Kinetics and Mechanisms Study of Congo red, Eosin B and Neutral red Adsorption from Aqueous Solutions on Kaolin

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Abstract

In this study, kaolin clay was used as the adsorbent for the removal of congo red, eosin B and neutral red from aqueous solutions. The effect of contact time was investigated and found that the adsorption process of dyes on kaolin surface was reached complete equilibrium within 60 min

The maximum uptake of congo red, eosin B and neutral red by kaolin clay were found to be 65.7%, 89.7% and 97.9%, respectively.

The kinetic data were well fitted to the lagergren, pseudo-second order models. The results obtained show that the second order rate constants of eosin – kaolin and neutral red – kaolin systems are much higher than that of congo red – kaolin system. This behavior was discussed depending on the chemical structure of dyes and kaolin surface.

The kinetics of dyes adsorption was also studied in terms of intraparticle diffusion model. The results indicated that intraparticle diffusion plays a significant role in the adsorption mechanism.

الخلاصة

يعنى هذا البحث بدراسة فعالية سطح الكاؤولين المتوفر محلياً لأمتزاز صبغة الكونغو الحمراء، الايوسين B و الاحمر المتعادل من محاليلها المائية، وكان الغرض من هذه الدراسة هو التعرف على ميكانيكيـة عمليـة امتزاز هذه الصبغات على سطح الكاؤولين.

أن الزمن اللازم لحدوث الاتزان في عملية امتزاز الاصباغ المذكورة أنفاً على سطح الكاؤولين هـو 60 دقيقة. وقد وجد ان كمية الامتزاز القصوى لصبغة الكونغو الحمراء ، الايوسين B و الاحمر المتعـادل علـى سطح الكاؤولين هي 65.7% ، 89.7% و 97.9% على التوالي.

أظهرت نتائج حركية الامتزاز بان عملية امتزاز الاصباغ على سطح الكـاؤولين تتبـع قـوانين

السرعة من المرتبة الاولى والثانية وقد بينت النتائج أن ثوابت السرعة لتفاعل المرتبة الثانية لانظمة (الايوسين B – كاؤولين) و(الاحمر المتعادل – كاؤولين) كانت أكبر مقارنة بثابت السرعة لنظام (الكونغـو الحمـراء – كاؤولين) وقد نوقشت النتائج على ضوء التركيب الكيميائي لكل من الاصباغ وسطح الكاؤولين.

طبق قانون الانتشار الضمني للدقائق لدراسة حركية امتزاز الاصباغ على سـطح الكـاؤولين وقـد أظهرت النتائج ان الانتشار الضمني للدقائق يلعب دوراً رئيسياً في عملية الامتزاز.

Introduction

Textile industries spend large amounts of water and chemicals for dyeing processes. Dye wastewater usually consist of a number of contaminants including acids, bases, dissolved solids, toxic compounds, and color. The colored compounds are not only esthetically displacing, but also impede ligh penetration in the pans, thus up setting the biological treatment process within the treatment plant. In addition, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. They, therefore, need to be removed or decolorized before the wastewater can be charged[1,2].

Adsorption is a widely used method for the treatment of industrial wastewaters containing colors, heavy metals and other inorganic and organic impurities[3-5]. The advantages of adsorption are its simplicity of operation, low costs (compared to other separation processes), and absence of sludge formation. Textile industries are the major consumers of water, and they release a fair amount of color in their effluents. Liquid-phase adsorption has been used effectively for the removal of dye form wastewater[5].

Sorption technology, including physical and chemical adsorption and ion exchange process technologies have the potential waters and industrial residues. In adsorption process, atoms or ions (adsorbates) contained in a fluid phase diffuse to the surface of a solid (adsorbent), where they are chemically bound to the surface or held there by intermolecular forces[6].

The most common adsorbents used for dye removal from wastewater are activated carbons[7,8]. Natural materials have also been investigated as potential industrial adsorption media[9-11]. Regarding the adsorption of dyes using clay minerals, kaolinite, bentonite and sepiolites have been described as adsorbents[12-14]. There are also reports on the removal of dyes by cotton[15,16], natural cellulose[17], sunflower stalks[18], agricultural wastes[19] and nanosize

modified silica[20].

