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Adsorption Characteristics of Acid Dyes by the Live Activated Sludge

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Adsorption is the one of the aspects of abiotic removal and in current work, the adsorption properties of two acid dyes by live activated sludge were examined in a batch system. The dyes tested for the adsorption by live activated sludge were Lanaset yellow 4GN and Lanaset red G. Both acid dyes adsorbed by the live activated sludge to some degree and the equilibrium was obtained with in 160 min. The data obtained from equilibrium studies fit to both Langmuir and Freundlich models. Based on the Langmuir model, q_{max} values were found 69.48 and 144.91 mg/g for Lanaset yellow 4GN and Lanaset red G, respectively. Gibbs free energies of adsorption were also calculated and negative values were found for each dye and sludge system. Intraparticle diffusion was found significant for both dyes tested and overall adsorption process was best described by pseudo second order model. Rate constants for each of the model were also calculated.

Key Words: Abiotic removal, Adsorption isotherms, Acid dyes, Adsorption kinetics.

INTRODUCTION

Dyes are one of those chemicals used in textile industry along with other chemicals and often receive most attention from many researchers in textile wastewater treatment due to the serious environmental problems they pose. Colours in receiving waters as well as toxicity are just some examples of those problems that dyes are causing. Dyes used in textile industry tend to be less biodegradable than many other carbonaceous wastes because the structures of dyes are designed to resist all kind of environmental conditions. This in turn makes dyestuff resistant to biological treatment as well. Therefore, dyes are subject to many different treatment technologies. However, in many cases treatment of textile wastewaters take place at municipal wastewater treatment plants using the activated sludge process. Hence, it is important to know the faith or the behaviour of the dyes in activated sludge treatment process since this is the common process in many parts of the world for the treatment of textile wastewaters.

According to Tchobanoglous *et al.*[1] for many toxic and recalcitrant organic compounds entering biological wastewater treatment processes, non-biological or abiotic losses may be more significant than biodegradation. Abiotic losses include adsorption of the compound to the mixed liquor solids in the reactor with subsequent transport out of the system by the waste sludge and volatilization with release of the compound to the surrounding atmosphere. For certain compounds adsorption can be more significant than biodegradation or volatilization[1]. Similarly, most of the dyes used in textile industry can be adsorbed by activated sludge[2,3]. Various workers[4-9] reported that adsorption is the main process for the partial or whole decolourization of wastewaters containing dyes. This sorption removal is often referred to as bio-elimination and its efficiency varies from dye to dye[3,10]. Several works[8,10-12] on dye adsorption by activated sludge indicated that adsorption depends on dye structure (molecular structure and the type and number of the position of the substituents in the dye molecule), colouring group and solubility for various group of dyes. For example, in basic dyes, the colouring group is cationic and shows good adsorption, while acid dyes where the colouring group is anionic, do not[12,13].

The adsorption properties of activated sludge were found to be similar to activated carbon in studies involving acid, direct, reactive, disperse and basic dyes[6]. Surface of the activated sludge is highly porous with a specific surface area of between 40-140 m^2/g dry solids[14]. In a recent work[13], a comparison of adsorption capacity of live activated sludge with same basic dye with various adsorbents showed that activated sludge has higher adsorption capacity than maize cob and bagasse pith while lower adsorption capacity than carbon, clay for the same basic dye. In a study by Zheng *et al.*[15] using aerobic granules for the adsorption of an acid dye (rhodamine B), it was demonstrated that acid dye was adsorbed by aerobic granules and the specific surface area of the aerobic granules for this acid dye was estimated as $18.57/m^2/g$ SS. The work also has demonstrated that based on the Langmuir constants, adsorption capacity of granules three times higher that flocks[15].

So far, it was already demonstrated that adsorption of various dyes from various classes by living or non-living activated sludge exhibit different adsorption properties[3,10,13,15-20]. The dyes used in this current work are currently being used in wool dyeing industry which is one of the subcategory of textile industry. Since the adsorption is the important part of abiotic removal of textile dyes during the biological treatment, aim of this work, therefore, is to investigate the adsorption properties of two acid dyes by live activated sludge.

