Removal of Azo Dye Reactive Black 5 By Adsorption onto ZnO and CaO

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Abstract

In this study, the adsorption of reactive black 5 dye was carried out by using various surfaces, namely ZnO and CaO. The validity of the adsorption was evaluated by using UV Spectrophotometry through the determination the amount of adsorbed dye. Various parameters such as pH, adsorbent weight, initial dye concentration and contact time were studied in terms of their effect on the reaction progress. Furthermore, Lagergren's equation was used to determine adsorption kinetics. It is observed that high removal of dye was obtained at pH=5. Removal of dye was increased by increasing initial dye concentration and contact time. High removal of dye was at the time equivalent of 70 min and reached equilibrium. Increasing of adsorbent weight leads to decrease dye adsorption where 0.1gm was the best weight. For kinetics the reaction onto CaO followed pseudo-first order Lagergren's equation while the reaction onto ZnO followed pseudo-second order Lagergren's equation and the adsorbed amount onto CaO surface was more than that of ZnO surface.

Keywords: Reactive black 5; Adsorption; Removal.

الخلاصة:

تم في هذا البحث دراسة امتزاز صبغة (RB5) باستخدام سطوح مختلفة وهي CaO و ZnO وقد تم قياس سرعة الامتزاز باستخدام جهاز قياس المطيافية من خلال تحديد كمية الصبغة الممتزة. كما تم دراسة العديد من العوامل المؤثرة في سرعة التفاعل منها: الدالة الحامضية، وزن السطح الماز، التركيز الابتدائي للصبغة وزمن التماس. بالإضافة الى ذلك تم استخدام معادلة Lagergren لتحديد حركيات الامتزاز. لقد لوحظ ان اعلى ازالة للصبغة كانت عند الدالة الحامضية pH=5 حيث ان ازالة الصبغة كانت تزداد مع زيادة التركيز الابتدائي للصبغة وزمن التماس والذي وصل الى الاتزان عند (70 دقيقة). كما أدت زيادة وزن السطح الماز الى تقليل الامتزاز حيث ان أفضل وزن كان (0.1 gm). أما بالنسبة الى حركيات الامتزاز فان التفاعل كان من الدرجة الاولى الكاذبة على سطح CaO ومن الدرجة الثانية الكاذبة على سطح ZnO وقد كانت كمية الامتزاز على سطح CaOأعلى من الكمية الممتزة على سطح ZnO .

1. Introduction

Dyes have been widely used in many industries including textile, paper printing, leather, color photography and cosmetics. Especially, reactive dyes are the most common type of dyes because of their unique properties such as bright colors. However, most of reactive dyes are non-degradable and toxic to environments and carcinogenic to human being. Even though it is treated with wastewater treatment, the solution contained reactive dyes with some color. Besides, traditional physicochemical and biological treatment methods are ineffective to remove reactive dyes(1-5).

The widely used methods to treat dyes-containing wastewater are chemical precipitation,ion-exchange, reverse osmosis, ozonation, solvent extraction, adsorption, membrane filtrations and flocculation. Within these techniques, adsorption technology has been widely applied to treat dyes wastewater using various adsorbents such as activated carbon (AC), peat, chitin, sludge, algae, clay, zeolite, fly ash and montmorillonite[2].

Azo dyes, one of the greatest groups of synthetic dyes, have one or more azo bounds (-N=N-) and because of their solubility, low expense, stability and color variety, are widely used in many applications[6-8]. Removal of azo dyes from colored effluents due to their complex composition, toxicity, poor degradability and high solubility, have attracted great interest in the last few years[9].

The purpose of this study is to investigate the ability of ZnO and CaO on adsorption of reactive black 5 (RB5), a toxic dye. Adsorption characteristics of RB5 were investigated by pH, adsorbent weight, dye concentration, contact time and kinetic study.

2. Materials and methods

2.1. Material

The molecular structure of RB5 in non-hydrolyzed form is illustrated in Fig.1. Initial maximum absorbance of RB5 solution was measured at 600 nm wavelength.

