

STUDIES ON THE USE OF ORANGE PEEL FOR ADSORPTION OF CONGO RED DYE FROM AQUEOUS SOLUTION

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ABSTRACT

Low-cost orange peel was prepared and used as adsorbent for the removal of Congo red dye from aqueous solution. The effect of contact time, adsorbent dose; adsorbent size, initial dye concentration, pH, and kinetics of adsorption were investigated. The adsorption process attained equilibrium after about 60 minutes. Dye removal increased with increasing contact time, and solution concentration; but decreased with increasing adsorbent size, adsorbent mass, and pH. The Langmuir isotherm equation fitted better than the Freundlich equation. The maximum adsorption capacity (q_m) was 18.94. The kinetic data were analyzed using the pseudo-first order, pseudo-second order, and intraparticle diffusion models. The result showed that the data fitted better to the pseudo-second order kinetic model. Orange peel, a low-cost and an easily available waste material can be an alternative for the more costly adsorbents for wastewater treatment.

Keywords: Adsorption; Aqueous solution; Isotherm; Congo red; Orange peel; Kinetics

1. INTRODUCTION

Dyes and pigments are commonly used by many industries in colouring their products. Such industries include textile, paper, carpets, rubber, plastics foods etc. The discharge of wastewaters from these industries into natural streams cause many significant environmental problems such as increasing the toxicity and chemical oxygen (COD) demand of the effluent, and also reducing light penetration; this causes a negative effect on photosynthetic processes of aquatic plants [1-2]. Some of the dyes and their breakdown products are either toxic, mutagenic, and/or carcinogenic [3-4]. Dyes may cause severe damage to humans, such as: dysfunction of the kidney, reproductive system, liver, brain, and central nervous system [5-7].

The removal of dyes/colours from wastewater before discharge into the environment is therefore an environmentally important challenge. There is therefore need to develop effective and efficient processes for the removal of dyes from industrial wastewaters. Many physical and chemical methods have been used for the treatment of dye-containing effluents; these include adsorption, coagulation, precipitation, filtration, and chemical oxidation; electrochemical and anaerobic microbial degradation. Adsorption appears to be the more preferred over all other methods because of its cheapness and the quality of the treated effluents especially for well-designed sorption processes [8]. Activated carbon has been the most widely used adsorbent for this process; however its use has been limited by its high cost [9-12]. This has necessitated the search for other alternative adsorbents. Various other alternatives have been tried with varying degrees of successes for the removal of colour from effluents; these include coal, fly ash, wood, silica gel, agricultural wastes (maize cob, coconut shell, rice husk, etc.) [13-14].

The purpose of this work is to test the adsorptive capacity of orange peel, a natural waste material, for the removal of Congo red dye from aqueous solution. Congo red is an anionic dye widely used in textile, paper, rubber and plastic industries. It is very stable in aqueous medium; moderately resistant to light and oxidizing agents, thus it is very difficult to be biodegraded [15]. Orange peel consists mainly of cellulose, pectin, hemicelluloses, lignin, chlorophyll, pigments and other low molecular weight hydrocarbons [16]. These components contain various functional groups such as carboxyl and hydroxyl groups which make orange peel a potential for removing metal ions [17-21]. The effects of contact time, adsorbent mass, adsorbent size, initial dye concentration, pH, and kinetics of adsorption were studied.

2. MATERIALS AND METHODS

2.1 Materials

Orange peels were obtained from a local fruit stall in Auchi, washed several times with distilled water to remove all dirt and adhering particles. The washed peels were air dried in an oven at 100 – 110 °C for 24 hours [22]. The dried materials were crushed and ground using a domestic blender. The adsorbent was sieved through 212 μ m and 100 μ m, and used without further treatment. Congo red (CI: 22120; chemical formula: $C_{32}H_{22}N_6O_6Na_2$; molecular weight: 696.9 g/mol; λ_{max} : 500nm), obtained from Sigma chemical company, USA was used without further purification. A stock solution of 1000 mg/L was prepared, and working solutions were prepared by diluting the dye stock solution to the required concentrations.

