



## Testing the Ability of Using Cement Kilns Waste for Removing Acid Dyes Wastewater by Adsorption

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**Abstract:** This investigation deals with the use of cement kiln dusts waste (CKD) as adsorbent for removal two kind of acid dyes from simulated wastewater. cement kiln dusts waste prepared by dried at 60°C. The effect of pH: 2-12, contact time: 20- 180 min, sorbent weight: 0.5- 4.0 g were considered. The optimal pH value for acid dyes adsorption was found to be 2.5 for acid red dyes(ARD)and 6.5 for acid blue dyes (ABD). The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Freundlich model was found to fit the equilibrium data very well with high-correlation coefficient ( $R^2$ ). The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation ( $R^2 > 0.95$  and 0.94) for acid red dyes(ARD) and acid blue dyes (ABD). respectively. The results showed that the cement kiln dusts waste was found to be an attractive low cost adsorbent for the treatment of wastewater.

**Keywords:** Cement Kilns Dust, Acid Dyes, Isotherms; Kinetics; Wastewater.

### اختبار قابلية الغبار المتساقط من محارق تصنيع السمنت في ازالة الصبغات الحامضية النسيجية باستخدام الامتزاز كعملية معالجة

**الخلاصة:** نفذت الدراسة الحالية لبحث ازالة صبغتين حامضيتين من المياه النسيجية الملوثة المصنعة هي: الصبغة الحامضية الحمراء و الصبغة الحامضية الزرقاء. تم استخدام عملية الامتزاز في المعالجة. تم استخدام مادة مازة معدومة الكلفة وهي بقايا مخلفات صناعة السمنت اي الغبار المتساقط من معامل صناعة السمنت والطابوق والذي يعتبر من مخلفات الصناعة و التي لا بد من التخلص منها. تم اجراء التجارب لدراسة تأثير الدالة الحامضية، الجرعة، وقت التلامس، والتركيز الابتدائي على عملية الامتزاز باستخدام مخلفات غبار السمنت، وجد ان افضل الظروف هي 2.5 للصبغة الحامضية الحمراء و 6.5 للصبغة الحامضية الزرقاء، 2غم، 40. دقيقة، 50 ملغم / لتر على التوالي وكفاءة الازالة هي 97%، 91% للصبغة الحامضية الحمراء والصبغة الحامضية الزرقاء على التوالي.

## 1. Introduction

Industries are concerned to dispose of a variety of toxic pollutants which involve dyes. Dyes can be fined in the wastewater of many industries such as, tannery, dyeing, textile, and paint industry [1]. Dyes can reduce light penetration in streams which impacts the ecosystem. Dyes in textile industry effluent are hardly to remove by conventional treatment methods since they are almost unaffected by light and oxidizing agents, and can resist the aerobic degradation.

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Many efficient systems have been developed using adsorption techniques to treat dyes in an economic manner, [2].

Textile industries utilize a large quantities of water. So a large amount of effluents was discarded as wastewater which needs efficient treatment.

Prominent types of dyes used in the textile industry are:

1. Acid dyes used for wool, and silk fibers; 2. Disperse dyes used for polyester and acetate fibers; 3. Direct and reactive dyes used for rayon, cotton, paper and linen.

The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [3].

Due to their good solubility, synthetic dyes are common water pollutants and also carcinogenic and toxic, and this will cause severe hazard to aquatic life, [4]. Dyes are recalcitrant organic matter, resistant to the biological treatment, stable to light, oxidizing agents and heat, [5].

Acid dyes contain organic sulphonic acids; sodium salts represent the commercial type which is soluble in water. Acid dyes are almost used with, wool polyamide, silk, polypropylene and acrylic fibers and they can use with a blends of the previous fibers with other fibers like, rayon, cotton, polyester. Acid dyes related to the following chemical groups: anthraquinone, azo, triphenylmethane, nitro, quinoline and pyrazolone. Azo dyes considered as a largest and most important group followed by anthraquinone and triarylmethane dyes, [6].

There are many conventional techniques for the removal of dyes from wastewater. These techniques can be: biological, physical and chemical, [3]. They all have advantages and disadvantages. Many of these methods have are not popular in treating dye wastewater because it is expensive, [7].