The Aim of Present Work:

The aim of the present work is to explore the feasibility of utilizing kaolin clay as adsorbent to removal congo red, eosin B and neutral red dyes. Equilibrium and kinetic analysis were conducted to investigate the mechanism of dye adsorption and optimization of various parameters in dye recovery.

Materials and Methods

Instruments:

1- Visible spectrophotometer.

2- Dunboff metabolic shaking Incubater GCA/ precision Scientific.

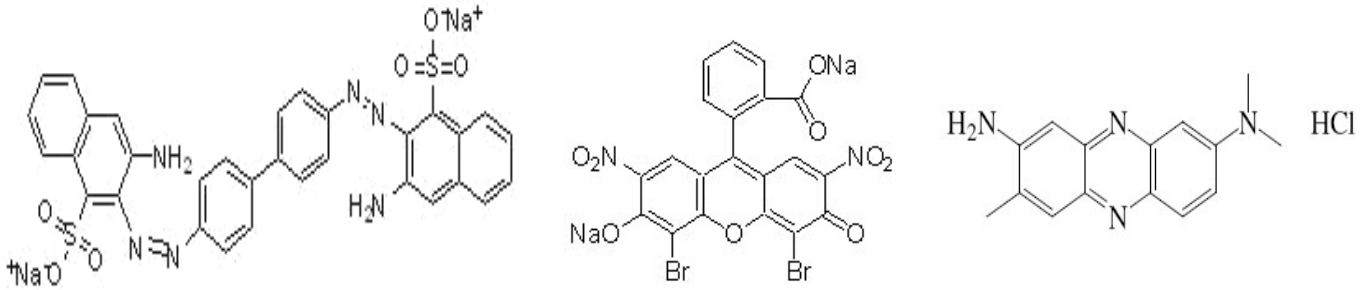
3- Centrifuge tubes. Hettich Universal (D-7200).

4- Electronic Balance, Sartorius Lab. L420 B, ±0.0001.

5- pH-Meter, HM-73, TDA Electronic Ltd.

Materials:

Sodium chloride, eosin B, neutral red and congo red (Figure (A)) were supplied by Fluka. Kaolin was obtained from "The General Company for Geological Survey and Mining".



-a- **-b-** **-c-**

Figure (A) The chemical structure of a- Congo Red b- Eosin B c- Neutral red

Methodology

The clay was washed with excessive amounts of distilled water, dried at 160°C for three hours. The clay was ground and sieved to a particle size of 75µm. Wavelength of maximum absorbancy (λ_{max}) for each dye was selected, and found 540nm for eosin B, 495nm for congo red and 520nm for neutral red. These values were utilized for estimation of quantity of dyes adsorbed.

Solutions of different concentrations for each dye were prepared by serial dilution. Absorbance values of these solutions were measured

at the selected λ_{max} value for each dye and plotted against the concentration values. The calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

Calculate the quantity adsorbed

The quantity of dyes adsorbed was calculated according to the following equation[21]:-

Q_e or $\frac{x}{m} = \frac{V(C_o - C_e)}{m}$ …… (1)

Where:

x : the quantity adsorbed.

m : weight of adsorbent (g).

C_o : initial concentration (mg/*l*).

C_e : equilibrium concentration (mg/ *l*).

V : volume of solution (L).

Kinetic Studies

The effect of contact time was determined by adding 0.2gm of adsorbent into 10ml dye solution, with initial concentration ($1x10^{-4}$M) under shaking. The temperature of solution was held constant at 20^oC with a thermostatic shaker. After different time intervals, the solutions were centrifuged and volumes of 1ml supernatant were taken for spectrophotometrically measurements of dye content.

Results and Discussion

To evalute the effectiveness of an adsorbate, the adsorption of congo red, eosin B and neutral red dyes on kaolin surface was studied as a function of contact time, and the results are shown in Figures (1) and (2). The adsorption rates of dyes onto kaolin are observed to be very fast within the first few minutes and gradually decrease and become almost constant after a period of 40min. for all dyes.