EXPERIMENTAL

Total suspended solids (TSS) were measured by the standard gravimetric technique[21]. Residual dye concentrations were measured spectrophotometrically (Bausch and Lomb, Spectronic 21) as the absorbance at 403 nm for Lanaset yellow 4GN and 496 nm for Lanaset red G, which were the wavelengths giving maximum absorbencies.

The activated sludge was obtained from a full scale activated sludge plant treating soft drink industry wastewater. The sludge was used on the same day as it was sampled. The dyes were used in this experiment Ciba's azo metal complex dyes and obtained from local textile factory in Adana, Turkey. These were used without any further treatment.

Batch sorption tests: The sorption tests were conducted at 20 °C in conical flasks (1000 mL) using an orbital shaker in a constant temperature room. The activated sludge (250 mL) was added to aqueous solutions (250 mL) either of Lanaset yellow 4GN or Lanaet red G. Total suspended solids (TSS) concentration of activated sludge was 1625 mg/L during all experiments. Initial dye concentrations varied between 25 to 400 mg/L were used and the incubation time of the flasks ranged from 10 to 160 min. The data for deriving the Langmuir constants were obtained by using sludge and dye concentrations of 25, 50, 100, 200 and 400 mg/L. The contact time was 160 min. In both cases, after contacting the sludge solids were removed by centrifugation (20 min at 6000 rpm). The dye concentrations were then measured in the spectrophotometer. The amount of dyes adsorbed by the live activated sludge was calculated using the following equation;

$$q = V(C_i - C_e)/W$$

where q (mg/g) = amount of dye sorbed by activated sludge, C_i and C_e (mg/L) = initial and equilibrium dye concentration in liquid phase, V = volume of solution (L) and W = dry weight of the activated sludge (g).

RESULTS AND DISCUSSION

Initial adsorption tests: Initial adsorption tests for various initial dye concentrations for both acid dyes are shown in Fig. 1. It is evident that both acid dyes adsorbed for some degree and specific adsorption increased with increasing dye concentrations. This initial adsorption experiments have also showed that equilibrium was obtained in 160 min. Therefore, this time was used for the batch equilibrium time for the subsequent batch experiments.

Acid dyes are also called anionic dyes because of the negative electrical structure of the chromophore group. Longmuir[22] reported that under normal biological treatment pH conditions electrostatic repulsion between the anionic dye molecule and the negatively charged sludge surfaces is responsible for the poor adsorption. The contact time required for equilibrium conditions to be established with activated sludge was found 10 min or less[22]. There

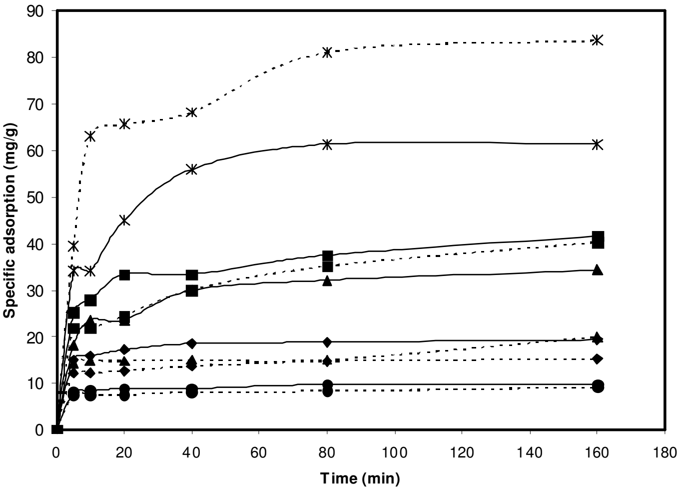

Fig. 1. Variation of specific adsorption for various initial dye concentrations (●) 25 mg/L, (♦) 50 mg/L, (▲) 100 mg/L, (■) 200 mg/L, (×) 400 mg/L (Lanaset yellow 4GN dotted line, Lanaset red G, solid line)

are various reports indicating the poor adsorption properties of acid dyes by activated sludge[11-13,17,22]. However, acid dyes used in this current study were adsorbed by activated sludge under pH conditions around 7.6.

Adsorption isotherms: Langmuir and Freundlich isotherms models were used in order to asses to nature of adsorption of acid dyes by live activated sludge. The linearized form of the Langmuir equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right)C_e$$

where C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e = equilibrium solid phase concentration (mg/g), K_L (L/g) and a_L (L/mg) = Langmuir constants.