2.2 Method

The effect of contact time on amount of dye adsorbed was investigated at 60 mg/L dye solution. For the other adsorption experiments, 50 cm³ of dye solution of initial dye concentration was stirred with a certain amount of adsorbent at desired pH and temperature at 1500 rpm for 80 minutes. The pH of solution was adjusted by adding 0.1M HNO₃ or 0.1M NaOH by using a Hanna Instrument pHep pH meter. At the end of an adsorption period, the mixture was centrifuged for 25 minutes at 4000 rpm. The supernatant solution was taken with a syringe and the equilibrium dye concentration was analyzed using a JENWAY 6505 UV/VIS spectrophotometer set at $\lambda_{max} = 500nm$.

The amount of dye adsorbed onto the peels was calculated by a mass balance relationship (Eq.1).

$$q_e = (C_i - C_e)V/m \quad (1)$$

where q_e is the amount of dye adsorbed at equilibrium per gram of adsorbent, C_i and C_e are the initial and equilibrium concentration of dye solutions respectively (mg/L), V is the volume of solution (L), and m is the mass of dry adsorbent used (g).

The procedure for the kinetics experiments were more or less the same as those of equilibrium tests. Aqueous samples were withdrawn at predetermined regular intervals, and the dye concentrations measured in a similar way.

3. RESULTS AND DISCUSSIONS.

3.1 Adsorption isotherms

Adsorption isotherms are required for the design of adsorption systems. The equilibrium relationship between the amount of adsorbate in solution and that adsorbed was studied. The results provide information about the capacity of the adsorbent (i.e. the amount of adsorbent) required to remove a unit mass of the adsorbate under the given conditions. The data obtained in the present study were analyzed using the Langmuir and Freundlich isotherm equations respectively. Equation (2) is the Langmuir isotherm:

$$C_e/q_e = 1/k_L q_m + (1/q_m)C_e \quad (2)$$

Where C_e is the concentration of the adsorbate at equilibrium (mg/L), q_e is the amount of the adsorbate removed at equilibrium per unit mass of adsorbent (mg/g). q_m is the monolayer adsorption capacity at equilibrium (mg/g), and k_L is the Langmuir equilibrium constant (l/mg). Their values were obtained from the slope and intercept respectively of the linear plot of C_e/q_e against C_e .

Equation (3) is the Freundlich isotherm:

$$\log q_e = \log k_f + 1/n \log C_e \quad (3)$$

where k_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. Their values are obtained from the intercept and slope respectively from the linear plot of $\log q_e$ against $\log C_e$.

The values of the Langmuir and Freundlich isotherm constants are presented in Table 1. From the values of the linear regression correlation coefficients R^2 , the adsorption of Congo red by orange peel seemed to have been slightly better described by the Langmuir isotherm than the Freundlich isotherm (0.9993>0.9954). This may suggest homogeneous monolayer coverage of the adsorbate on the adsorbent surface [23]. On the other hand, the value of the Freundlich constant $1/n$, (0.501: <1) suggests a favourable adsorption intensity.

Table 1. Langmuir and Freundlich isotherm parameters for adsorption of Congo red by orange peel.

Langmuir constants		Freundlich constants			
q_m (mg/g)	k_L (L/mg) R^2	k_f	$1/n$	R^2	
18.94	0.06	0.9993	2.236	0.501	0.9954

3.1.2 Effect of initial concentration with respect to time.

The adsorption of dye on orange peel was shown to increase with time; dye adsorption rate initially increased rapidly, and attained equilibrium after about 60 minutes and thereafter remained almost constant. The amount of dye adsorbed at equilibrium, q_e increased with increase in initial dye concentration as shown in Figure 1. Dye uptake is concentration dependent. The increase in loading capacity of the adsorbent for dye ions may be due to a higher driving force for mass transfer at a higher initial dye concentration, the more concentrated the solution, the better the adsorption [24].

