

# NOVEL COMPOSITE OF PLASTER KILN DUST-Fe<sub>3</sub>O<sub>4</sub> MAGNETIC NANOPARTICLES AS SORBENT TO UPTAKE CADMIUM (II) IONS FROM CONTAMINATED WATER

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## ABSTRACT

This study was aimed to use composite magnetic plaster kiln dust (MPKD) as a novel low-cost adsorbent reused of by-product plaster kiln dust (PKD) that was considered a source of air pollution. The removal efficiency of cadmium (II) ions was studied as a function of pH (4-7), MPKD mass (0.5- 8 g/L), initial ion concentration (50- 350 mg/L), and shaking time (5- 180 min). The adsorption kinetics of the MPKD was detected as chemical sorption due to the experimental uptake data best fitted with the pseudo-second-order model, also the intraparticle diffusion of ions did not significantly exert effects on the adsorption. The maximum adsorption uptake was 48 mg/g depending on the Langmuir model. Compared with other adsorbents, the MPKD was considered a promising adsorbent in the field of water treatment.

**Keywords:** water treatment, coating, low-cost, heavy metals, langmuir and pseudo-second-order.

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مركب جديد من غبار فرن الجص - الجسيمات النانوية المغناطيسية باعتباره مادة مازة لاممتازز أيونات الكاديوم الثنائية من المياه الملوثة

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المستخلص

تهدف هذه الدراسة إلى استخدام مركب غبار فرن الجص المغناطيسي (MPKD) كمادة مازة جديدة منخفضة التكلفة معاد استخدامها من غبار فرن الجص (PKD) الذي يعتبر مصدرًا لتلوث الهواء. تمت دراسة كفاءة إزالة أيونات الكاديوم الثنائية كدالة لـ pH (4-7)، كتلة MPKD (0.5 - 8 جم/ لتر)، تركيز أيون أولي (50 - 350 مجم/ لتر) ووقت الرج (5 - 180 دقيقة). تم الكشف عن نوعية الامتزاز لـ MPKD على أنها امتزاز كيميائي بسبب بيانات الامتزاز التجريبية وكانت أكثر توافقًا مع موديل المرتبة الثانية، كما ان انتشار الايونات داخل جسيمات الوسط الماز لم يؤثر بشكل كبير على الامتزاز. ان الحد الأقصى لسعة الامتزاز هو 48 ملجم/ جم اعتمادًا على موديل Langmuir. بالمقارنة مع المواد المازة الأخرى ، تم اعتبار MPKD مادة مازة واعدة في مجال معالجة المياه.

الكلمات المفتاحية: معالجة المياه، طلاء، واطيء الكلفة، عناصر ثقيلة، Langmuir، موديل المرتبة الثانية.

## INTRODUCTION

The presence of polluted water restricts the survival of ecosystems (5). Industrial wastewater contains higher amount of heavy metals that can pollute the water when it is discharged to the nature (28). Specific gravity of the heavy metals is more than five times of that for water (32). The rapid pace of both amplification of industrial infrastructures and populations increase led to the global demand for metals in developing countries. As a consequence of huge pollution, it was predicted today that just 3% of the Earth's water was fresh (6). Heavy metals are chemical elements poisonous or toxic even at low concentrations. In terms of toxicity, the cadmium is classified as the second most dangerous toxic element and only preceded by mercury (12). Therefore, heavy metal wastewater must be stringently treated before the drainage. One of the common methods to treat heavy metal wastewater is used as efficient adsorbent (34). As a result of the huge and continuous increases of heavy metals in wastewater drainage, it is necessary to invent new, low cost, sustainable, and effective absorbents. Many researchers in recent years used different low-cost materials as adsorbents, such as tea waste (8, 24), bentonite (2, 22), gypsum (27), Tamarind wood (1), cement kiln dust (30, 33), bone char (10, 21), lignite (13, 25), and attapulgit (36). Many factors affect the adsorbent property such as intrinsic properties and modification of the adsorbent can change to large extent functional groups, specific surface area, and pore size distribution (11). The waste adsorbent (especially clays) is removed from the solution after adsorption process with considerable difficulties because of their high dispersion. So, the clay particles can be magnetized (coated) by magnetite and recovered from the water with magnetic separation (20). Compared to the normal separation ways (filtration, centrifugation, and sedimentation), magnetic separation is taken into account to be a quick and efficient separation method. Another advantage acquired from the coating by magnetic nanoparticles is increasing adsorption uptake due to both of high surface area of nanoparticles and a new functional group of