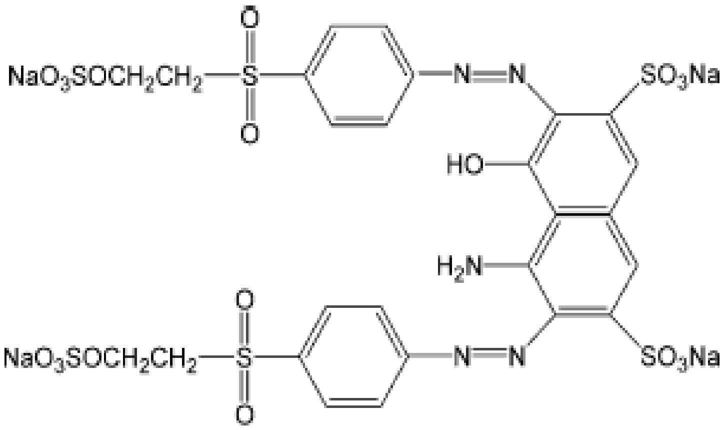


Fig.1 Chemical structure of RB5 in non-hydrolyzed form

2.2. Methods

2.2.1. Experimental Procedure

Reactive black 5 was dissolved in distilled water to prepare a stoke solution (100 ppm) , and then a practical solutions were prepared from a stock solution in an appropriate concentration (10, 20, 30, 40, 50) ppm. For the experiments, 25 ml of dye solution was added to a given amount of ZnO and CaO, with a magnetic stirrer. At a predetermined time interval, the sample was taken and after filtration (Wathman), the final concentration of dye was determined by using UV/VIS spectrophotometer (model 1700, Shimadzu Japan) at a maximum absorbance wavelength (λ_{max}) of 600 nm for RB5 and calibration curve as in Fig.2.

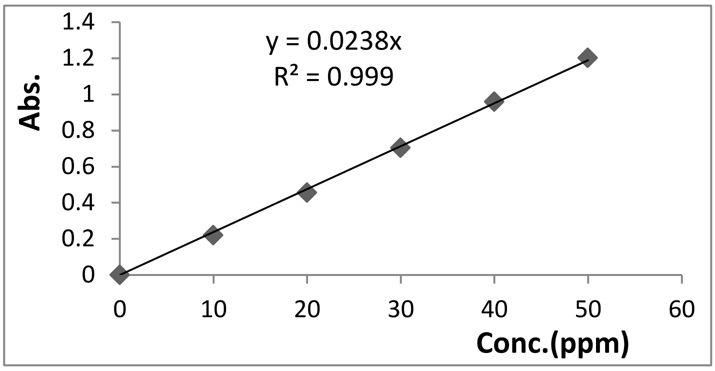


Fig.2 Calibration curve for aqueous solution of RB5

2.2.2. Kinetics and Equilibrium Study

To investigate adsorption kinetics, (50 mg/L) of RB5 solution was added to (0.1 g) of surface (ZnO and CaO), then the mixture was agitated at room temperature for (70 min) with a magnetic stirrer.

Amount of dye adsorbed on ZnO or CaO surfaces was calculated as following equation:[10]

$Q_e = (C_o – C_e) V/ m$ (1)

Where Q_e : the amount of dyes adsorbed (mg/g).

C_o and C_e : the initial and equilibrium concentrations (mg/L) of the adsorbate dye in solution, respectively.

V : the volume of solution (L) and (m) the mass of adsorbent(g).

3. Results and Discussion

3.1. Effect of Contact Time

The removal of dye was investigated at time intervals of 10, 20, 30, 40, 50, 60 and 70 min from initial time. Results showed that by lapse of time, dye removal was increased and reached equilibrium point at (70 min) for both surfaces. Fig.3& 4 shows the effect of contact time on dye removal.

