)
R^2 correlation coefficient
1/n adsorption intensity

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