new composite (14). This fact is clearly appeared in many publications such as (11) who found that the removal efficiency enhanced by 10.3% higher than the removal efficiency of raw sorbents, (20) discovered that the removal efficiency increased six times higher than nature clay, and (34) reported that the adsorption capacity rose by 15% after coating nature bentonite by  $\text{Fe}_3\text{O}_4$  nanoparticles. Plaster kiln dust (PKD) is emitted through the smoke chimney during converting (at a temperature in the range from 120 °C to 165 °C, sometimes 200 °C) raw materials gypsum into the end product gypsum plaster or stucco. The PKD quantities in some countries are estimated at 40 kg/ton of dryer-calciner stack. In my country, it is estimated about 7% of plaster produced according to statistical information of the ministry of environment. The PKD is a solid, alkaline powder removed from the exhaust gas of plaster kiln and collected by bag filters or precipitators. From the environmental viewpoint, the PKD adversely effects on the ecosystem. Industrial emissions are associated with risks to human health and the natural environment (4, 7). The aim in the present study is to reuse a low-cost by-product PKD by coating with  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles. The unique composite magnetic plaster kiln dust (MPKD) is used in the adsorption technique to remove Cd (II) ions from synthetic wastewater.

## MATERIALS AND METHODS

### Adsorbent preparation

The by-product PKD was collected and reused from local factories located in Iraq. The PKD was coated by the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles (Merck USA; 10- 20 nm size) to produce magnetic plaster kiln dust (MPKD) through impregnation method represented in (11, 20). The  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles powder was scattered and sonicated in deionized water for 3 min using sonication (1200W Ultrasonic Homogenizing and Mixing Liquid Chemicals-MSK-USP-12N). Then the PKD was added to the magnetic fluid to achieve a percent of  $\text{Fe}_3\text{O}_4$  to bentonite as (20%). The new mixture was sonicated again for 10 min and stirred for 1 h using magnetic stirrer (SH-3) in order to adsorb magnetite onto the PKD. The synthesized adsorbent

(MPKD) was separated by an external magnetic field and dried at 100 °C for 1 day and then milled for 60 min at a speed of 500 rpm. The EDS test was conducted to show that the adsorption of Cd (II) ions was done on the surface of Fe<sub>3</sub>O<sub>4</sub>.

### Chemicals

Analytical grade cadmium sulfate of purity 99.5% (chemical formula: CdSO<sub>4</sub>·xH<sub>2</sub>O; molecular weight = 208.46 g/mol purchased from Kanto Chemical CO., INC. Japan) was used to prepare an inventory of solution 1000 mg/l of Cd (II) ions by dissolution an amount of the salt in de-ionized water. This solution was kept in the refrigerator (temperature <5 °C) and acidic pH to avoid Cd (II) ions precipitation. NaOH and HCl solutions were used to adjust the pH of the solutions.

### Adsorption studies

It was conducted batch experiments to investigate the adsorption of the Cd (II) ions by the MPKD as a function of the pH (4- 7), shaking time (5- 180 min), initial ion concentration (25- 350 mg/L), and sorbent dosage (0.5-8 g/L). All experiments were conducted using several flasks of 250 mL containing 100 mL of Cd (II) ions solution under the shaking speed of 200 rpm. The adsorbent was recovered using a magnet. Atomic absorption spectrophotometer (AA-6200 Shimadzu, USA) was used to determine the residual ion concentration after the adsorption process. The pH was adjusted by 0.1 M HCl or/and 0.1 M NaOH and measured with a pH meter (HI2020-01 edge Hanna). The temperature during the experiment was controlled by using water bath shaker (Julabo SW23, Germany). The adsorption capacity (q<sub>e</sub>, mg/g) at equilibrium and the removal efficiency (Re%) were calculated using Equations (1) and (2), respectively (22).

$$q_e = \frac{(C_i - C_e) \times V}{W} \quad (1)$$

$$R_e = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Where C<sub>i</sub> and C<sub>e</sub> are the initial and equilibrium ion concentration (mg/L), respectively; V is the volume of ion solution (L), and W is the weight of adsorbent (g).

## RESULTS AND DISCUSSION

**EDS test:** The iron element (Fe) in the MPKD was about 2.81% as shown in Figure 1 a. After adsorption (Figure 1 b), this percentage decreased and new peaks of the Cd (II) ions appeared. This indicated that adsorption occurred on a surface of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

### Batch adsorption of Cd (II) ions

**Effect of pH :** The solubility of ions and the interaction between functional groups and metal ions could be affected by pH solution (18). This information clearly appeared in the study of the effect of pH as shown in Figure 2. The removal efficiency changed dramatically from 74.3% at pH 4 to 98.12% at pH 6.5. The Cd (II) ions removal were studied as a function of pH with fixing MPKD dosage (6 g/L), initial concentration (100 mg/L), and shaking 110 min. The Cd (II) ions removal during the lowest pH values decreased due to competition between heavy metal ions and H<sup>+</sup> protons that absorbed onto the MPKD surface. The removal efficiency increased with increasing pH. However, the experiments were stopped after pH of 6.5 (natural pH) to avoid chemical precipitation (1, 12).