The use of physical method currently in industries treated effluent with a research focus on based on cheaper and effective alternatives for bio. In physical the processing, it has acquired the technology adsorption of more importance because of its high efficiency in the removal of dyes from effluent and is for an economically viable process compared to membrane filtration, ion exchange, and irradiation and chemical and electrical ways. Activated carbon is the the most commonly used on a large scale intensive to remove color and processing of liquid textile waste but due to its high price is not used on a large scale [8]

The process of adsorption involves the ions, atoms or molecules of the adsorbate to transfer and adhere to the surface of the adsorbent creating a thin film. The adsorbate can be images, liquid or dissolved solute phases. Adsorption technique can be divided into physical and chemical adsorption. Physisorption is an another term of physical adsorption process and it is controlled by physical forces such as Van der Waals forces, hydrophobicity, hydrogen bond, polarity, static interaction, dipole –dipole interaction,  $\Pi$ -  $\Pi$  interaction etc. In the physical adsorption, pollutants get accumulated on adsorbent surface by the above mentions interactions while chemical adsorption (Chemisorption or Langmuir adsorption) is defined when the adsorb ate is chemically bound to the adsorbent's surface due to the exchange of electrons[9]. Adsorption process is a very effective separation technique and it is considered to be superior

compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances [10,11,12].

Cement is an inorganic non-metallic powder. Cement is the main ingredient of concrete, is the second most used material even after the water in all parts of the world. It includes cement production, heating and calcining and sintering of a mixture of limestone and clay Typically, to make clinker, which is then cooled and foundations with the addition of gypsum to make cement. And it is used on a large scale dry process production process, which gradually replace the wet process .

Fine dust CKD (cement kiln dust) was generated from the kiln. The composition of the CKD varies along the process and even along the time from a single kiln line, it composition contain fine particles include the raw material at different stages of burning and particles of clinker. CKD is also obtained from alkali bypass systems (installed to avoid excessive build-up of alkali, sulphur and chloride), bypass dust consists of calcined kiln feed material[13].The objective of this study was to study the effect of operating parameters like initial dye concentration, sorbent dosage, contact time and temperature on the sorption efficiency. In addition, kinetic studies were conducted to determine the contact time required to reach equilibrium. The equilibrium studies were also performed.

## 2. Materials and methods

### 2.1. Materials

A stock solution of acid dye with concentration of 1000 mg/L were prepared using 1g of the dye and dissolved in 1 L of distilled water. The prepared solution was kept at room temperature and used as stock solution to prepare the desired concentrations after dilution with distilled water. UV-vis spectrophotometer was used to measure the concentration of dye dissolved in water before and after adsorption. Acid red dye(ARD) was detected at wavelength of (540 nm) and (466nm) for acid blue dye(ABD) .

### 2.2 Sorbent preparation

A Cement kiln dust was used as an adsorbent in the present work. It was obtained from Al-Kufa Cement Factory at Al-Najif Government. The chemical composition of the CKD constituents was performed in the lab of Geological Survey Company and is listed in Table (1).

Table 1 X-ray analysis of CKD

Substance	Mass or Volume
SiO <sub>2</sub>	9.92
Al <sub>2</sub> O <sub>3</sub>	5.22
Fe <sub>2</sub> O <sub>3</sub>	1.92
CaO	39.32
MgO	3.23
SO <sub>3</sub>	9.15
Loss on Ignition	24.64
Total	93.4

The Cement kiln dust was dried in an oven at 80°C for 24 hours and then it was kept in desiccators until use.

### 2.3. Analytical method

A UV-V is spectrophotometer was used for measuring dye concentration at 595 nm. Equation 1 was used to calculate the dye removal efficiency.

$$\text{Color removal efficiency (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

Where  $C_0$  (mg/l) and  $C$  (mg/l) are the concentration of the dye before and after treatment respectively.

### 2.4 Batch Experiments for Acid Dye

#### 2.4.1 Effect of contact time, pH, agitation speed and CKD dosage

100mL of acid blue and red dye with concentration of 50mg/L was placed in flask of 250mL volume. One gram of CKD was added. The apparent pH value was measured to be 12. The mixture was shaken at 200rpm for 180 min. 10ml sample was taken every 30 min to study the effect of contact time on the adsorption process. To measure the concentration of the remaining acid dyes in the solution, the sample was centrifuged for 5 min to separate the supernatant from the CKD, then the supernatant analyzed spectrophotometrically.

