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Adsorption of Ecotoxicological Congo Red Dye onto Kaolin Clay

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Abstract

This study was conducted to evaluate the adsorption ability of kaolin clay mineral to remove Congo red (CR), an anionic dye with ecotoxicological effects, from aqueous solution. In order to optimize the variables in the adsorption system, pH, adsorbent amount, contact time, and initial CR concentration factors were investigated. Adsorption kinetics and equilibrium isotherm of kaolin clay were investigated using Pseudo first order, Pseudo second order and Intra-Particle Diffusion kinetic equations and Freundlich, Langmuir and Temkin isotherm models. The obtained results were tested with 5 different error functions. Accordingly, it was determined that the adsorption of CR dye onto kaolin clay fit the Freundlich model with an R^2 value of 0.999 and the Pseudo second order model with an R^2 value of 0.999. In addition, the q_{max} value was calculated as 7.984 mg/g kaolin. For morphological examination, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy(SEM) images of raw and CR-loaded kaolin were examined. As a result, it was revealed that kaolin clay can be used as a low-cost alternative for the removal of resistant dyes from wastewater.

Keywords: Adsorption, Congo red, Isotherm, Kaolin, Kinetic

1. Introduction

The rapid development of the global production printing and dyeing industry in the world has increased the need for different dyes [1]. In industrial production, synthetic dyes are used intensively in sectors such as leather, paper, and textile industries due to their coloring properties [2], [3]. Dye molecules are compounds with complex chemical structures that can transfer their colors by binding to the surfaces or fabrics they affect and are highly resistant to environmental conditions [4]. CR dye, one of the dyes widely used in the dyeing industry, is preferred in various sectors due to its high chromaticity [1]. The textile industry, one of the sectors that uses the most dyes, has an important place in uncontrolled dye discharges into the aquatic ecosystem [5]. According to the World Bank report, approximately 17-20% of water pollution caused by industrial production is caused by the textile sector [6].

When dyes are discharged into the receiving environment in an uncontrolled manner, they remain in the ecosystem for a long time. These discharges are dangerous for flora and fauna, even in low concentrations, and cause significant environmental problems [7], [8]. Dyes that give color to water reduce the clarity and aeration of water, create negative effects on the photosynthesis system and cause the amount of dissolved oxygen to decrease [9]. Therefore, they must be treated before being discharged into the receiving environment.

Different removal methods are used for CR removal from aquatic environments. Various treatment processes such as ozonation [10] nanoparticles [11], ultrafiltration [12], electrochemical treatment [13], UV degradation [14], aerobic treatment [15] adsorption [16] have been frequently applied for CR removal. Researchers continue to search for cost-effective materials and methods for retaining dyes from wastewater. Among the alternative methods for CR removal, the adsorption process is used intensively due to its simple design and operation, effectiveness, and low cost [17], [18]. A wide variety of adsorbent materials are used in the adsorption process. Kaolin clay is also used effectively as a sorbent in the removal of dyes from wastewater due to its cheap and environmentally friendly nature. Clay materials attract the attention of researchers due to their environmentally friendly nature in the removal of dyes from aquatic environments [19].

In this study, the removal of CR dye from aqueous solutions by kaolin clay in a batch adsorption process was investigated. In the adsorption studies carried out with kaolin, a natural and easily available material, 3 different kinetic and isotherm models were tested. In addition, FTIR and SEM images of raw and CR-loaded kaolin were examined. The results show that kaolin clay is an environmentally sustainable material for CR removal from aqueous solutions. This fundamental study, which was carried out with kaolin clay, which is quite cheap compared to other commercial adsorbents, will provide researchers with ideas to design a sustainable adsorbent for sectors that use and discharge ecotoxicological paints with high environmental destructive power, such as the textile industry.

2. Materials and Methods

2.1. Chemicals

All chemicals used in experimental studies are of analytical grade. Powder Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, 696.66 g/mol, Sigma-Aldrich), pellet sodium hydroxide (NaOH, 40.00 g/mol, ≥99.0%, Sigma-Aldrich) and liquid sulfuric acid ($H_2(SO_4)_3$, 1.81 g/cm^3, ≥ 90-91 %, Merck) was used.

