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Sorption Kinetics for Dye Removal From Aqueous Solution Using Natural Clay

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Abstract

The kinetics of the adsorption of Congo red onto natural clay has been studied in an agitation batch adsorber. The Furusawa model has been used to determine the external transfer coefficient for the system and the effect of several experimental variables have been investigated: these include agitation, initial dye concentration, clay mass and clay particle size. The mass transfer coefficient has been correlated with the system variable by the following equation: $k_f = A(\text{variable})^B$.

Keywords: dyes, adsorption, mass transfer, clay

1. Introduction

Synthetic dyestuffs can exist in the effluents of wastewater from different industries such textiles, paper, leather, plastics, etc. [1]. Discharge of wastewater into natural streams and rivers from the industries using dyes poses severe environmental problems. Even small quantities of dyes can color large water bodies, which not only affects aesthetic merit but also reduces light penetration and photosynthesis. In addition, most of dyes are either toxic or mutagenic and carcinogenic [2, 3]. For these reasons, the removal of dyes from process or waste effluents becomes environmentally important.Conventional wastewater treatment plants are not suited to remove the dyes due to their non-biodegradable features [4]. Therefore, alternative methods have been developed to remove the dyes from wastewater, namely, coagulation and flocculation [5], membrane separation [6], oxidation or ozonation [7, 8], electro-coagulation [9], and adsorption [10, 11].Among these methods, adsorption currently appears to offer the best potential for entire treatment [12]. Although activated carbon is the most widely used adsorbent for wastewater treatment, it is very expensive and has high operating costs due to the high price of the activated carbon and to the high water flow rate always involved.

Those costs can be greatly increased when there are a locally lack of carbon regeneration [13]. Consequently, in recent years, considerable attention has been devoted to the study of different types of low-cost materials in order to remove the pollutants from aqueous phase [14, 15]. Many workers have employed the perlite [16], biomaterial [17], recycled alum sludge [18], zeolites [19], clay [20], agriculture waste residues [21] for removing the dyes from wastewater. Previously, efforts have been concerned by equilibrium adsorption isotherms of certain dyes on clay [22-24]. Data have mainly served to predict capacity of dye adsorption systems using natural clay. However, this work studies kinetics of the adsorption of congo red on natural clay.

2. Material and Methods

2.1 Clay

The Tunisian clay used was essentially in the sodium form and could therefore be described as sodium bentonite. It contained ca, 56-68% of sodium smectite which is the most valuable type of smectite. The total amount of non-claymaterialsreachs up 20%. Quartz, some calcite and a small amount of kaolinite form a major impurity. The external surface area of the clay's crude sample $71 m^2/g$ was recorded using a Carlo Erba Sorptomatic 1800 surface analyzer with nitrogen as the sorbent. Based on mercury porosimetry usage and specific gravity bottles, the porosity and density of the adsorbent were determined as 36% and

2.05g/cm^3, respectively [22].
The cation-exchange capacity of the clay as determined by the copper-ethylenediamine method was ca. 80 mequiv/100g calcined material. The adsorbent was not labour during low demand seasons is considered a waste of resources. Absenteeism is the measure of unplanned absences from workplace due to some reasons like personal emergency, accident, illness, etc. Turnover occurs when an active worker resigns from the company of his own accord, thus leaving a vacant post until a replacement is found. If such disturbance has caused a large number of tasks become unattended and overdue, the company is then vulnerable to overtime cost, shrunk capacity and productivity, extra queuing time, lost business income, etc. In order to prevent these deteriorative effects, optimising the number of workers can be helpful. As a fundamental branch of knowledge in manufacturing business, workforce management will never fall behind the times. Therefore, it is worth an attempt to incorporate a novel methodology, such as HMS, into the state of the art of workforce sizing.

subjected to any form of pre-treatment other than washing the clay with distilled water to remove adhering impurities and drying at 160°C.

2.2 Congo red

Congo red (CR) labeled Merck (C.I. 22120), was retained as an anionic disazo direct dye, containing NH_2 and SO_3 functional groups (see Fig.1). It has a maximum absorbency at wavelength 500nm on a UV vis spectrophotometrer. The chemical formula and molecular weight of CR is $C_{32}H_{22}N_6$ $Na_2O_6S_2$ and 696.7g/mol respectively.