The same procedure were conducted to examine the effect of other parameters (pH, agitation speed and CKD dosage) on the adsorption process, by varying the pH from 2-12, the agitation speed from 150-300rpm and CKD dosage from 1-5g.

## 3. Results and Discussion

### 3.1. Effect of Initial pH

Usually, the pH of solution plays a significant role in the sorption process. For the purpose of study the impact of pH on the removal of acid dyes by using CKD as sorbent; 100 mL of 50 mg/L acid dyes solution was used.

Experiments were performed in pH of 2, 4, 6,8,10 and 12. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustment,[14].

The initial pH of the solution represents an important task on the adsorption of dyes, time 180 min, 200rpm and 10g/L CKD were used. The result was plotted in Figure (1). It can be observed from this figure that the removal efficiency increases with decrease pH from 4 to 2 and decreasing at pH > 4 for (ARD) and The removal efficiency increases with increase pH from 4 to 6.5 and decreasing at pH > 6.5, for (ABD). From Figure (1) it is seen that for 50 mg/L of dye the removal is almost 92% at pH 2.5 for (ARD) and 97% at pH 6.5 for (ABD). This refers to the existence of such powers

between the ABD, ARD and CDK interaction that is not H<sup>+</sup> or OH<sup>-</sup> ions can affect the ability of adsorption, and did not involve ion-exchange mechanism [14].

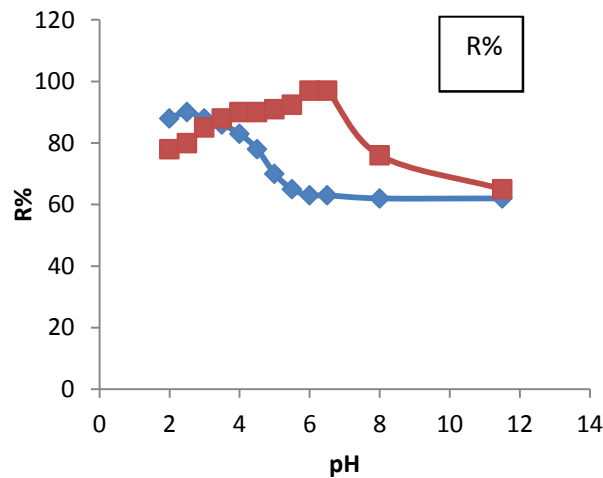


Figure 1. Effect of pH on the removal efficiency of acid dye.  
ARD , ABD conc.=50mg/L, dose=10g/L, rpm=200, cont. time=180 min

### 3.2 Effect of Contact Time

Adsorption of the acid dye was studied as a function of contact time. ARD and ABD concentration=50mg/L, pH=2.5, 6.5, respectively , 200 rpm and 10g/L CKD were used. The result was plotted in Figure (2). This figure explained that the removal efficiency has increased rapidly after 40 minutes, and then remain constant thereafter until the end of the experiment after 180 minutes. This revealed that CKD good adsorbent with fast kinetics to remove all acid dyes compared to other adsorbent. Consequently, adsorption experiments conducted in other batches with 40 minutes contact time.

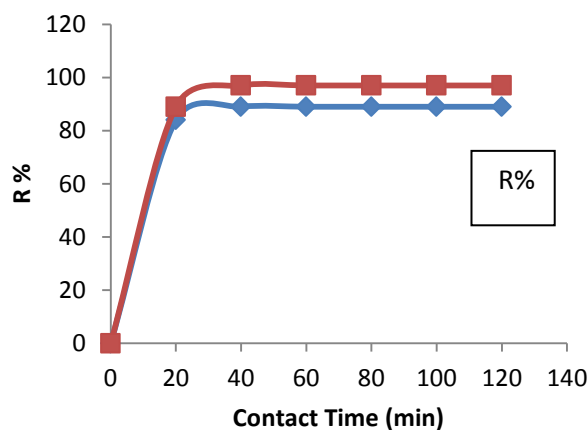


Figure 2. Effect of contact time on removal efficiency of acid dye.  
Acid red dye conc.=50mg/L, pH= 2.5, dose=10g/L, rpm=200 ,  
Acid blue dye conc.=50mg/L, pH= 6.5, dose=10g/L, rpm=200 .