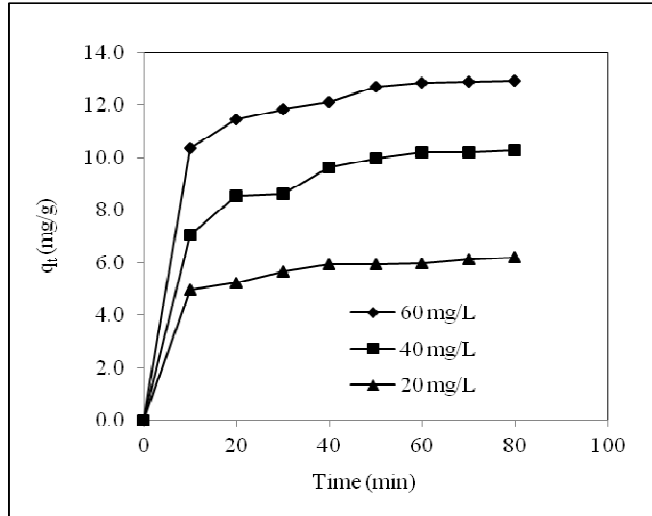


Fig. 1. Effect of initial dye concentration on adsorption of Congo red onto orange peel:
 (Temp. = 28 °C; pH = 7; adsorbent dose = 0.1g adsorbent size = 100 μ m)

3.1.3 Effect of adsorbent mass.

Adsorbent dosage is an important factor in adsorption. It determines the capacity of an adsorbent for a given initial adsorbate concentration. There was an increase in the percentage of dye adsorbed; this was due to the increase in adsorption sites at the surface of the adsorbent as the adsorbent dosage was increased [25]. However as shown in Figure 2, the amount of dye adsorbed per unit mass of adsorbent decreased as the adsorbent dosage was increased. This decrease is explained by fact there is a split in the flux or concentration gradient between the concentration of dye in solution and the dye on the surface of the adsorbent [26].

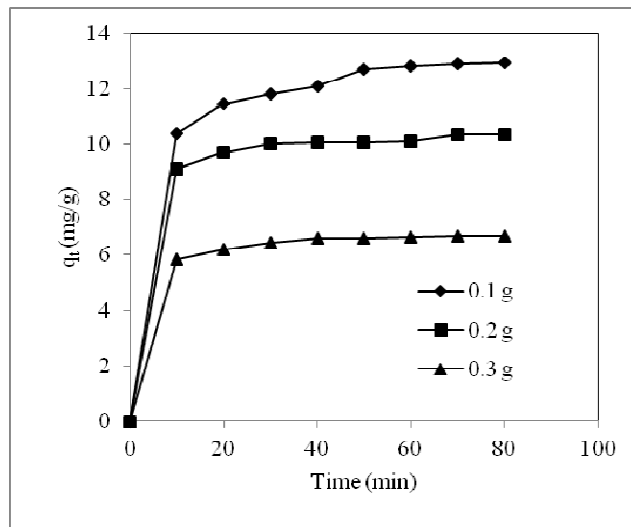


Fig. 2. Effect of adsorbent dose on adsorption of Congo red onto orange peel:
 (Temp. = 28 °C; pH = 7; conc. = 0.60mg/L; adsorbent dose = 0.1 g; adsorbent size = 100 μ m)

3.1.4 Effect of adsorbent particle size.

The amount of dye adsorbed per unit mass of adsorbent increased as the adsorbent size decreased. This is shown in Figure 3. The relatively higher adsorption with smaller adsorbent particle size may be due to the fact that smaller particles yield larger surface areas. This meant that the number of available adsorption sites increased accordingly, thereby leading to the increase in adsorption capacity.