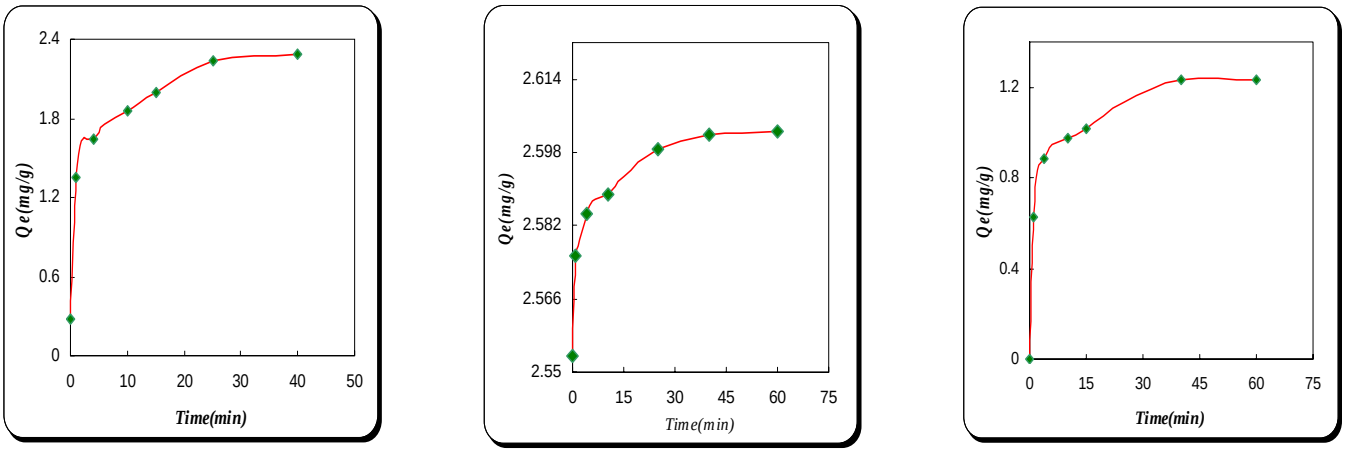


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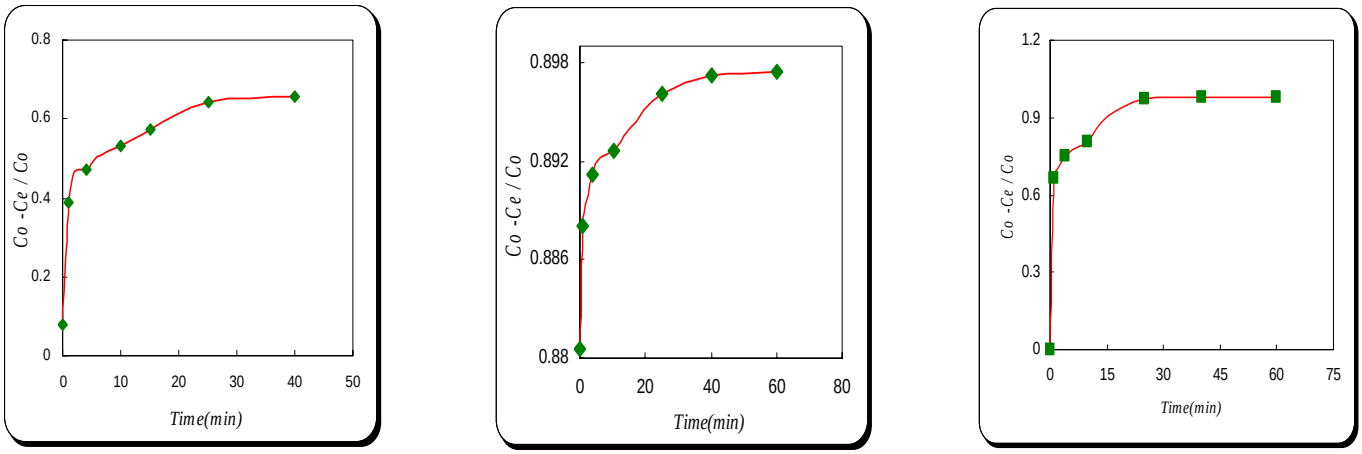
Figure (1) a- Adsorption kinetics of a- Congo red b- Eosin B c- Neutral red on Kaolin