### 3.3 Effect of Agitation Rat

The effect of agitation rate on CKD adsorption of acid dye was examined by varying the rate of agitation from 100 to 300 rpm. Acid dyes concentration= 50mg/L, contact time 40 min, pH=2.5,6.5 for ARD, ABD respectively and 10g/ L CKD were used. The results are plotted in Figure (3).

From this figure it can be noticed that the removal efficiency at 100 rpm is 88% while for 200rpm it equal to 90% for (ARD) and equal to 95 at 200 rpm for (ABD) then it remain constant for higher agitation speeds.

This can be explained as follows: under low agitation speed a thick boundary layer is established around the CKD particles making the acid red dye removal a slow diffusion controlled process.

When agitation rate increases, the boundary layer becomes thin and the dye can reach easily the external particle surface and be adsorbed on its active site, thus improve the removal efficiency of the dye. For further experiments 200rpm was applied.

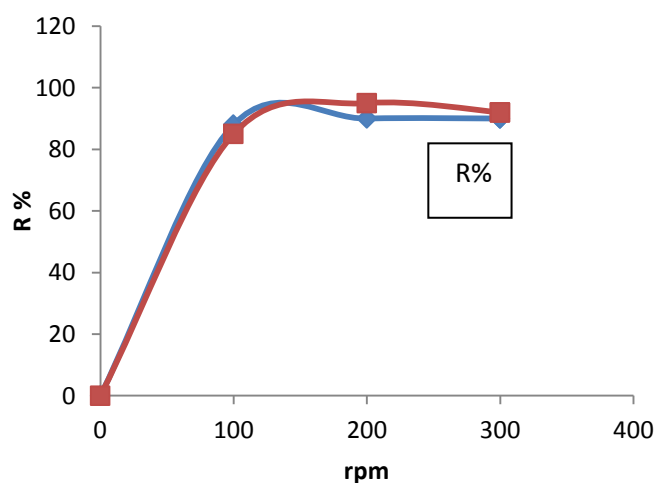


Figure 3. Effect of agitation rate on removal efficiency of acid red dye.  
 Acid red dye conc.=50mg/L, dose=20g/L, pH=2.5, contact time = 40 min.  
 Acid blue dye conc.=50mg/L, dose=20g/L, pH=6.5 , contact time = 40min.

### 3.4 Effect of Dyes Concentration

The dyes concentration was changed from 25- 300mg/ L in order to find its influence on the removal efficiency of acid red dye=95% for 50mg/L, Acid red dye concentration equal, The CKD= 10g/L, contact time 40min, pH=2.5 and 200rpm were used, the removal efficiency of acid blue 96% for 50m g/L of dye concentration the CKD= 10g /L , contact time 40min, pH=6.5 and 200rpm were used . The results are plotted in Figure (4).

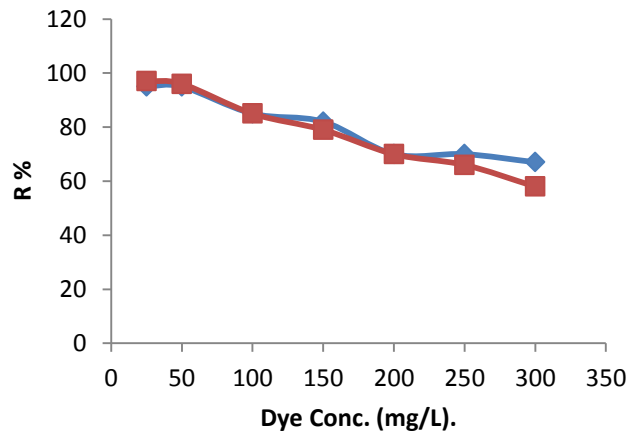


Figure 4. Effect of CKD dosage on the removal efficiency of acid red dye.  
 Acid red dye , the CKD dose =10 g/L, rpm=200, pH=2.5, contact time=40min.  
 Acid blue dye, the CKD dose =10 g/L, , rpm=200 pH=6.5, contact time=40min.