The linearized form of the Freundlich model can be written as:

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e)$$

where C_e = equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e = equilibrium solid phase concentration (mg/g), K_f (L/g) and n = Freundlich constants. The initial batch sorption experiments showed that equilibrium had been achieved with in 160 min (Fig. 1). Therefore, this was used as the contact time for the subsequent work which derived values of Langmuir and Freundlich constants. The data obtained from further batch experiments conformed well to both models and plots of the linearized form Langmuir and Freundlich models for both dyes are shown in Figs. 2 and 3. The results of regression analysis are shown in Table-1. A comparison on q_{max} values obtained from Langmuir model showed that Lanaset red G was adsorbed significantly better than Lanaset yellow 4GN by live activated sludge. Various researchers[3,11,12] have showed that acid dyes can bind to activated sludge and adsorption properties acid dyes mainly depend on dye structures. Presence of hydroxyl, nitro, azo groups and size molecules increase adsor-ption while presence of sulfonic acid groups effect adsorption in a negative manner. Dyes used in this current work are not in pure form and they are mixture azo metal complex dyes. Therefore it is difficult to speculate these different adsorption properties of each dye. In fact it was the main aim of this work to investigate the faith of these commercial dyes in activated sludge treatment plant as it is used. Therefore, data should be treated in this way.

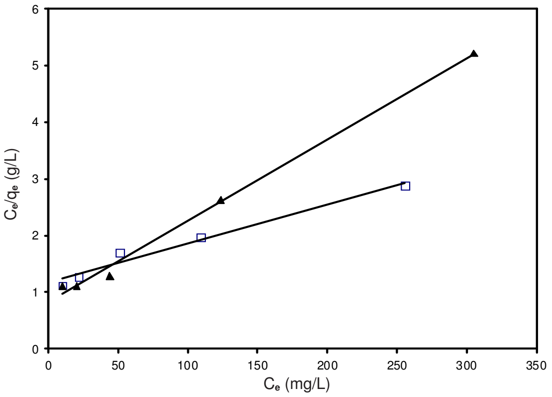

Fig. 2. Linearized Langmuir plots for Lanaset yellow 4GN (▲) and for Lanaset red G (□)

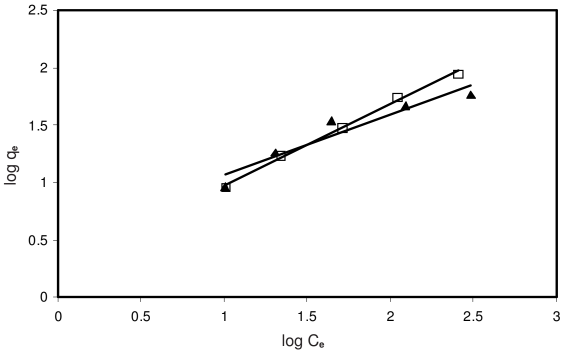

Fig. 3. Linearized Freundlich plots for for Lanaset yellow 4GN (▲) and for Lanaset red G (□)

TABLE-1
COMPARISON OF LANGMUIR AND FREUNDLICH CONSTANTS FOR VARIOUS DYE SLUDGE SYSTEMS

Absorbent	Dyes	Langmuir constant				Freundlich constants		
		q_{max} (mg/g)	a_L (L/mg)	K_L (L/g)	r	K_f (L/g)	n	r
Live activated sludge (current)	Lanaset yellow 4GN	69.48	0.0175	1.216	0.998	3.45	1.890	0.956
	Lanaset red G	144.91	0.0059	0.855	0.986	1.85	1.409	0.998
Dried activated sludge[16]	Reactive blue 2	250.0	0.0067	1.675	0.999	1.40	1.160	1.000
	Reactive yellow 2	333.3	0.0029	0.966	0.992	3.14	1.340	0.997
Live activated sludge[13]	Maxilon red BL-N	123.2	0.057	6.97	0.99	-	-	-

r = Correlation coefficient.