3. Theory

3.1 Kinetic Studies

It is necessary to study the kinetics of adsorption in batch systems in order to determine the rate limiting step in the adsorption process. The mechanism of solute adsorption onto an adsorbent consists on several steps. However, for the purposes of this work the overall adsorption processes is assumed to occur in the following three steps;

(i) mass transfer of solute from bulk solution to the particle surface;
(ii) adsorption of solute onto sites; and
(iii) internal diffusion of solute via either a pore diffusion model, or homogenous solid phase diffusion.

In the process of establishing step, step (ii) is assumed rapid and thus not considered in any kinetic analysis. Consequently, the two rate limiting steps considered are external mass transfer and intraparticle diffusion.

The development of models based on two such mass transport steps is quit complex, requiring a coupling equation and its subsequent solution. Initially, therefore, simplifying assumptions were made attempts to describe the adsorption processes in terms of an external mass transfer coefficient have been undertaken

3.2 External Mass Transfer Furusawamodel [25]

In a well agitated adsorber mixing the liquid phase is rapids.Hence, the concentration of a solute in the liquid phase and the concentration of adsorbent particles in *the liquids are essentially uniform throughout the vessel. A more rapid method of determining the external mass transfer coefficient, k_f, is possible, from the boundary condition shown in equation (1).*

$$\left[\frac{d\,C_t/C_0}{dt}\right]_{t=0} = -k_f A_p \qquad (1)$$

A_p is the external surface area of the clay particles. Thus $k_f$could be obtained simply by drawing a tangent to the curve, C_t/C_0versus time, through the origin.The k_f values can be correlated by the following equation:

$k_f = A\ (variable)^B$
or in the logarithmic form:

$$Ln(k_f) = ln\ (A) + B\ ln\ (variable) \quad (2)$$

Where the variable can represent agitation speed, initial dye concentration, clay mass or clay particle size.

3. Results and discussion

4.1. Effect of agitation

Figure 2 shows the experimental results obtained from a series of contact time studies for the adsorption of (CR) on clay in which the degree of agitation, N, was varied. The curves represent concentration-time profiles for moderately contact times.

The experiments were conducted over a 3h period. The results indicate that the rate of adsorption of CR dye is controlled by the degree of agitation. Thus, the boundary layer resistance to mass transfer is reduced by increasing agitation. The external mass transfer coefficients, k_f, have been determined using equation (1) and were plotted as ln (k_f) versus ln(N) as shown in Fig.3. From this figure, alinear variation can be observed.The data indicates that the external adsorption of dye on clay controlled by the degree of increasing agitation diminishes the boundary layer resistance to mass transfer and increase the mobility of the system. From k_f values shown in Table 1 we found: A=1.26 10^{-9} and B = 1.81 .

4.2 Effect of Initial Dye Concentration

The initial dye concentration of an effluent is important since a given mass of mass clay can only adsorb a certain amount of dye. Therefore, the more concentration an effluent, the smaller is the volume of effluent that a fixed mass of clay can purify. The influence ofinitial dye concentration was studied and the range of concentrations was varied depending on the amount of colouring matter in the commercial salt. Experimental results are shown in Fig.4 for the adsorption of (CR) on clay. At high concentrations the lines lie close together and fractional adsorption is low. However, for low concentrations the initial uptake of dye is rapid, indicating a rapid surface reaction. Consequently, the concentration of dye in effluent will greatly affect the extent and rate of dye uptakes on clay.

Fig.4. Effect of initial dye concentration.The external mass transfer coefficients, k_f, were determined as before and were plotted as ln(k_f)versus ln(C_0) as shown in Fig.5. Linear variation was observed. The results are presented in Table 1.The external mass transfer coefficients are increasing as C_0 decreases for the dye CR being adsorbed onto clay. The values of A and B are respectively equal to 17.10^{-5} and-0.66.

4.3 Effect of Particle Size Range

The influence of contact time on dye ranges of particle size of clay was investigated using the size ranges listed in Table 1.The experimental results are shown in Fig.6. The data shows an increase in the rate of dye uptake as the mean diameter of clay decreases. This observation is in agreement with the proposed mechanism, as the large external surface area removes more dye in the initial stages of the adsorption process than large particles.