-a- **-b-** **-c-**

Figure (2): Effect of contact time of a- Congo red b- Eosin B c- Neutral red

The data for Q_e versus t during the initial hour of contact shows avery fast increase in Q_e with time, initially followed by a gradual plateau at quasi-equilibrium situations. The initial uptake is attributed to surface adsorption. When the dye adsorption at the exterior surface reached the saturation level, the dye begins to enter the pores of the kaolin surface and is adsorbed by the interior surface of the adsorbent particles. The interior surface seems to be very active and have a very high affinity toward dye molecules. Hence, a high dye uptake by kaolin is observed. As the surface saturates with dye molecules, the adsorption rate decreases due to an increase in the diffusion resistance. This means that the pore diffusion is the rate-controlling step during dye adsorption[22].

The effect of contact time on the removal of dyes by kaolin is shown in Figure (3). This Figure showed rapid

adsorption of dyes in the first 25 min., and thereafter, the adsorption rate decreased gradually. Nearly 65.4%, 89.7% and 97.2% of congo red, eosin B and neutral red, respectively, are removed from an aqueous solution within 40 min.

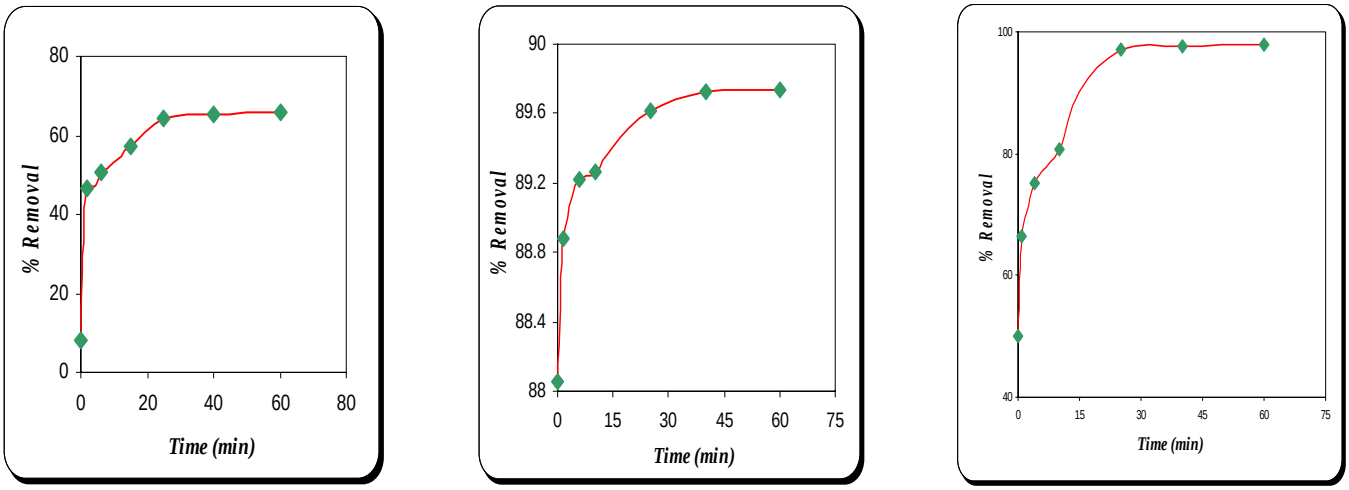


Figure (3): Effect of contact time on the removal of a) Congo red b) Eosin B and c) Neutral red by kaolin

Numerous kinetic models have been proposed to elucidate the mechanism by which pollutants are adsorbed. The mechanism of adsorption depends on the physical and / or chemical characteristics of the adsorbent, as well as on the mass – transport process. The rate constants of the dyes removal from the solution by kaolin were determined using first order and pseudo – second order equations.