Table 1 Effect of contact time on adsorption RB5 dye by ZnO surface

Time (min)		10	20	30	40	50	60	70
C_o =50 ppm	C_e (mg/L)	49.369	46.554	46.176	43.445	39.201	37.352	35.420
	Q_e (mg/g)	0.157	0.861	0.956	1.638	2.699	3.162	3.645

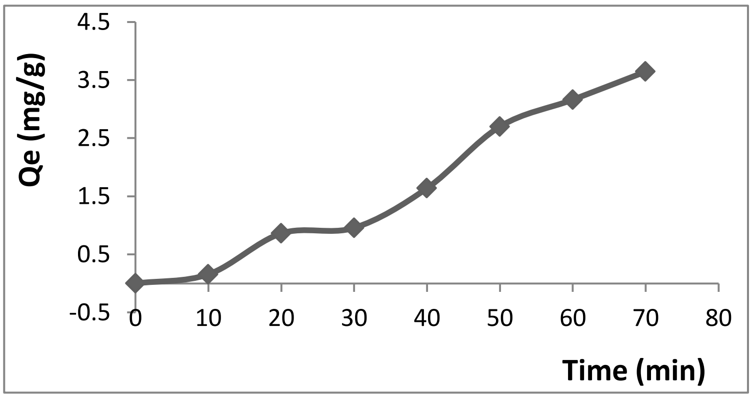


Fig.3 Effect of contact time on adsorption RB5 dye by ZnO surface

Table 2 Effect of contact time on adsorption RB5 dye by CaO surface

Time (min)		10	20	30	40	50	60	70
C_o =50 ppm	C_e (mg/L)	36.218	31.638	29.621	24.327	21.050	17.016	15.378
	Q_e (mg/g)	3.445	4.590	5.094	6.418	7.237	8.246	8.655

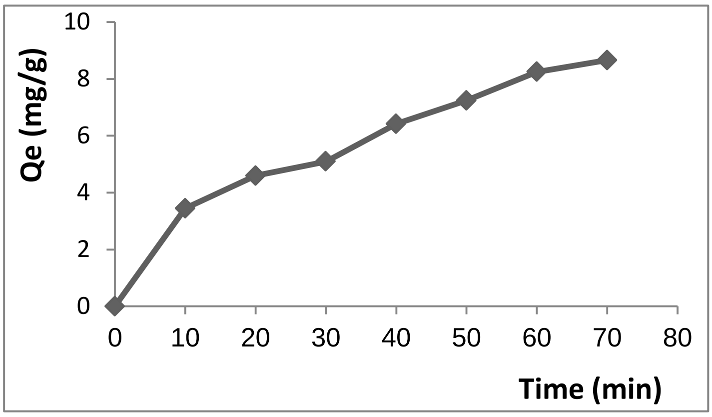


Fig.4 Effect of contact time on adsorption RB5 dye by CaO surface

3.2. Effect of Initial RB5 Dye Concentration

RB5 solution of (10, 20, 30, 40 and 50) mg/L was used for the study of initial dye concentration on removal efficiency. It is observed that initial dye concentration has a significant effect on dye removal (Fig.5& 6). The results showed that by increases in the initial dye concentration, the removal efficiency was increased. The reason for the effect of the initial dye concentration can be explained by the chemical structure of dye where active sites and free hydroxyl ions were increased with RB5 concentration increasing.

Table 3 Effect of Initial RB5 Dye Concentration by ZnO surface

C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)
10	5.462	1.134
20	14.411	1.397
30	20.882	2.279
40	29.411	2.647
50	35.420	3.645

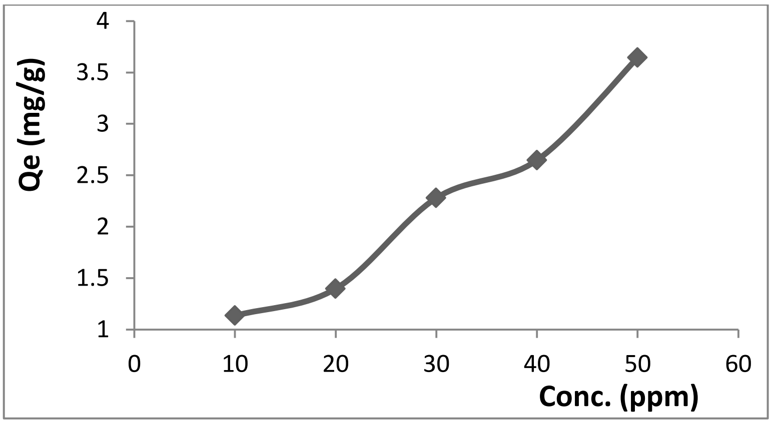


Fig.5 Effect of Initial RB5 Dye Concentration by ZnO surface

Table 4 Effect of Initial RB5 Dye Concentration by CaO surface

C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)
10	0.252	2.437
20	0.126	4.968
30	2.815	6.796
40	7.310	8.172
50	15.378	8.655