The external mass transfer coefficients, k_f, were determined as before and are listed in Table 1. Figure 7 shows the ln(k_f) versus ln (dp) correlation of dye (CR), and a linear graph was obtained indicating that k_f varies with dp in a definite logarithmic manner. It is observed that increasing the mean particle diameter, dp, results in a decrease in the external mass transfer coefficient, k_f.

The values of A and B are respectively equal to 57, 9 10^{-5} and -0.71.

4. 4. Effect of Clay Mass

The effect of clay mass was studied on the dye (CR) when experimental conditions were maintained constant. In all cases the rate of dye uptake increased with increasing clay mass; the results are shown in Fig.8 as plot of C_t/C_0 versus time. The external mass transfer coefficient depends on the driving force per unit area, and in this case, since C_0 is constant, increasing the mass of clay increases the surface area for

adsorption and hence the rate of dye removal is increased. Since the particle size range is constant the surface area will be directly proportional to the mass of clay in the system. From figure 9 we found: A = 2610^{-5} and B = 0.8.

4.5 Comparison with Various Adsorbent.

The comparison of the external mass transfer coefficient k_f of Tunisian bentonite clay with various adsorbent is given in Table 2. Even studied couple's diversity, the external mass transfer coefficient, k_f, remains in the range 10^{-5} - 10^{-4} m/s.

5. Conclusion

The external mass transport phenomena which influence the extent and initial rate of uptake of congo red (CR) on clay have been studied. A general model has been proposed which enables the external mass transfer coefficient to be determined. The external mass transfer coefficient has been found to vary linearly with agitation, initial dye concentration, clay particle size, mass of clay, according to the general equation: k_f= A (variable) ^{B}. The constants A and B have been determined for each variable. It appears that the rate of dye removal increases with the agitation speed, the particle size and mass of adsorbent but it decreases with the initial concentration. The external mass transfer coefficient, k_f, and the results shows that this coefficient is in the range of 10^{-5} - 10^{-4} m/s.

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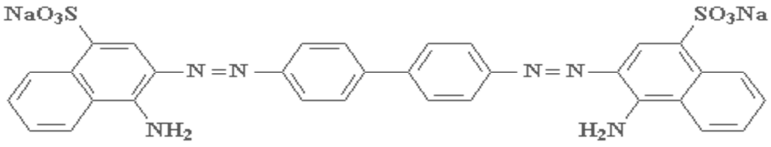

Figure1. Structure of Congo red Dyestuff.

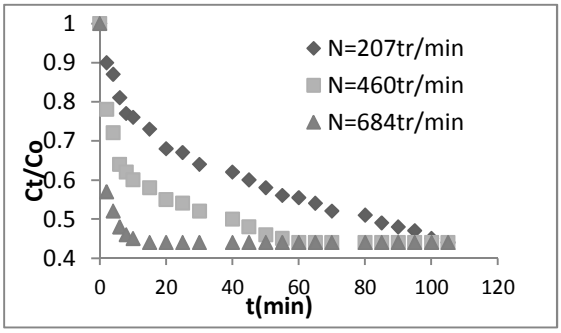

Figure2. Effect of Agitation.

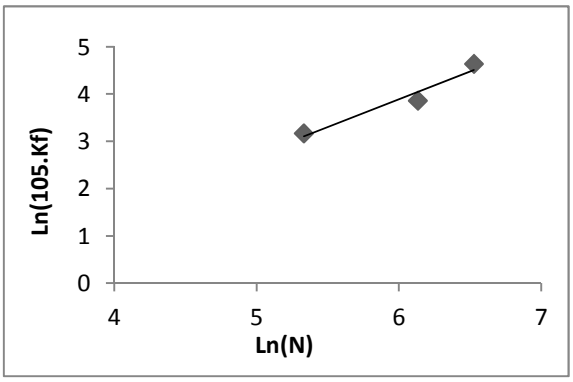

Figure 3. Plot of ln (k_f) versus ln (N).