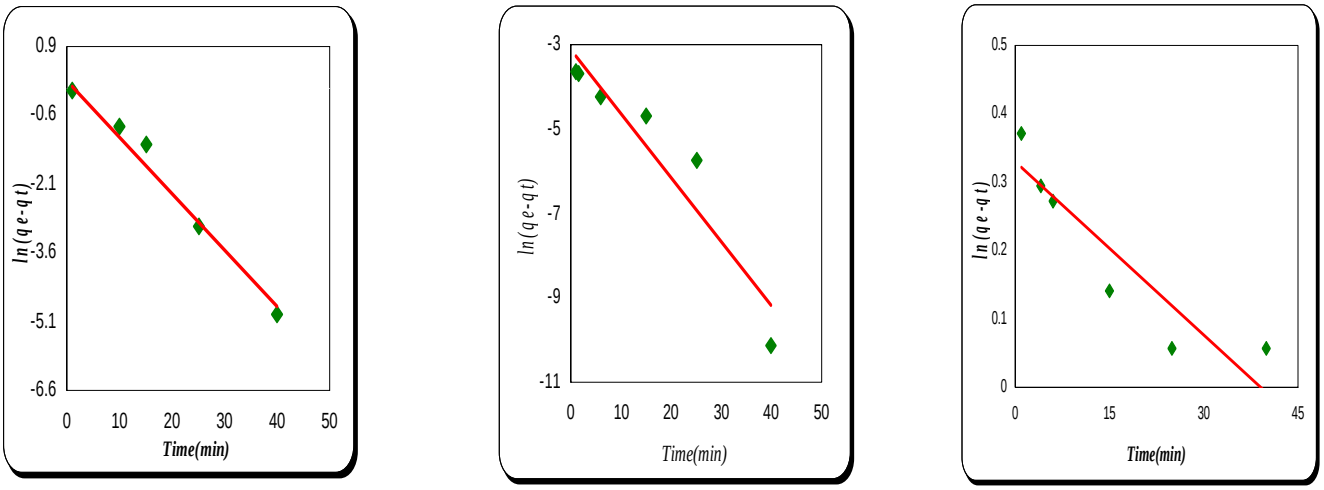
The lagergren first order rate equation was used to fit the experimental results. The integral form of the model is[23]:

$$ln(q_e - q_t) = ln\, q_e - k_1\, t \quad \ldots\ldots(2)$$

Where q_e (mg/g) is the equilibrium sorption capacity and q_t (mg/g) is the amount of dye adsorbed at time t (min), and k_1 is the equilibrium first-order constant. Values of k_1 for dyes - kaolin systems were obtained from the slope of the plot of $ln(q_e-q_t)$ vs. t (Figure (4)). The adsorption kinetic parameters from Figure (4) are indicated in Table (1).

Table (1): Adsorption kinetic parameters of dyes on Kaolin

	Pseudo-first order			*Pseudo-second order*			
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 ($g.\ mg^{-1}.min^{-1}$)	q_e (mg/g)	R^2	h ($mg.\ g^{-1}.min^{-1}$)
Congo red	0.123	1.144	0.977	0.255	2.353	0.996	3.915
Eosin B	0.151	0.0446	0.898	11.709	2.604	1	0.085
Neutral red	0.0084	1.391	0.859	0.581	1.269	0.997	1.721



-a- **-b-** **-c-**

Figure (4): The applicability of the first order kinetic model to a) Congo red, b) Eosin B and *c) Neutral red adsorption on kaolin.*

The adsorption data were also analyzed in terms of a pseudo-second order mechanism[24,25]. The linearized-integral form of this model is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad \text{.....(3)}$$

Where k_2 ($g.mg^{-1}.min^{-1}$) is the rate constant of the pseudo – second order adsorption.

If the initial adsorption rate is

$$h = k_2 q_e^2$$

Then equation (3) becomes.

$$\frac{t}{q_t} = \frac{1}{h} + (\frac{1}{q_e})t \quad \text{.....(4)}$$

By plotting t/q_t versus t (Figure (5)), a straight line could be obtained and q_e, k_2 and h can be calculated. The adsorption kinetic parameters from Figure (5) are listed in Table (1).