### Effect of sorbent dose

Figure 3 represents the effect of the mass of adsorbent (dose value) on removal efficiency. This effect was studied with fixing pH 6.5, ion concentration (100)

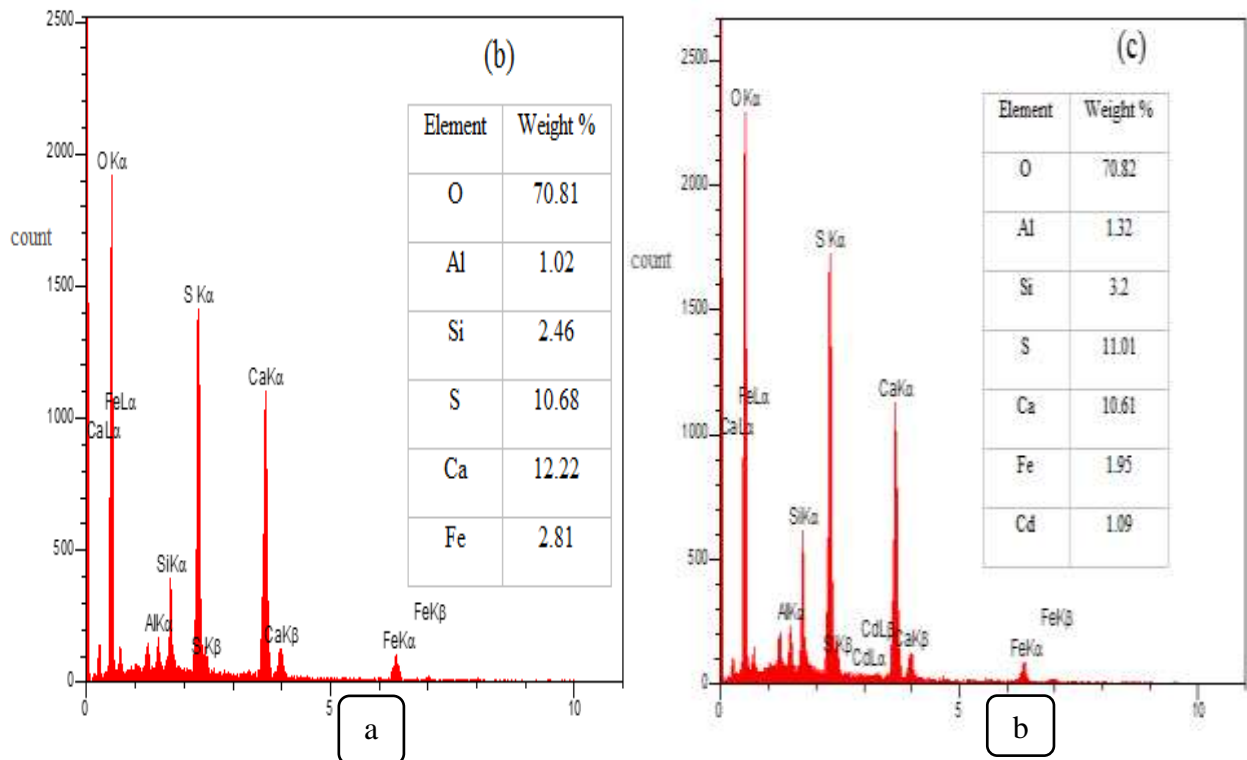


Figure 1. The EDS test of the MPKD (a) before and (b) after the Cd (II) ions adsorption