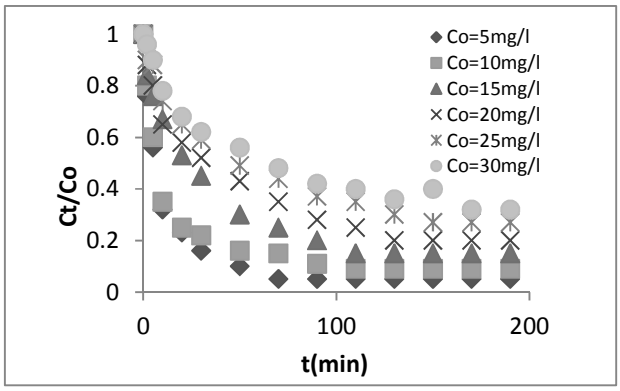

Figure 4 Effect of Initial Dye Concentration.

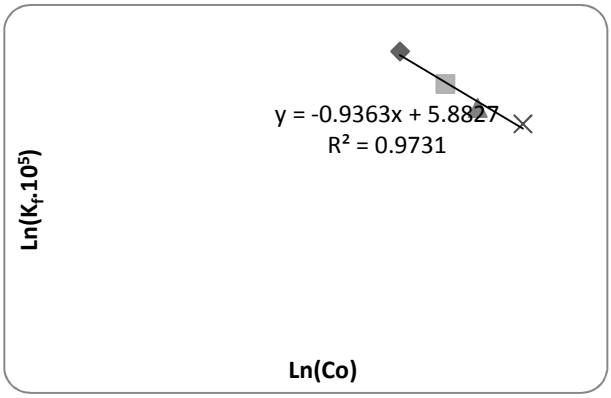

Figure 5. Plot of ln (k_f) versus ln (C_0).

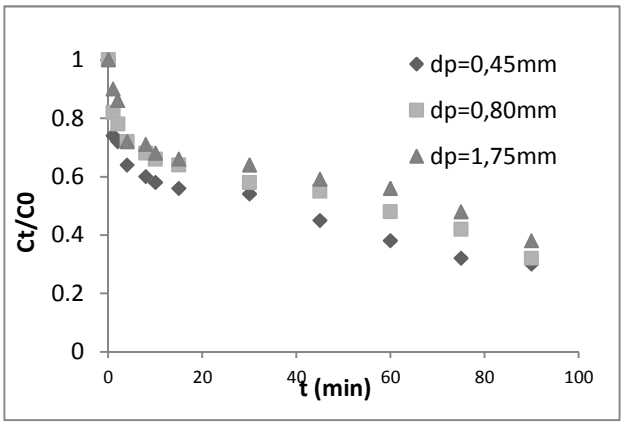

Figure 6. Effect of particle size range

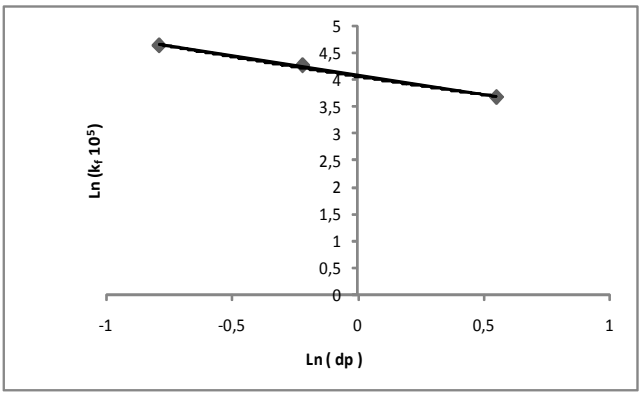

Figure7. Plot of ln (k_f) versus ln (dp).

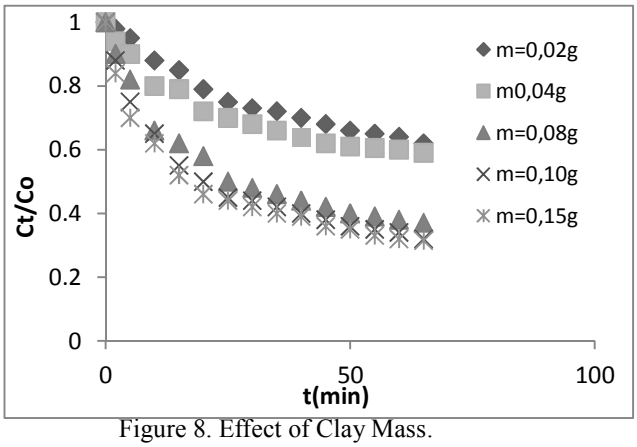

Figure 8. Effect of Clay Mass.