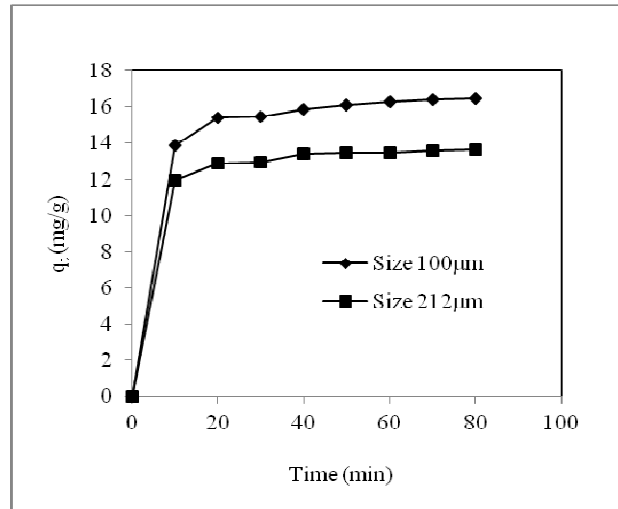


Fig. 3. Effect of adsorbent size on adsorption of Congo red onto orange peel:
(Temp. = 28 °C; pH = 7; conc. = 0.60mg/L; adsorbent dose = 0.1 g)

3.1.5 Effect of solution pH.

The pH is a measure of the acidity ($\text{pH} < 7$) or alkalinity ($\text{pH} > 7$) of an aqueous solution. The pH of the dye solution is a very important factor in the adsorption process, especially on adsorption capacity [27]. The effect of pH on the adsorption of Congo red by orange peel with respect to time is shown in Figure 4. The solution pH was found to affect the amount of dye adsorbed. The dye adsorption increased with decrease in pH. As the pH solution decreased, the positive charge on the solution interface increased, and thus the adsorbent surface became more positively charged; this enhanced the adsorption of the negatively charged Congo red dye through electrostatic forces of attraction.

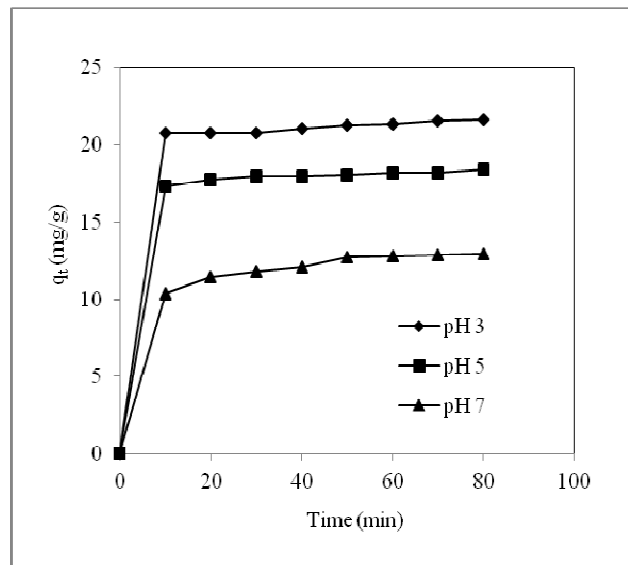


Fig. 4. Effect of pH on adsorption of Congo red onto orange peel:
(Temp. = 28 °C; conc. = 0.60mg/L; adsorbent dose = 0.1 g; adsorbent size = 100µm)

3.2 Adsorption kinetics

The adsorption kinetics was studied in order to have a better understanding of the dynamics of adsorption of the dye ions onto the orange peel adsorbent. The applicability of the pseudo-first order, pseudo-second order, and intraparticle diffusion models were tested for the adsorption of Congo red onto orange peel powder. The best-fit model chosen was based on the values of the linear regression correlation coefficient, R^2 .

Figure 1 shows the plot of the amount of dye adsorbed (mg/g) against time at different initial dye concentrations (20 mg/L, 40 mg/L, 60 mg/L). It was observed that the amount of dye adsorbed increased with contact time at all concentrations. In addition, the amount of dye adsorbed increased with increase in concentration. It was also observed that dye adsorption was rapid for the first 10 minutes and thereafter proceeded at a slower rate and finally became constant (i.e. reached saturation). These observations showed that the equilibrium time was independent of initial dye concentration

The pseudo-first order kinetic model is one of the kinetic models that have been widely used to predict dye adsorption kinetics. A linear form of it was described by Lagergren [28] (under initial and end boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$) as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (4)$$

where

q_e and q_t are the amount of dye adsorbed (mg/g) at equilibrium and at time t respectively, k_1 is the pseudo-first order rate constant of adsorption (min^{-1}).