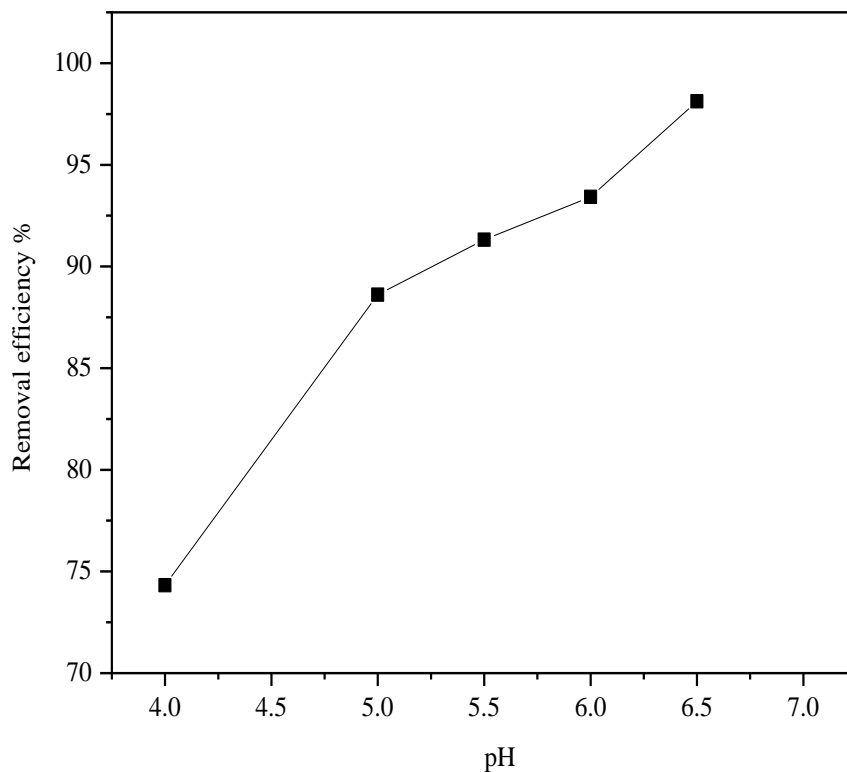


Figure 2. Effect of the pH on the Cd (II) ions adsorption.

mg/L) and shaking time 150 min. It can be observed that Cd (II) ions removal efficiency increased sharply from 51.6% at MPKD dose 0.5 g/L to 97.24% at MPKD dose 5 g/L and afterward approximately stayed constant.

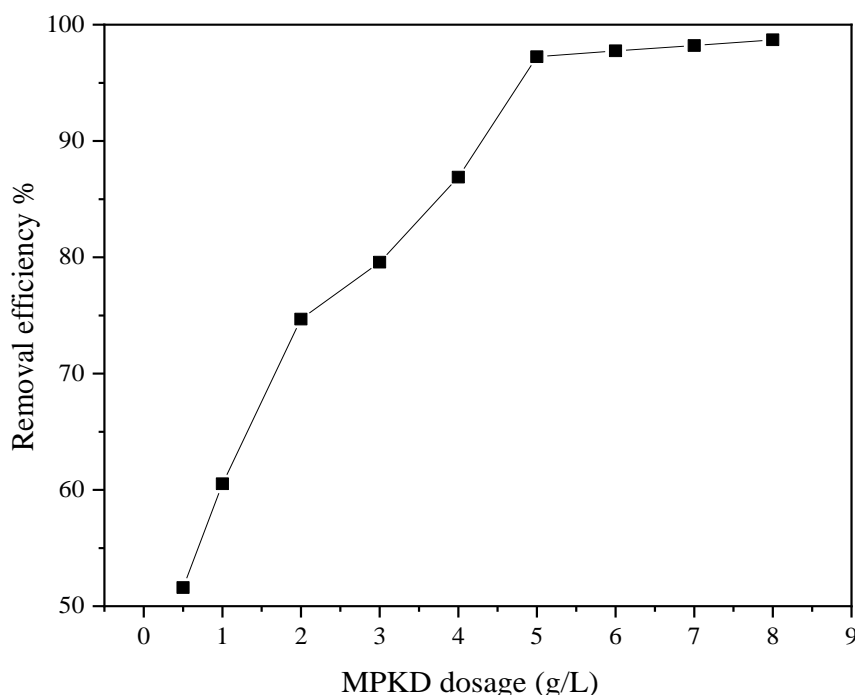
**Effect of sorbent dose**

Figure 3 represents the effect of the mass of adsorbent (dose value) on removal efficiency.

This effect was studied with fixing pH 6.5, ion concentration (100 mg/L) and shaking time 150 min. It can be observed that Cd (II) ions removal efficiency increased sharply from 51.6% at MPKD dose 0.5 g/L to 97.24% at MPKD dose 5 g/L and afterward approximately stayed constant. This acceleration and deceleration in the removal

efficiency were due to increase adsorption active sites with increasing mass of the MPKD. Later, the agglomeration of composite

particles developed in the solution with more mass of the MPKD (35).