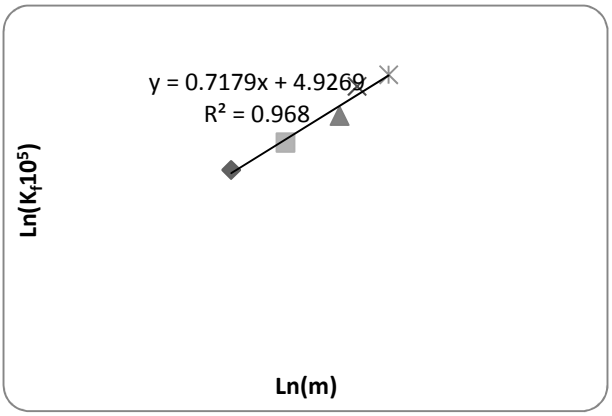

Figure 9. Plot of ln (k_f) versus ln (m).

Table 1. External Mass Transfer Coefficients k_f.

Effect of		$k_f(10^{-5}$ m/s)
N (tr/min)	207	1.90
	460	8.33
	684	16.30
C_0 (mg/l)	5	5.10
	10	4.90
	15	2.65
	20	2.50
	25	1.90
	30	1.67
m (g)	0.02	0.80
	0.04	1.60
	0.08	2.80
	0.10	3.80
	0.15	4.50
dp (mm)	0.45	0.28
	0.80	0.19
	1.75	0.11

Table 2. Comparison of the External Mass Transfer Coefficient k_f with Various Adsorbent.

Adsorbent	Variable	Dyes	Variable				Ref.
			N (tr/min)	C_0 (mg/l)	m (g)	T (K)	
Peat	$20 \leq C_0 \leq 1000$mg/l $100 \leq N \leq 600$rpm $291 \leq T \leq 353$ K	Telon Blue	$K_1 N^{0.26}$	$K_2 C_0^{-1.1}$	-	$K_3 T^{5.5}$	[27]
Maize cob	$75 \leq C_0 \leq 400$mg/l $75 \leq N \leq 600$ rpm $0.85 \leq m \leq 3.40$ g	BB 69	$6.610^{-4} N^{1.223}$	$0.734\ C_0^{-1.30}$	$25.410^{3} m^{0.4}$	-	[28]
		BR 22	$5.0210^{2} N^{0.69}$	$0.080\ C_0^{-0.83}$	$5.0510^{1} m^{0.5}$	-	
Bagasse pith	$25 \leq C_0 \leq 300$mg/l $100 \leq N \leq 600$ rpm $0.425 \leq m \leq 3.40$ g $293 \leq T \leq 353$ K	AB 25	$10^{-3}\ N^{0.993}$	$9\ C_0^{-0.67}$	$0.553\ m^{-0.154}$	$0.2^{8} T^{6.28}$	[29]
		AR 114	$410^{-3}\ N^{0.897}$	$22\ C_0^{-0.792}$	$0.631\ m^{-0.081}$	$0.3^{10} T^{3.7}$	
		BB 69	$1.410^{-2} N^{0.981}$	$84\ C_0^{-0.644}$	$3.28\ m^{-0.19}$	$0.1^{10} T^{4.9}$	
		BR 22	$2\ 10^{-3}\ N^{1.19}$	$128\ C_0^{-0.771}$	$2.93\ m^{-0.224}$	$0.4^{15} T^{6.2}$	
Kaolinite	$C_0 \leq 50$ mg/l	BM	$10.59\ C_0^{-1.02}$				[30]
Bentonite	$5 \leq C_0 \leq 30$mg/l $207 \leq N \leq 684$ rpm $0.02 \leq m \leq 0.15$ g $0.45 \leq dp\ 1.75$mm	RC	$17.110^{-5}\ C^{-0.66}$ $1.26\ 10^{-9}\ N^{1.81}$ $26\ 10^{-5}\ m^{0.88}$ $57.910^{-5}\ dp^{-0.71}$				This work