A plot of $\log(q_e - q_t)$ against t of equation (4) should give a linear relationship from which q_e , and k_1 can be determined. Figure 5 is the result of plotting $\log(q_e - q_t)$ against t . The calculated q_e , k_1 , and the corresponding linear regression correlation coefficient R_1^2 values are also shown in Table 2.

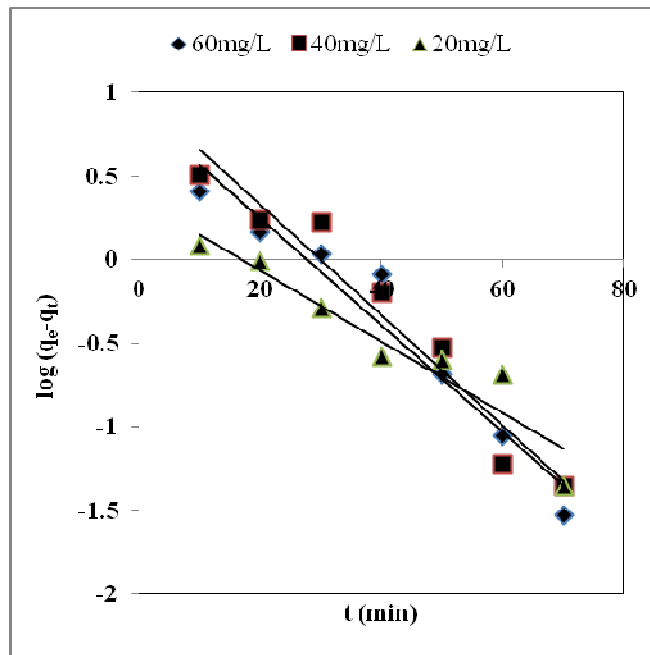


Fig. 5. Pseudo-first order plots of adsorption of Congo red on orange peel
 (Temp. = 28 °C; pH = 7; adsorbent dose = 0.1 g; adsorbent size = 100 μ m)

The adsorption experimental data were also analyzed using Ho's pseudo-second order kinetic model [28]. Under the initial and end boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the linear form is represented as:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (5)$$

where k_2 is the pseudo-second order rate constant of adsorption (g/mg min.).

If the initial adsorption rate, h (mg/gmin) = $(k_2 q_e^2)$ then equation (4) becomes:

$$t/q_t = 1/h + t/q_e \quad (6)$$

A plot of t/q_t against t of equation (6) should give a linear relationship from which q_e , and k_2 can be determined from the slope and intercept respectively of the plot.

Figure 6 is the result of plotting t/q_t against t . The calculated values of q_e , k_2 , h , and the corresponding linear regression correlation coefficient R_2^2 are also shown in Table 2. The linear regression correlation coefficients for the pseudo second-order kinetics model R_2^2 , are greater than 0.99. This shows that the adsorption reaction can be approximated with the pseudo second-order kinetics model.

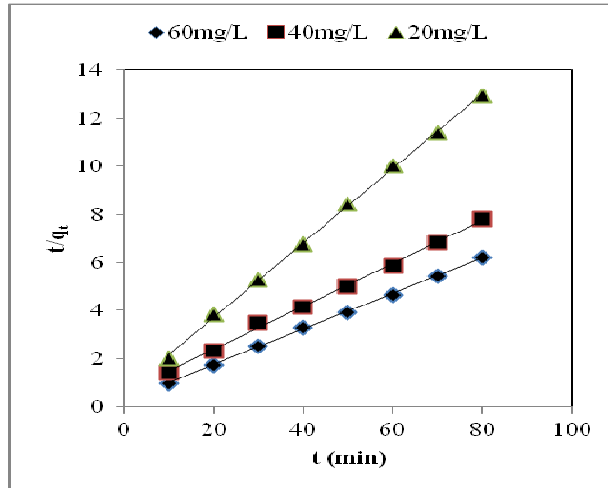


Fig. 6. Pseudo-second order plots of adsorption of Congo red on orange peel
 (Temp. = 28 °C; pH = 7; adsorbent dose = 0.1 g; adsorbent size = 100 μ m)