**Figure 3. Effect of the MPKD dosage on the Cd (II) ions adsorption**

#### Effect of shaking time

The effect of shaking time with two initial Cd (II) ions concentrations (100 and 200 mg/L) was investigated with 5 g/L of MPKD and exhibited in Figure 4. With the increasing contact time from beginning to 20 min, the adsorption was very fast. At this stage, the driving force was higher due to the concentration gradient and bare adsorption sites. After a while, the adsorption of Cd (II) ions became slower and required time to reach equilibrium due to slow ions diffusion in the adsorbent pores bulk (1, 12). There was a consensus between these results and the results of (23, 24). For kinetics study, it was chosen 120 min as equilibrium time.

#### Effect of initial ion concentration

Figure 5 illustrates the removal efficiency of Cd (II) ions as a function of initial ion concentration. As the initial concentration increased from 50 mg/L to 350 mg/L, the removal efficiency decreased from 98.56 to 68.7% respectively. Low initial ion concentrations did not apply a remarkable effect on the removal efficiency. Otherwise, deterioration of the removal efficiency was

significant during high concentration levels. This behavior ascribed to the competition of surplus Cd (II) ions on available adsorption active sites of the MPKD with the deficit of binding sites at high Cd (II) ion concentrations. These results were in a good agreement with (31).

#### Kinetics study

The sorption mechanism (mass transfer, chemical reaction, and diffusion control) and reaction pathways could be visualized through the kinetic models for assessment the MPKD adsorption of Cd (II) ions in wastewater treatment system (22, 23). The results (in the effect of sorbent dose) were modeled by commonly used models that were pseudo-first-order (Equation 3) and pseudo-second-order (Equation 4). Another model was used to predict the intraparticle diffusion rate (Equation 5) (16, 22).

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad (3)$$

$$K_1 = -\text{slope}, q_e = e^{\text{intercept}}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