2.2. Preparation of Kaolin Clay

The kaolin clay used in adsorption studies was ground and then sieved in a sieve with a pore size of 75 microns. Then it was washed with pure water to remove impurities. Then it was dried in an oven at 60^{0}C for 24 hours and stored in a closed container.

2.3. Adsorption Studies

Batch adsorption studies were carried out on an orbital shaker with a stirring speed of 250 rpm (Heidolp, Unimax1010, Germany). A stock solution of CR dye with a concentration of 500 mg/L was prepared and a calibration curve was created at a wavelength of 497 nm on a UV-Visible spectrophotometer (Hach DR6000, Germany) by diluting the solution at the required rates [20]. The curve equation was calculated as y = 0.0414x + 0.0079 (R^2 = 0.999) and all experimental results were calculated with the help of this equation.

To determine the removal capacity of CR dye and its performance under environmental conditions, pH (3-11), initial kaolin amount, contact time and initial CR concentration were determined and kinetic and isotherm calculations were made according to these values. The obtained results were evaluated using equations 1 and 2.

$$R(\%) = \frac{C_0 - C_e}{C_0}.100 \quad \textbf{(1)}$$

$$q_e = \frac{(C_0 - C_e).V}{m} \quad \textbf{(2)}$$

Here, the R expression expresses the removal efficiency of CR dye in %, while the C_0 and C_e expressions express the CR concentration in the solution at the beginning and end of the experiments in mg/L. In addition, the q_e expression represents the amount of CR dye removed per gram of kaolin in mg (mg/g), the V expression represents the solution volume in L, and the m expression represents the amount of kaolin in g.

2.3.1. Adsorption Kinetics

Kinetic studies are carried out to determine the rate at which the adsorbent removes the pollutant and to have an idea about the removal mechanism[21]. In this context, 300 mg of kaolin was added to a 100 mL solution with an initial CR concentration of 3 mg/L at neutral pH and samples were taken at certain times to calculate the CR concentration with the help of the previously obtained calibration curve. The results were examined with the help of Pseudo first order, Pseudo second order and Intra-Particle Diffusion kinetic models Table 1.

Table 1. Kinetic Models Used in CR Adsorption on Kaolin Clay.

	Model	Equality	References
Kinetic models	Pseudo-first-order	$q_t = q_e(1 - e^{-k_1 t})$	[22]
	Pseudo-second-order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	[22]
	Intra-particle diffusion	$q_t = K_{id} t^{1/2} + C$	[23]

The q_t expression in the table above represents the amount of CR removed by the cation at a certain time t (mg/g), and the q_e expression represents the amount of removal at equilibrium (mg/g). In addition, the k_1, k_2, and K_{id} expressions represent the constant of each model.

2.3.2. Adsorption Isotherms

A reasonable isotherm modeling performed in adsorption studies provides information on the capacity of a given biosorbent to adsorb a unit mass of a solute under specified operating conditions [23]. In 6 different test tubes with a volume of 10 mL under the same environmental conditions, CR dye was added at concentrations ranging from 6.71 to 217.6 mg/L in the initial CR concentration range and kaolin was added at 1 g/L each. At the end of the period, centrifugation was performed and the CR concentration in the upper phase liquid was read. The obtained results were tested with the isotherm models given in Table 2.

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Table 2. Isotherm Models Used for CR Adsorption on Kaolin Clay

	Model	Equality	References
Isotherm models	Freundlich	$q_e = K_F {C_e}^{1/n}$	[24], [25]
	Langmuir	$q_e = \dfrac{q_{max} K_L C_e}{1 + K_L C_e}$ $R_L = \dfrac{1}{1 + a_L C_e}$	
	Temkin	$q_e = B ln(A_T C_e)$ $B = \dfrac{RT}{b_T}$	

When the table above is examined, q_e (mg/g) represents the amount of CR adsorbed at equilibrium, C_e (mg/L) represents the CR concentration at equilibrium, and q_{max} (mg/g) represents the maximum adsorption capacity. K_f (mg/g) (L/mg) is the Freundlich constant $1/n$; n is a dimensionless constant and indicates the adsorption density. The terms K_L and a_L are the Langmuir constants. R_L is the dispersion constant. In addition, B in the Temkin model represents the model constant, b_T (J/mol) represents the heat of adsorption, T (K) represents the temperature, and R (8.314 J/mol.K) represents the universal gas constant.