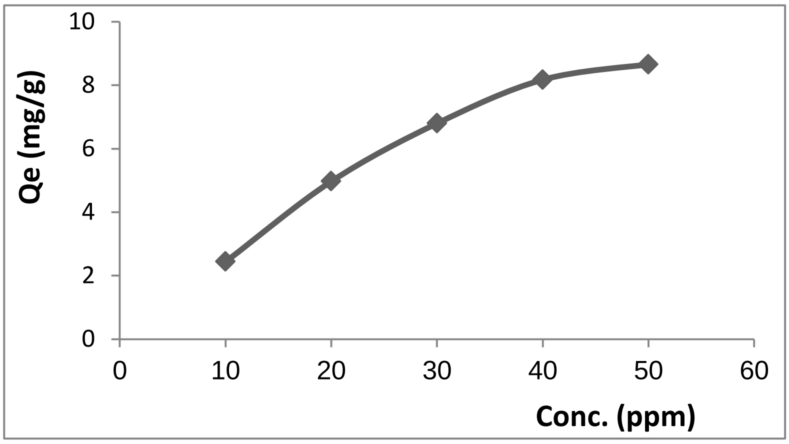


Fig.6 Effect of Initial RB5 Dye Concentration by CaO surface

3.3. Effect of Adsorbent Weight

The effect of adsorbent weight was investigated by adding different weights of ZnO and CaO (0.1, 0.3, 0.5, 0.7 and 0.9)gm. into (50 ml) of dye solution; respectively. The results showed that by increasing the adsorbent weight, dye removal was decreased (Fig.7& 8). So removal efficiency can be decreased. The reason for this case was that accumulated some particles of the surface above others so the pores and active sites of surface can be closed and leads to decrease dye adsorption(11).

Table 5 Effect of adsorbent weight on adsorption by ZnO surface

Wt. (gm)	C_e (mg/L)	Q_e (mg/g)
0.1	35.420	3.645
0.3	34.369	1.302
0.5	33.571	1.041
0.7	20.840	0.825
0.9	20.294	0.821

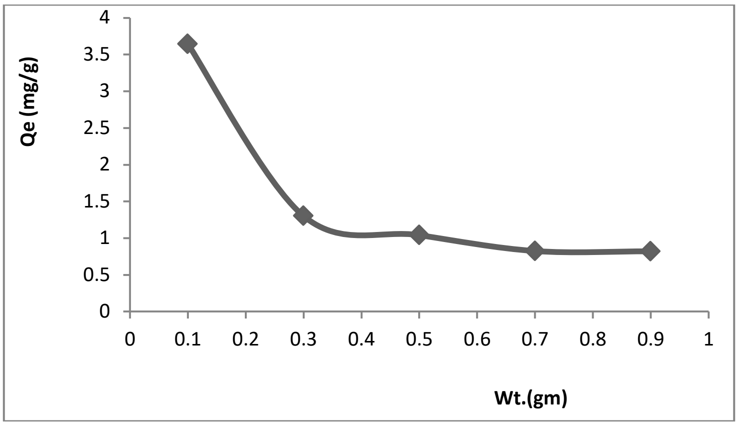


Fig.7 Effect of adsorbent weight on adsorption by ZnO surface

Table 6 Effect of adsorbent weight on adsorption by CaO surface

Wt. (gm)	C_e (mg/L)	Q_e (mg/g)
0.1	15.378	8.655
0.3	2.142	3.988
0.5	5.042	2.247
0.7	3.991	1.643
0.9	4.789	1.255