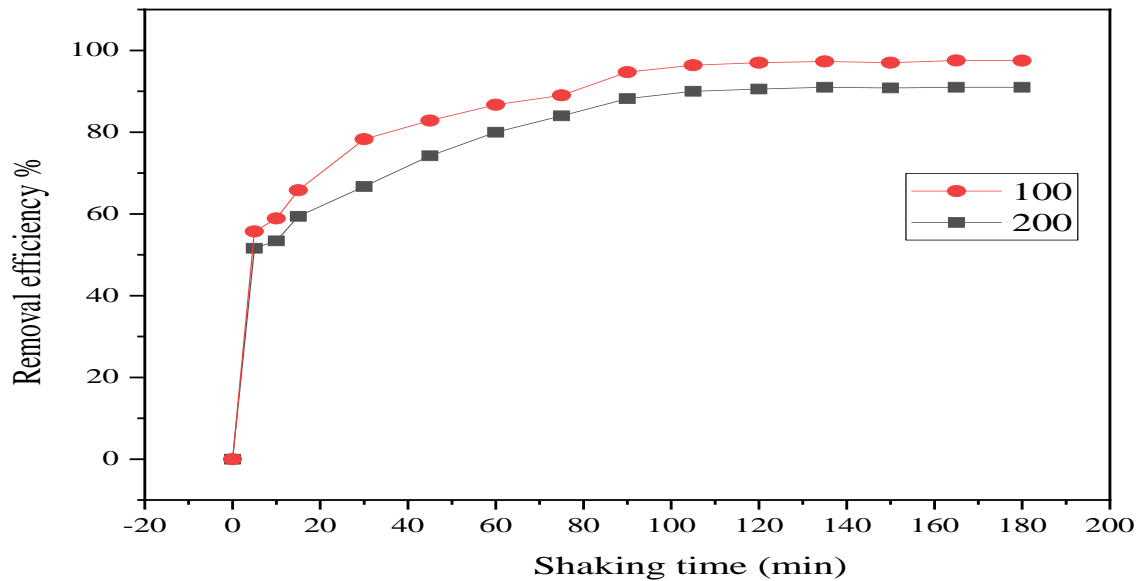


Figure 4. Effect of contact time on the Cd (II) ions adsorption

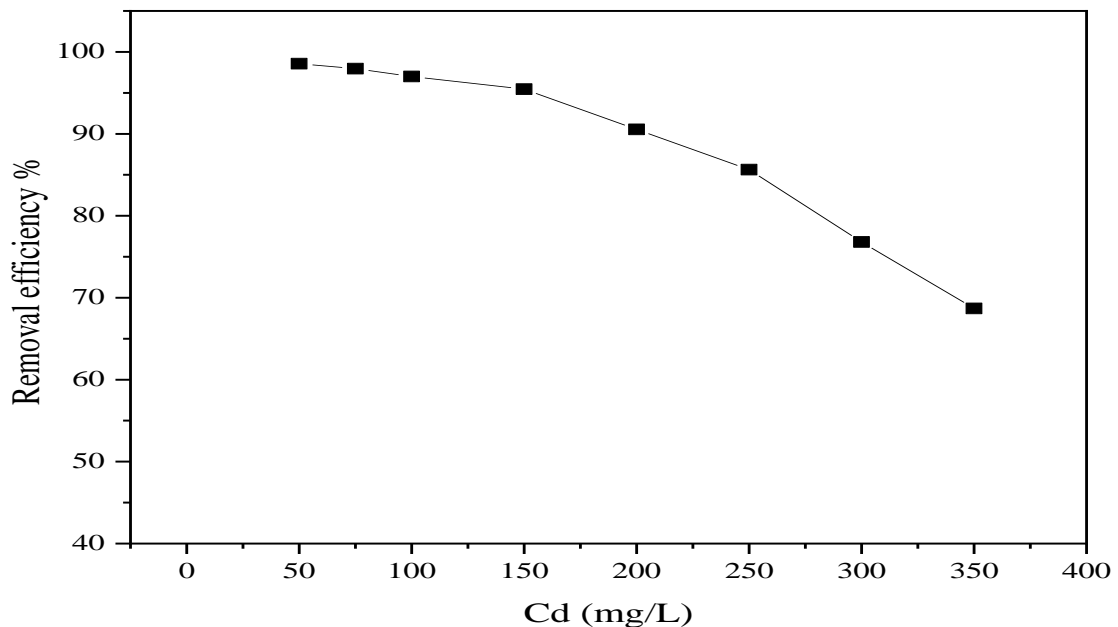


Figure 5. Effect of initial ion concentration on the Cd (II) ions adsorption

$$K_2 = \text{slope}^2/\text{intercept}, q_e = 1/\text{slope}$$

$$q_t = K_3 t^{0.5} + C \quad (5)$$

$$K_3 = \text{slope}, C = \text{intercept}$$

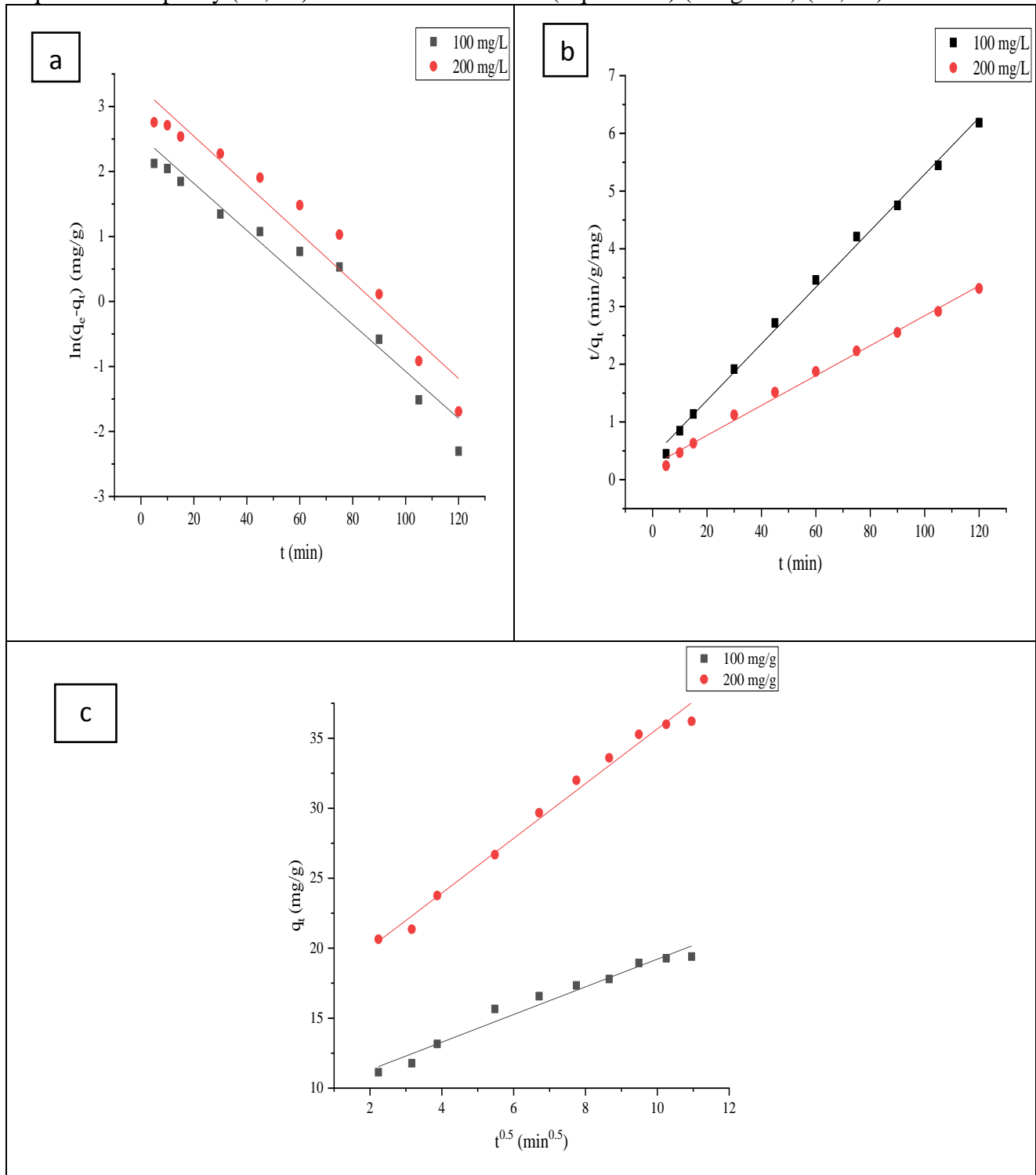
Where  $q_t$  is the amount of Cd (II) ions sorbed (mg/g) at time  $t$  (min),  $K_1$  is the equilibrium rate constant of pseudo-first-order model ( $\text{min}^{-1}$ ),  $K_2$  is the equilibrium rate constant of the pseudo-second-order model (g/mg.min),  $K_3$  is the intra-particle diffusion rate constant, and  $C$  is a constant related to the thickness of the boundary layer (mg/g). The three models were fitted and shown in Figure 6 and table 1 included statistical kinetics analysis. The agreement between practical observed uptake values and the pseudo-first-order model was