### 3.5 Effect of CKD Dosage

The CKD dosage was changed from 10- 40g/ L in order to find its influence on the removal efficiency of acid red dye=92% for 10 g/L of CKD , Acid red dye concentration equal 50mg/L, contact time 40min, pH=2.5 and 200rpm were used, the removal efficiency of acid red dye=95% for 10 g/L of CKD , Acid blue dye concentration equal 50mg/L, contact time 40min, pH=6.5 and 200rpm were used . The results are plotted in Figure (5), the increase in the removal efficiency with the increase in the adsorbent dosage can be related to more available surface area and binding sites. Further increase in CKD dosage may increase the linkage between surface active sites which reduced the uptakes and the removal efficiency. The CKD dosage of 10g/L was used in the next experiments.

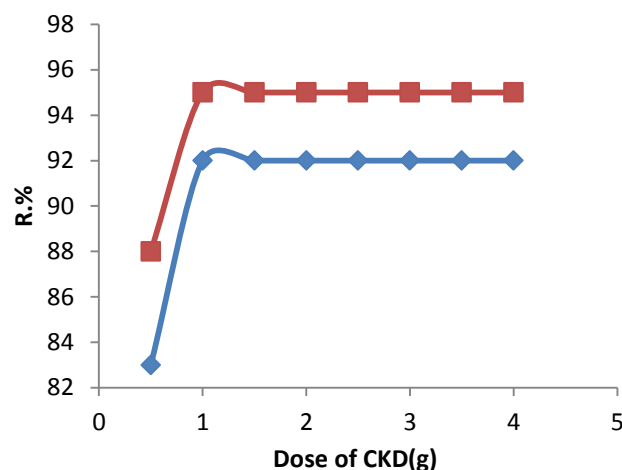


Figure 5. Effect of CKD dosage on the removal efficiency of acid dyes.  
 ARD conc. 50mg/L, rpm=200, pH=2.5, contact time=40min.  
 ABD conc. 50mg/L, rpm=200, pH=6.5, contact time=40min.

### 3.6 Adsorption Isotherms

In order to find an equation which suitable for the results and can be used for design purposes; Langmuir and Freundlich isotherm equations have been used for the equilibrium modeling of adsorption systems. The form of Langmuir (linear form) is:

$$\frac{ce}{q_e} = \frac{1}{bQ_0} + \frac{ce}{Q_0} \quad (2)$$

Where  $C_e$  is the equilibrium concentration of the metal in solution (mg/L),  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $Q_0$  (mg/g) and  $K$  (L/mg) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum sorption capacity ( $Q_0$ ) represents monolayer coverage of sorbent with sorbate and  $b$  represents the enthalpy of sorption and should vary with temperature. A linear plot was obtained when  $C_e/q_e$  was plotted against  $C_e$  over the entire concentration range of dyes investigated.

The Freundlich adsorption form (linear form) is:

$$\log q_e = \log K_f + \frac{1}{n} \log ce \quad (3)$$

where  $q_e$  is the amount of metal ion adsorbed at equilibrium per gram of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of metal ion in the solution (mg/L),  $k_f$  and  $n$  are the Freundlich model constants [15]. Freundlich parameters,  $k_f$  and  $n$ , were determined by plotting  $\log q_e$  versus  $\log C_e$ . The Langmuir and Freundlich adsorption isotherms of dyes are given in Figure( 6,7) and Table 2.

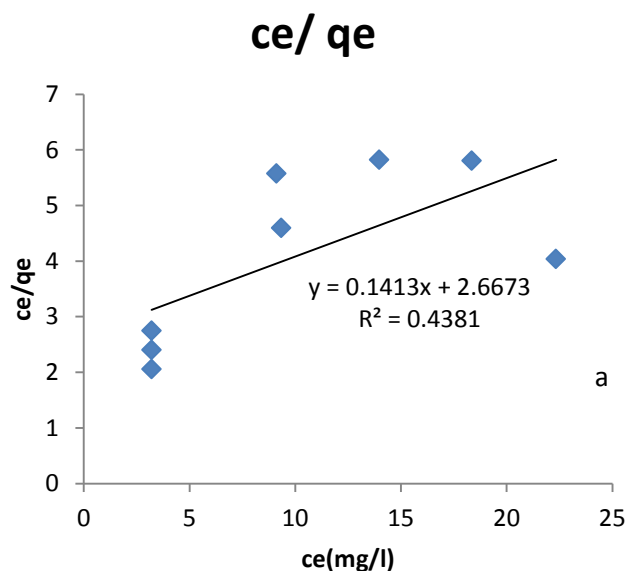


Figure 6. Langmuir plots of CKD sorption on (a) ARD (b) ABR.