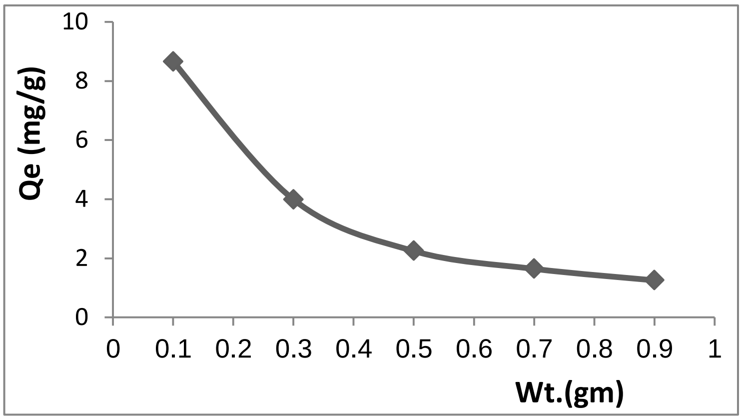


Fig.8 Effect of adsorbent weight on adsorption by CaO surface

3.4. Effect of pH

To determine the optimum pH, pH was changed in the range of (5, 7 and 9). Fig.9& 10 shows the effect of pH solution on dye removal. In view of this figure, it is clear that the pH of the solution has a significant effect on dye removal. In both surfaces, high removal occurred at pH=5, while low removal occurred at pH=9. The reason was that in acidic pH the active sites were free while in basic pH the dye was precipitated.

Table 7 Effect of pH on adsorption by ZnO surface

pH	C_e (mg/L)	Q_e (mg/g)
5	33.319	4.170
7	35.714	3.571
9	36.554	3.361

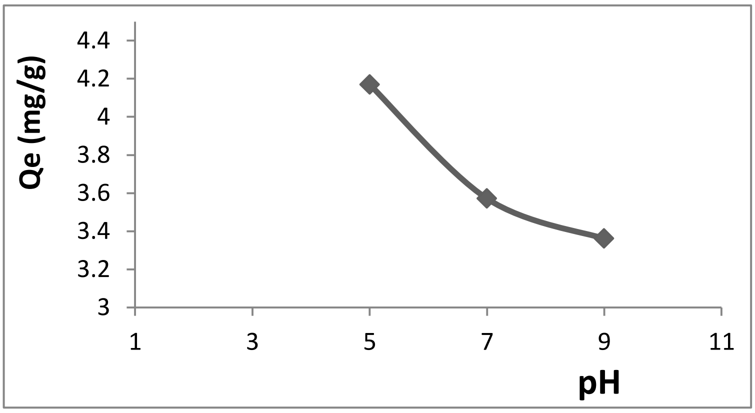


Fig.9 Effect of pH on adsorption by ZnO surface

Table 8 Effect of pH on adsorption by CaO surface

pH	C_e (mg/L)	Q_e (mg/g)
5	23.697	6.575
7	24.831	6.292
9	25.714	6.071

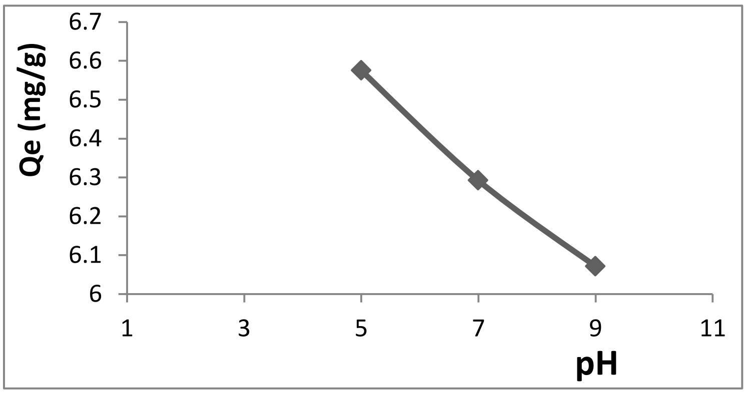


Fig.10 Effect of pH on adsorption by CaO surface

3.5. Adsorption Kinetics

The adsorption kinetics of RB5 onto two adsorbents was investigated to determine the order of reaction. To investigate sorption characteristics of RB5, two kinetic equations were applied: pseudo- first order and pseudo-second order. Two kinetic equations can be expressed as follows:[12]

Pseudo-first order Lagergren's equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303}\, t \qquad (2)$$

Pseudo- second order Lagergren's equation:

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{1}{q_e}\, t \qquad (3)$$

where q_e and q_t (mg/g) are the amount of adsorbed RB5 at equilibrium and time t, respectively. K_1 and K_2 are the first order rate constant (min^{-1}) and the second order rate constant (g/mg. min), respectively.