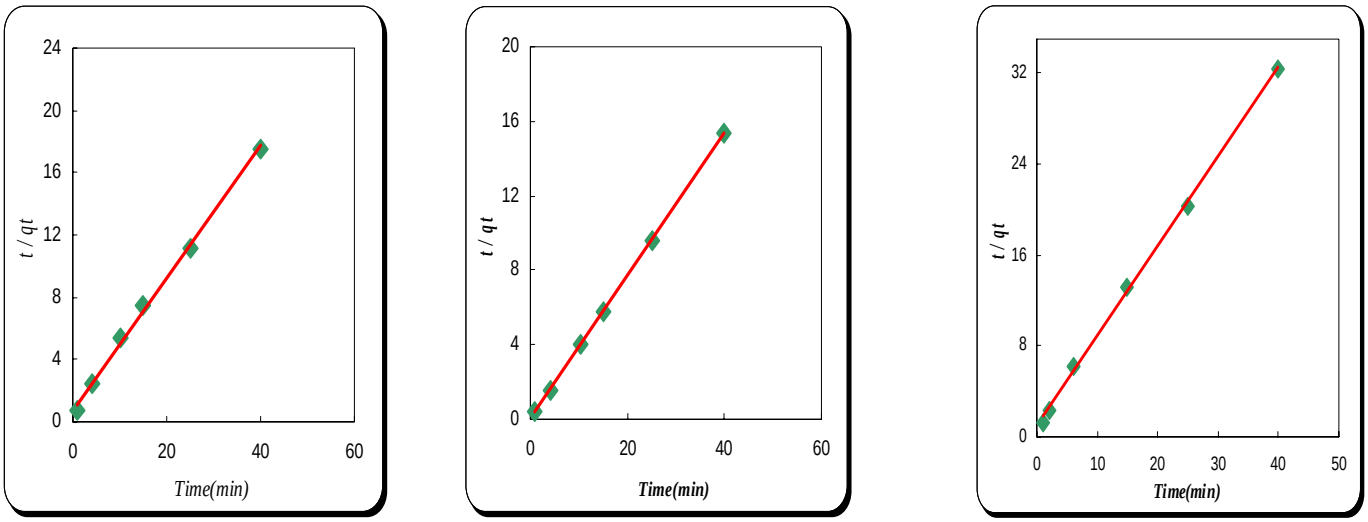


Figure (5): The applicability of the second order kinetic model to a) Congo red, b) Eosin B and c) Neutral red adsorption on kaolin.

The linearity of these plots indicates the applicability of the two models. However, the correlation coefficients, R^2, show that the pseudo-second order model fites the experimental data slightly better than the pseudo-first order model. The second order rate constants for eosin B-kaolin and neutral red – kaolin systems were found to be greater than those for congo red – kaolin system. This is normally attributed to enhanced association of the dye cations with the negatively charged kaolin surface. In aqueous medium, the exchangeable alkali and other metal cations on the surface and in the interlayer region of the clay undergo hydration creating a hydrophilic environment[26]. The dyes used in this work differ in the molecular size, chemical class, and functional groups in the molecule (Figure (A)), so, the differences in the chemical structure between the dyes can explain the results obtained in Table (1).

If the movement of the solute from the bulk liquid film surrounding the adsorbent is ignored, the adsorption process for porous solids can be separated into three stages, viz, (1) mass

transfer (boundary-layer diffusion), (2) sorption of ions onto sites and (3) intraparticle diffusion. In many cases, three is a possibility that intraparticle diffusion will be the rate-limiting step, which is normally determined using the equation proposed by weber [27] :

$q_t = k_p t^{1/2} + C$ …..*(5)*

Where q_t (mg/g) is the amount adsorbed at time *t*, k_p is the intraparticle rate constant ($mg.min^{1/2}.g^{-1}$) and C is the intercept.

q_t was found to be linearly correlated with $t^{1/2}$. The k_p values were calculated using correlation analysis (Table (2)). The R^2 values are close to unity, indicating the appropriateness of the application of this model. This reveals the occurrence of an intraparticle diffusion process[27]. The intraparticle diffusion plots are presented in Figure (6). It can also observed that the plots did not pass through the origin, this was indicative of some degree of boundary layer control (the larger the intercept, the greater the boundary-layer effect) and this further showed that the intraparticle diffusion was not the only rate – limiting step, but other processes might control the rate of adsorption.