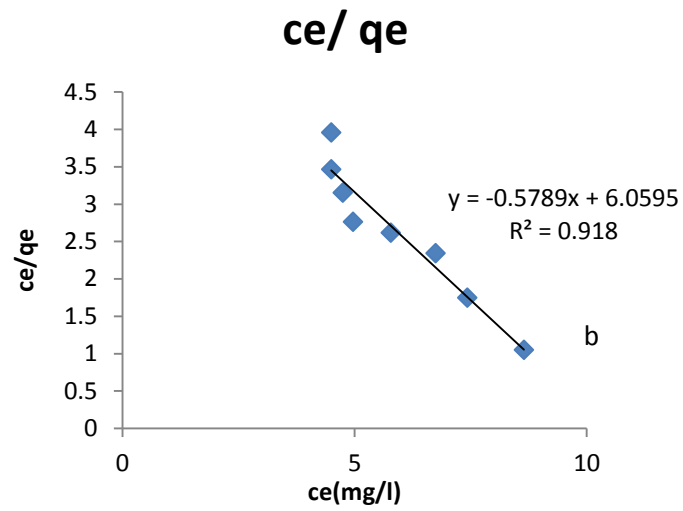


Figure 6. Continued.

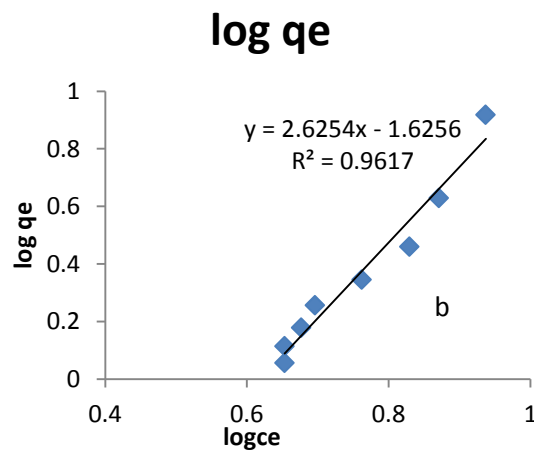
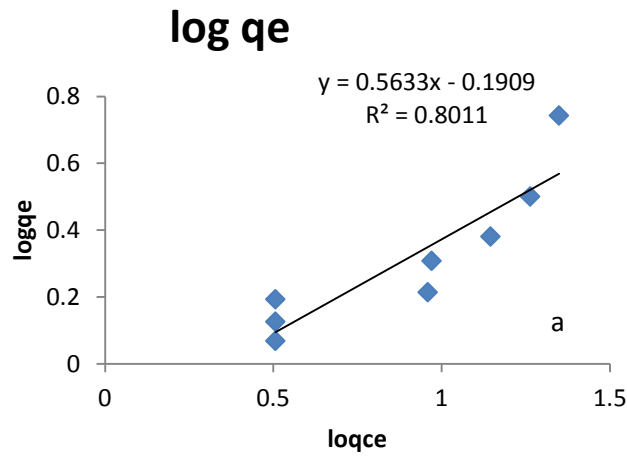


Figure 7. Freundlich plot of CKD sorption on (a) ARD (b) ABR.