To determine the order of reaction the pseudo-first order Lagergren's equation and the pseudo- second order Lagergren's equation were applied then the theoretical q_e was found and compared with the experimental q_e whichever was fitted or approximated that's mean the reaction had that order.

The results showed that q_e theoretical obtained from pseudo-first order Lagergren's equation was (6.480) and its far on q_e experimental onto ZnO surface that was (3.645). As for CaO surface q_e theoretical obtained from pseudo-first order Lagergren's equation was (10.987) and its nearby q_e experimental that was (8.655) as illustrated in Fig.11& 12.

Table 9 Experimental data of pseudo-first order Lagergren's equation of adsorption RB5 onto ZnO surface

C_o = 50 ppm	Time (min)	10	20	30	40	50	60
K_1=0.038 min^{-1}	Log ($q_e - q_t$)	0.542	0.444	0.429	0.302	-0.024	-0.316

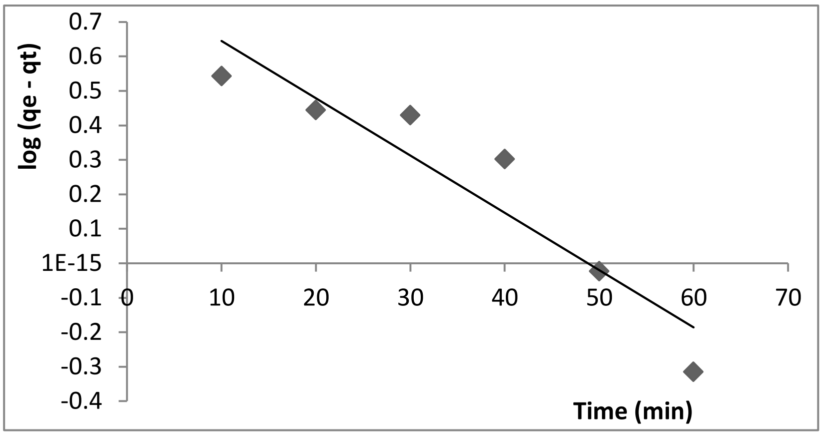


Fig.11 pseudo-first order Lagergren's equation of adsorption RB5 onto ZnO surface

Table 10 Experimental data of pseudo-first order Lagergren's equation of adsorption RB5 onto CaO surface

C_o = 50 ppm	Time (min)	10	20	30	40	50	60
K_1=0.046 min^{-1}	Log ($q_e - q_t$)	0.716	0.609	0.551	0.349	0.151	-0.388

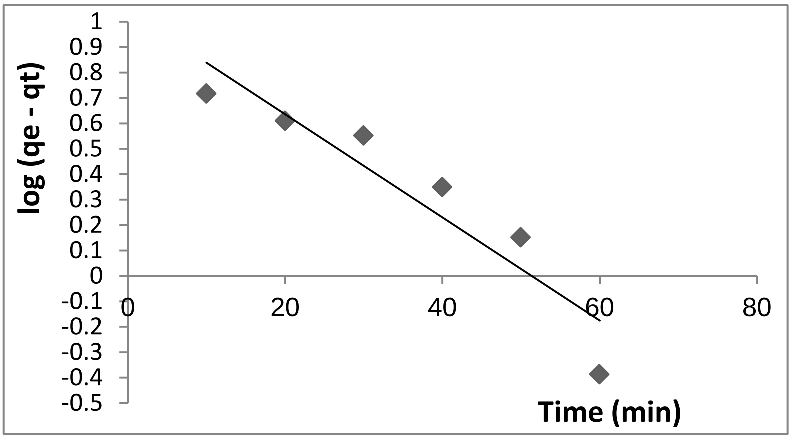
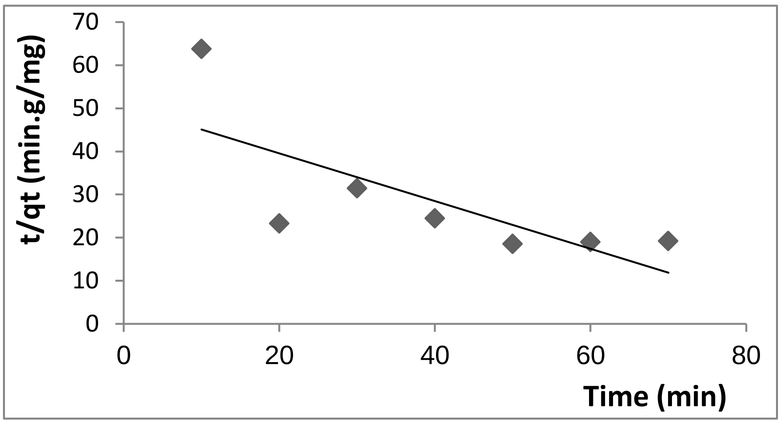