Adsorption process also incorporates the transport of adsorbate species from the bulk of the solution into the pores of the adsorbent through an intraparticle diffusion process [29]. Intraparticle diffusion could be the rate-limiting step in this case. This was tested by using the intraparticle diffusion model [30]:

$$q_t = k_{id}t^{1/2} + C$$

where C is the intercept, and k_{id} is the intraparticle diffusion rate constant. The values of q_t were plotted against those of k_{id} ; linear relationship was observed (Figure 7). The values of k_{id} , C , and the corresponding linear regression correlation coefficients R_3^2 are shown in Table 2. The value of the intercept is an idea of the thickness of the boundary layer; the larger the intercept, the greater the boundary layer effect [31]. Though the plots were slightly linear (R_3^2 values between 0.9334, 0.9128, and 0.9343), the intercepts were greater than zero. This showed that intraparticle diffusion may not have been a prominent rate controlling step [32].

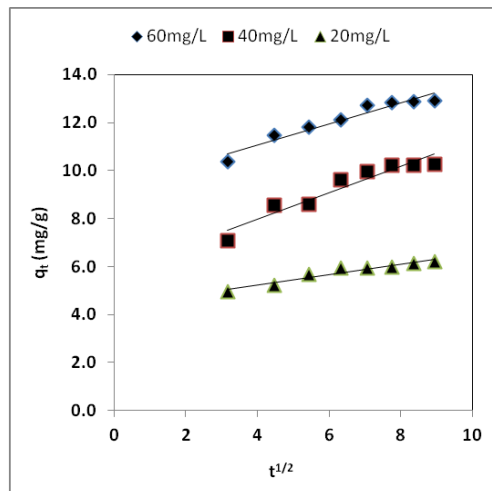


Fig. 7. Intraparticle diffusion plots of adsorption of Congo red on orange peel
 (Temp. = 28 °C; pH = 7; adsorbent dose = 0.1 g; adsorbent size = 100 μ m)

Table 2. Adsorption Kinetics parameters for the adsorption of Congo red by orange peel at different initial concentrations (mg/L).

	Conc. (mg/L)		
	20	40	60
Pseudo-first-order:			
k_1	0.0737	0.0762	0.0493
q_e	7.714	9.7051	2.3153
R_1^2	0.9446	0.9466	0.9089
Pseudo-second-order:			
K_2	0.02003	0.0136	0.0392
q_e	13.532	11.173	6.459
R_2^2	0.9995	0.9982	0.9993
h	3.668	1.668	1.635
Intraparticle diffusion:			
K_{id} (mg/g min ^{1/2})	0.215	0.552	0.436
C	4.375	5.759	9.324
R_3^2	0.9334	0.9128	0.9343

4. CONCLUSIONS

The use of orange peel for the adsorption of Congo red from aqueous solution was studied. Langmuir and Freundlich isotherm equations were used in testing the adsorption process. This study showed that orange peel, an agricultural waste material can be used as an adsorbent for the removal of Congo red dye from aqueous solution. It was found that the Langmuir isotherm equation, based on the value of the linear regression correlation coefficient R^2 , described the process better than the Freundlich isotherm equation. This showed the homogeneity of the surface of the orange peel adsorbent and the monolayer adsorption nature of Congo red on the orange peel adsorbent. The amount of dye adsorbed (mg/g) was found to increase with increase in contact time, initial dye concentration, and adsorbent dose; but decreased with increase in adsorbent size, adsorbent mass, and pH (i.e. increased with decrease in adsorbent size, adsorbent mass, and pH). The adsorption process was found to follow the pseudo second-order kinetics model with a good correlation.

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