The dimensionless constant separation factor or equilibrium parameter (R_L)[23] is given by;

$$R_L = \frac{1}{1 + a_L C_0}$$

where a_L = Langmuir constant and C_0 = initial dye concentration. Values of R_L obtained for the various initial concentrations indicate favourable adsorption of both acid dyes on activated sludge because all the R_L values were between 0 and 1 (Table-2).

TABLE-2
VALUES OF R_L FOR EACH DYE TESTED

C_0 (mg/L)	Lanaset yellow 4GN	Lanaset red G
25	0.695	0.871
50	0.533	0.772
100	0.363	0.628
200	0.222	0.458
400	0.125	0.297

Thermodynamics of adsorption: It is well known fact that Gibbs free energy would define system spontaneity. Gibbs free energy (ΔG^{o}) can be calculated[24] from the following equations:

$$K_c' = C_a/C_e$$

$$\Delta G^{o} = -RT \ln K_c^{o}$$

where, K_c' = equilibrium constant, K_c^{o} = thermodynamic equilibrium constant, C_a = solid phase concentration in equilibrium (mg/L), C_e = equilibrium concentration in solution (mg/L), R = universal gas constant (J/mol K) and T = temperature (K). Thermodynamic equilibrium constant (K_c^o) can be calculated from the equilibrium constant by plotting equilibrium constant against initial dye concentration[25,26]. Values of Gibbs free energy calculated on this basis are -1.056 and -0.736 kJ/mol for Lanaset yellow 4GN and Lanaset red G, respectively. This negative value of the Gibbs free energy indicates the spontaneity of the sorption of the Lanaset yellow 4GN and Lanaset red G on to live activated sludge.

Kinetics of adsorption: It was already demonstrated that activated sludge has highly porous surface area[14]. For these types of adsorbent structures intraparticle diffusion may be rate limiting step[27]. In order to asses this option equation described by Weber and Morris[28] can be used:

$$k_p = \frac{q}{t^{1/2}}$$

where q (mg/g) = amount of dye adsorbed at time t and k_p intraparticle rate constant (mg/g $min^{-0.5}$).

Values of k_p for various initial dye concentrations are shown in Table-3. High correlation coefficients were obtained for both dyes. This indicates that intraparticle diffusion playing significant role for the adsorption of acid dyes. In fact in a recent work by Ho and McKay[29] using an acid dye and pith reported that "without the capability for ion exchange reactions the uptake capacity of acid dye is much less and the mechanism is possibly physical diffusion which is well represented by the intraparticle diffusion". This is in good agreement with work because both acid dye and live activated sludge has net negative electrical charge. Therefore, physical diffusion is playing significant role which is well represented with by high correlation coefficients. Table-3 also shows that intraparticle rate constants increased with increasing dye concentrations for both dyes.

TABLE-3
INTRAPARTICLE RATE CONSTANTS FOR VARIOUS INITIAL CONCENTRATIONS FOR LANASET YELLOW 4GN AND LANASET RED G

Initial concentration (mg/L)	Lanaset yellow 4GN		Lanaset red G	
	kp (mg/g per $min^{0.5}$)	r	kp (mg/g per $min^{0.5}$)	r
25	0.143	0.915	0.167	0.986
50	0.339	0.893	0.336	0.969
100	1.227	0.939	0.502	0.980
200	1.298	0.963	1.984	0.989
400	5.493	0.978	2.380	0.959

r = Correlation coefficient.

Kinetics of adsorption of both acid dyes by activated sludge was tested for first order Lagergren model, pseudo second order and second order models. It was already reported that for the adsorption of many materials pseudo second order model provides better fit than first order Lagergren or second order model[13,30-32]. Data in present work were examined for all three models. However, it was found that both first order Lagergren and second order model were not applicable to all data. Therefore no further consideration given to both models.

For the pseudo second order

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where q_t = amount of dye adsorbed (mg/g) by activated sludge at time t (min), q_e = amount adsorbed at equilibrium time (mg/g) and K (min^{-1}) = pseudo second order rate constant of adsorption (g/mg min)[30]. Linear plots of t/q_t *vs.* t are shown in Figs. 4 and 5 for Lanaset yellow 4GN and Lanaset red G, respectively. Values were derived for reaction rate constants and correlation coefficients for each initial dye concentration are shown at Table-4.