Fig.12 pseudo-first order Lagergren's equation of adsorption RB5 onto CaO surface

When applying pseudo-second order Lagergren's equation the results showed that the theoretical q_e was that (1.808) and its nearby the experimental q_e onto ZnO surface was that (3.645). As for CaO surface the theoretical q_e obtained from pseudo- second order Lagergren's equation was (12.5) and its far on the experimental q_e was that (8.655) as observed in Fig.13& 14.
That's mean the reaction had pseudo-first order for CaO surface and pseudo- second order for ZnO surface.

Table 11 Experimental data of pseudo-second order Lagergren's equation of adsorption RB5 onto ZnO surface

$C_◦$ = 50 ppm	Time (min)	10	20	30	40	50	60	70
K_2= 0.006 g/mg. min	t/q_t (min. g/mg)	63.694	23.228	31.380	24.420	18.525	18.975	19.204



[**Fig.13** pseudo-second order Lagergren's equation of adsorption RB5 onto ZnO surface

Table 12 Experimental data of pseudo-second order Lagergren's equation of adsorption RB5 onto CaO surface

$C_◦$ = 50 ppm	Time (min)	10	20	30	40	50	60	70
K_2= 0.002 g/mg. min	t/q_t (min. g/mg)	2.902	4.357	5.889	6.232	6.908	7.276	8.087

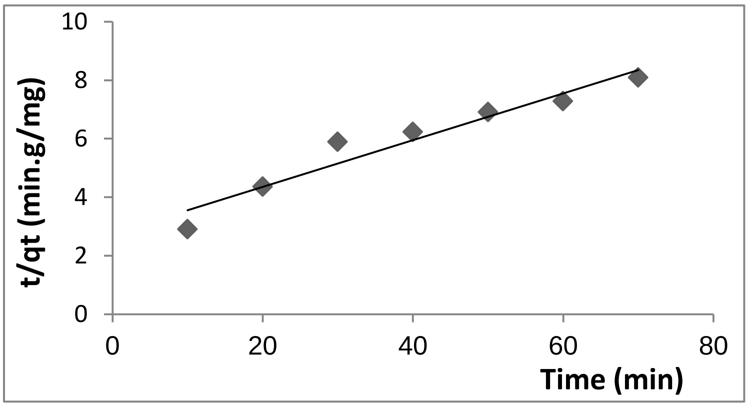


Fig.14 pseudo-second order Lagergren's equation of adsorption RB5 onto CaO surface

4. Conclusions

This work was one of the applications of adsorption for the effective removal of RB5 dye from aqueous solution. The following are the main results:

- In this study dye adsorption reached to equilibrium point at (70 min) for both surfaces ZnO and CaO.
- Increasing the initial dye concentration leads to increase adsorbed amount so increasing removal efficiency, where the best dye concentration was (50 mg/L).
- Adsorbent weight has significant effect in adsorption process, its observed that by increasing the adsorbent weight; adsorption was decreased, where the best adsorbent weight was (0.1gm).
- High removal for RB5 dye from aqueous solution was obtained at pH=5.
- The adsorbed amount onto CaO surface (8.665 mg/g) was more than that of ZnO surface (3.645mg/g).
- The order of reaction for CaO surface was pseudo-first order, while was pseudo- second order for ZnO surface.

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