Table (2): The intraparticle rate constants for the adsorption of dyes onto kaolin

	k_p $(mg.g^{-1}.min^{-1/2})$	*Intercept*	R^2
Congo red	0.212	1.187	0.985
Eosin B	0.0057	2.570	0.979
Neutral red	0.039	0.842	0.965

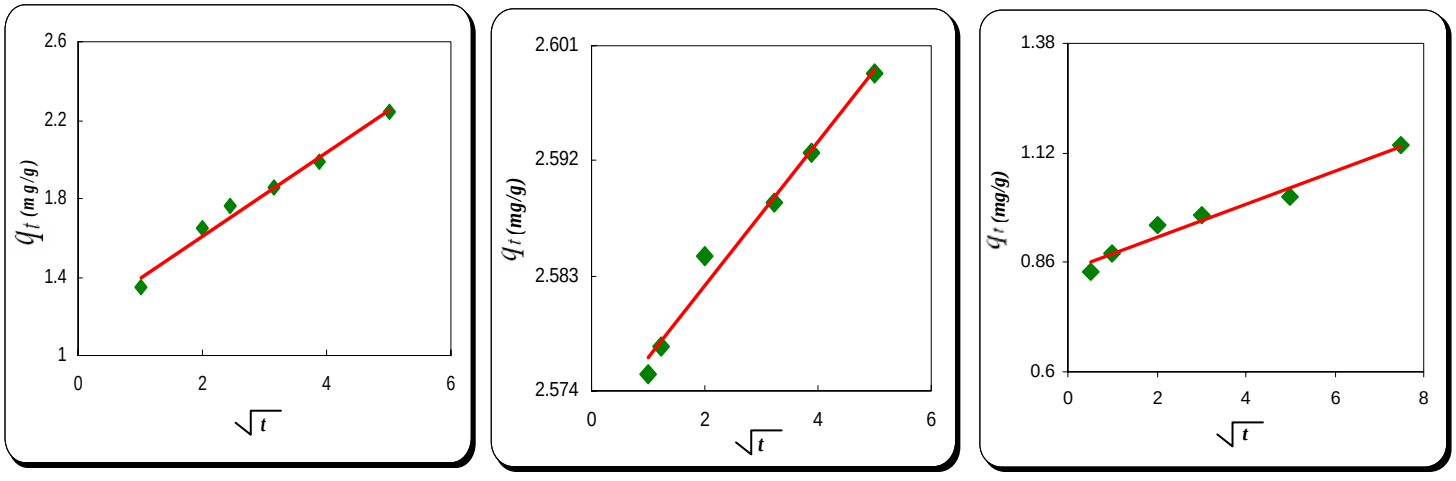


Figure (6): a) Congo red, b) Eosin B and c) Neutral red uptake by kaolin according to the intraparticle diffusion model.

The initial process, when a dye is added to the clay suspension, is the adsorption of the molecules on the external surface of the particles. This increase significantly the local concentration, giving rise to the formation of dye aggregates. With time, the dye molecules can migrate to the interlamellar region resulting in the disaggregation of the aggregates and restoring protonated monomers because of the higher acidity in this region, and so the adsorption proceeds through an ion pairing mechanism[28,29].

Conclusions

1. The kaolin clay could be employed as adsorbent in wastewater treatment for the removal of congo red, eosin B and neutral red dyes.
2. The process of adsorption is relatively fast and nearly 64.3%, 89.7% and 97.2% of congo red, eosin B and neutral red, respectively, removal are achieved within 25 min. of contact between clay and the dye solution.
3. The kinetic of dyes adsorption followed pseudo – first and second - order rate expressions and demonstrated that intraparticle diffusion plays a significant role in the adsorption mechanism.

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