poor. The pseudo-second-order model characterized by higher predicted values of  $R^2$  (0.996-0.994) than the first and third models. For the intraparticle model, the smaller value of  $C$  the smaller boundary layer effect, also the higher values of  $K_3$  the more rapid adsorption phenomena. Due to the  $C$  values were greater than zero (the straight line from plotting  $q_t$  versus  $t^{0.5}$  not passing the origin point), the intraparticle diffusion did not dominate the mechanism for the adsorption of Cd (II) ions (19). So, the adsorption of Cd (II) ions in this study was fitted better with the pseudo-second-order model besides the type of adsorption was chemisorption as (1) mentioned. At chemical

sorption, there are chemical bonds between the MPKD and Cd (II) at sites which increase to a higher extent the coordination number with the surface and cause rate-limiting step (RLS). RLS is slowest step of a chemical reaction that restricts the rate at that the overall reaction continues. So, the uptake depends on sorption equilibrium capacity (34, 22).

**Adsorption isotherm**

Equilibrium data with constant temperature were commonly used to predict the maximum capacity of adsorbent (the MPKD). There were many isotherm models but the most famous and successful for describing the sorption were Freundlich (Equation 6) and Langmuir (Equation 7) (Langmuir) (22, 23).



**Figure 6. Fitting of the pseudo-first-order (a), pseudo-second-order (b), and intra-particle diffusion (c) kinetic models for Cd (II) ions sorption onto the MPKD at different initial concentrations**

**Table 1. Kinetic parameters of the Cd (II) ions adsorption on the MPKD**

Kinetic models	Cd (II) ion concentrations (mg/L)	
	100	200
qe, exp (mg/g)	19.5	36.4
<b>Pseudo-first-order</b>		
qe (calc.) (mg/g)	12.6816	26.789
K <sub>1</sub> (min <sup>-1</sup> )	0.03615	0.03726
R <sup>2</sup>	0.93973	0.94228
<b>Pseudo-second-order</b>		
qe (calc.) (mg/g)	20.42	38.59
K <sub>2</sub> (g/mg.min)	0.00607	0.00269
R <sup>2</sup>	0.99663	0.99425
<b>Intraparticle diffusion</b>		
qe (calc.) (mg/g)	20.149	37.529
K <sub>3</sub> (mg/g/min <sup>0.5</sup> )	0.988	1.955
C (mg/g)	9.327	16.114
R <sup>2</sup>	0.9656	0.9859