Table 2. Langmuir and Freundlich constants for adsorption of CKD sorption on Acid dyes

	Isotherm Models					
	Langmuir			Freundlich		
	R <sup>2</sup>	a	b	R <sup>2</sup>	1/n	K
ARD	0.413	0.7604	0.485	0.8117	0.5773	1.5819
ABD	0.918	2.0399	0.09134	0.9072	2.4156	26

### 3.7 Kinetic Modeling

Two kinetic models namely pseudo-first-order, and pseudo-second-order models have been discussed to identify the rate and kinetics of adsorption of acid dyes on prepared cement kilns adsorbent. The linear form of pseudo-first-order (Lagergren rate equation) equation is given in Eq. (4) [16]:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \quad (4)$$

And the linear pseudo-second-order model is given as:

$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \right) \quad (5)$$

Where  $q_e$  is the amount of acid dyes sorbed at equilibrium (mg/g);  $q_t$  is the amount of acid dyes sorbed at time  $t$  (mg/g); and  $k_1, k_2$  is the equilibrium rate constant of pseudo first sorption (1/min).

Figure 8 (a, b) show a plot of pseudo-first and second-order kinetic model of acid dyes adsorption on prepared adsorbent, compiled in Table 3 along with correlation coefficient ( $R^2$ ) values.

It is seen from Table 5 that the theoretical  $q_e$  (cal) values calculated from the pseudo-first-order model did not give reasonable values with regard to the experimental uptake ones,  $q_e$  (exp). Further, the correlation coefficient ( $R^2$ ) is less than 0.99 suggesting that the present adsorption system does not follow pseudo-first-order process, while pseudo-second-order model is the best to describe our study.

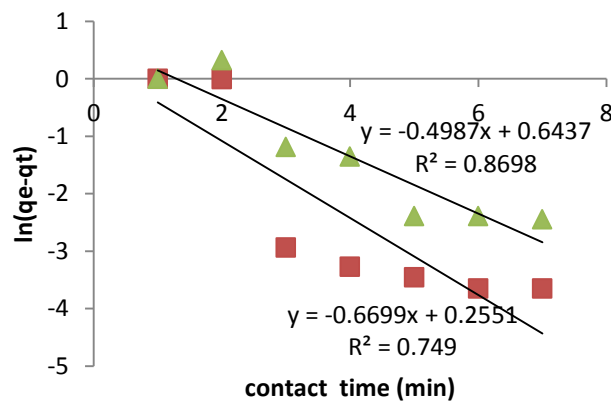


Figure 8a. Pseudo-first order kinetic for adsorption of acid dyes on CKD.

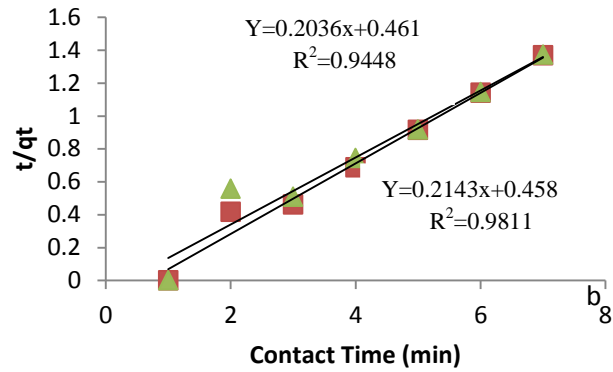


Figure 8b .Pseudo-second order kinetic for adsorption of acid dyes on CKD.

Adsorbent	Pseudo-first-order				Pseudo-second-order		
	$q_e \text{ exp.}$	$k_1 \text{ 1/min}$	$q_e \text{ calculated}$	$R^2$	$k_2 \text{ /min}$	$q_e \text{ calculated}$	$R^2$
	mg/g		mg/g			mg/g	
ARD	2.194	-0.4987	1.90217	0.8698	0.2143	2.1786	0.9811
ABD	2.1885	-0.6699	1.2916	0.749	0.2036	2.169	0.9448

#### 4. Conclusions

The adsorption of acid dyes for concentrations ranging from 50 to 300 mg/L was studied in the present work using cement kilns dust from Al-Kufa Cement Factory at Al-Najif Government. The results show that The adsorption of acid dyes occurred at all concentrations. The time required for utilizing acid dyes varies between 0-180min. depending on the initial concentration of acid dyes. The time  $t_f$  increases as the initial concentration of acid dyes increase..The experimental results equilibrium studies confirmed that the Freundlich form and Pseudo-second-order reaction kinetic has provided a realistic description of removal of acid dyes salts with closer experimental and calculated values of uptake capacity. Also correlation coefficients are higher in pseudo-second-order kinetics.

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