TABLE-4
PSEUDO SECOND ORDER RATE CONSTANTS FOR VARIOUS INITIAL CONCENTRATIONS FOR LANASET YELLOW 4GN AND LANASET RED G

Initial concentration (mg/L)	Lanaset yellow 4GN		Lanaset red G	
	K (g/mg min)	r	K (g/mg min)	r
25	0.0661	0.999	0.0398	0.998
50	0.0289	0.999	0.0254	0.999
100	0.0055	0.998	0.0084	0.987
200	0.0049	0.997	0.0029	0.994
400	0.0032	0.998	0.0024	0.998

r = Correlation coefficient.

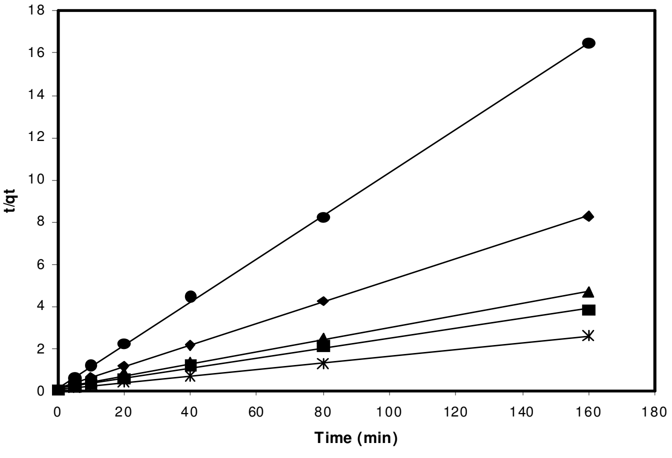

Fig. 4. Pseudo second order rate plots for Lanaset yellow 4GN
(●) 25 mg/L, (♦) 50 mg/L, (▲) 100 mg/L, (■) 200 mg/L, (✕) 400 mg/L

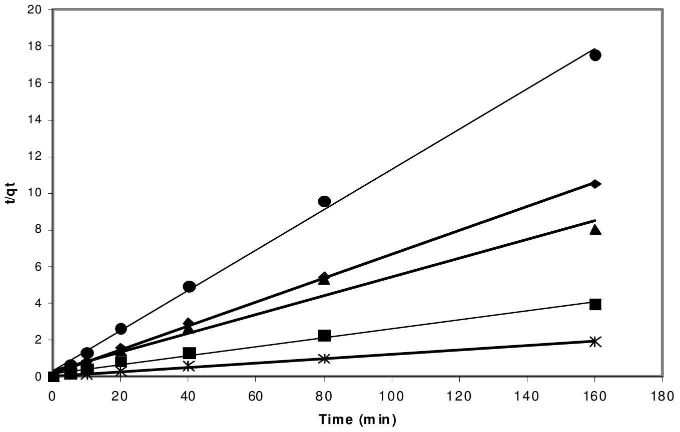

Fig. 5. Pseudo second order rate plots for Lanaset red G
(•) 25 mg/L, (♦) 50 mg/L, (▲) 100 mg/L, (■) 200 mg/L,
(×) 400 mg/L

It was seen that data derived from regression analysis pseudo second order reaction rate was the best describing with the correlation coefficient 0.999 for all initial dye concentrations. This is in good agreement with previous work performed by Basibuyuk and Forster[13] with live activated sludge and a basic dye.

Conclusion

Results from the work presented here showed that two acid dyes used in this work were adsorbed by live activated sludge. Although acid dye adsorption by live activated sludge is expected to be poor due to the negative charge in both acid dyes and activated sludge, however, the dyes used in current work were adsorbed to some degree and both acid dyes exhibited different adsorption results. Based on Langmuir constants, maximum removal capacities were 69.48 mg/g for Lanaset yellow and 144.91 mg/g for Lanset red G. This along with negative free energy results calculated for both dyes shows that abiotic removal is possible for these particular acid dyes when activated sludge treatment is applied.

According to results obtained, film diffusion was found to be playing important role for the initial adsorption and also intraparticle diffusion was significant. Examination of kinetic models for both acid dyes indicated that overall adsorption process was best described by the pseudo second rate model rather than second order model or first order Lagergren model.

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