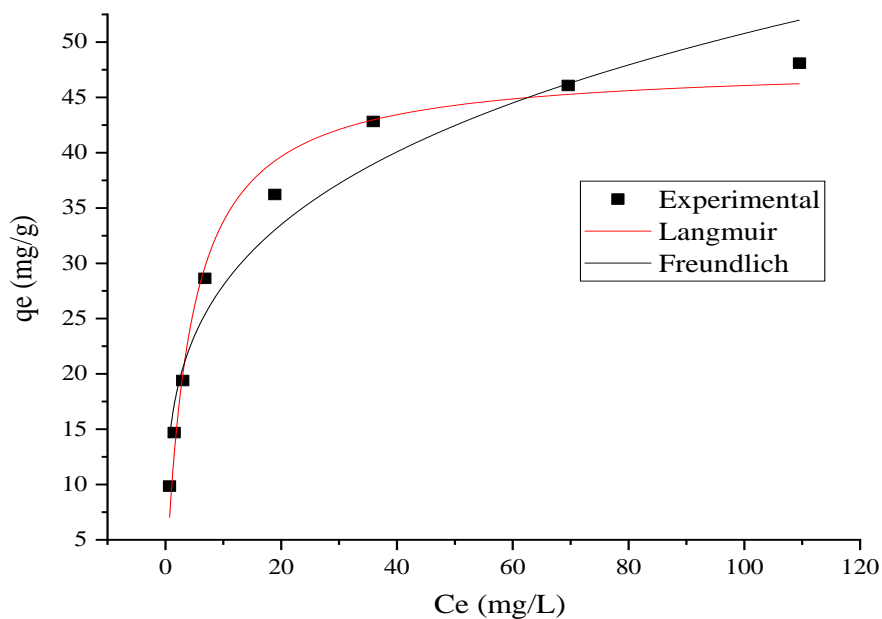
These models possessed two parameters which could be determined by nonlinear regression analysis.

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

$$\frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

Where K<sub>F</sub> is the Freundlich constant related to overall adsorption capacity (mg/g), 1/n is the constant related to a surface heterogeneity; q<sub>m</sub> is the maximum adsorption capacity (mg/g), and K<sub>L</sub> is the Langmuir constant reflecting the

affinity between the sorbent and sorbate (L/mg). It could be decided which one of these isotherm models were more suitable depending on the square of the correlation coefficient (R<sup>2</sup>). The adsorption isotherm models and statistical analysis results of Cd (II) ions adsorption on the MPKD were represented in Figure 7 and table 2, respectively. The results discovered that the relationship between the capacity data



**Figure 7. Isotherm data of the Cd (II) ions adsorption onto the MPKD (pH = 6.5, shaking speed = 200 rpm, adsorption dose 5 g/L, and initial ion concentrations = 50- 350 mg/L).**

**Table 2. Isotherm model parameters and regression coefficients for the adsorption of the Cd (II) ions onto the MPKD**

Model	Parameter	value
Langmuir	q <sub>m</sub> (mg/L)	48.016
	K <sub>L</sub>	0.23
	R <sup>2</sup>	0.979
Freundlich	K <sub>F</sub>	15.44
	n	3.86
	R <sup>2</sup>	0.941



and remaining at equilibrium was nonlinear. Also, the Langmuir model was more suitable to fit the experimental data with maximum uptake (48.016 mg/g). According to the theory of the Langmuir model, there was a monolayer of Cd (II) ions sorbed onto uniform active sites of the MPKD surface. Besides, the  $n$  value was

greater than unity referring to chemisorption of Cd (II) ions (22). Using the MPKD in the adsorption of Cd (II) ions did not mention previously as shown from the literature survey. So, it could be considered as an efficient adsorbent compared to other publications in table 3.

**Table 3. Comparison of the adsorption capacity of the different adsorbents for Cd (II) ions removal**

Adsorbent	$q_m$ (mg/g)	Reference
Fe <sub>3</sub> O <sub>4</sub> /Bentonite	21.7	(Yan et al. 2016)
Cashew nut shell	22.11	(Kumar, Ramalingam, and Sathyaselvabala 2012)
Fe <sub>3</sub> O <sub>4</sub>	11.698	(12)
<i>C. vulgaris</i>	111.1	(3)
OPP	35.71	(Gupta and Nayak 2012)
Mungbean husk	35.41	(Saeed, Iqbal, and Höll 2009)
Tobacco dust	29.60	(Qi and Aldrich 2008)
MPKD	48.016	This study

The by-product PKD was coated by Fe<sub>3</sub>O<sub>4</sub> and the new composite (MPKD) used for removal Cd (II) ions from aqueous solutions. Chemisorption was the type of the sorption in this study as verified by the kinetics study model pseudo-second-order. This fact was also confirmed by the Freundlich isotherm constant  $n$ . Although the Langmuir model did not provide any mechanistic understanding of the sorption phenomena, it was properly used to estimate the maximum capacity from the experimental data (48 mg/g).

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