2.3.3. Error Function Test Describing

Statistical error functions are used to evaluate the fit of isotherm and kinetic equations to experimental equilibrium data during the adsorption process [26]. The error functions used for this purpose are presented in Table 3. A total of five error functions were used, namely, Sum of Square Error (SSE), Average Relative Error (ARE), Hybrid Fractional Error Function (HYBRID), Marquardt's Percentage Standard Deviation (MPSD) and Chi-Square test (X^2).

Table 3. Error Functions Tests

Error function	Equation	References
SSE	$\sum (q_{e,cal} - q_{e,exp})^2$	[27]
ARE	$\dfrac{1}{n}\sum_{i=1}^{n}\left\lvert\dfrac{q_{e,cal} - q_{e,exp}}{q_{e,exp}}\right\rvert$	
HYBRID	$\dfrac{1}{N-P}\sum\left\lvert\dfrac{q_{e,exp} - q_{e,cal}}{q_{e,exp}}\right\rvert$	
MPSD	$\sqrt{\dfrac{\sum\left\lvert(q_{e,exp} - q_{e,cal})/q_{e,exp}\right\rvert^2}{N-P}}$	
X^2	$\sum\dfrac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}}$	

3. Results and Discussion

3.1. Material Characterization

3.1.1. SEM Images

Surface morphology was examined before and after CR dye adsorption. Morphological images of raw and CR loaded kaolin clay are presented in Figure 1. According to the images obtained, Figure 1a Surface morphology shows a relatively regular, crystalline structure. The image contains pores among the particles. However, when we look at the image of the CR loaded particles, Figure 1b. The surface is rough and blurred. Further disintegration, irregularity and heterogeneity are seen on the surface. Connecting the dye to the Kaolin surface may have increased roughness by covering the surface. This occupancy and density in the pores may indicate that the adsorption process is successful [28], [29].

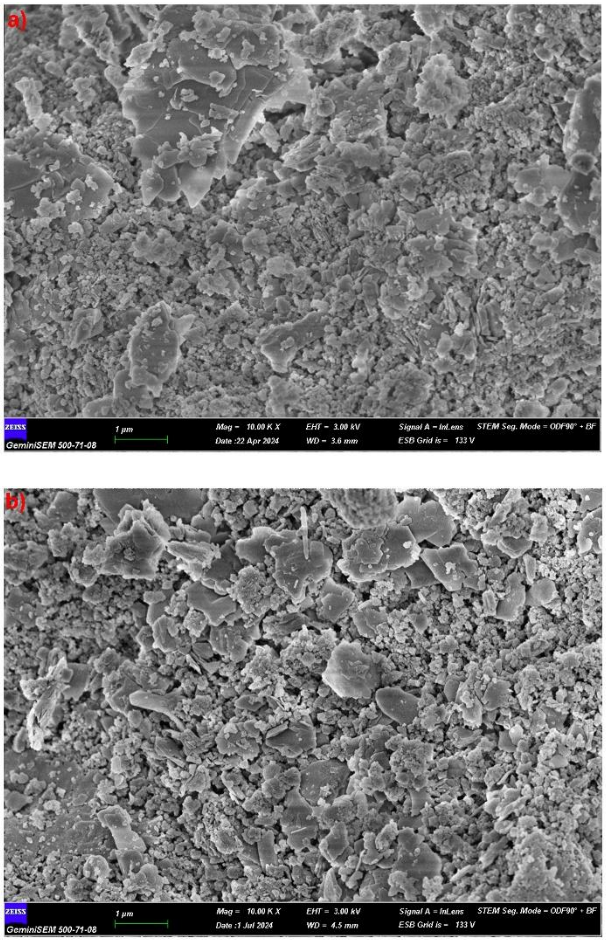

Figure 1. SEM images of kaolin clay before and after reaction; a) Raw kaolin clay, b) CR charged.

3.1.2. FTIR

FTIR analysis was performed to determine the adsorption functional group on the kaolin clay surface before and after CR adsorption. The spectra obtained for raw and CR-loaded kaolin clay are presented in Figure 2.

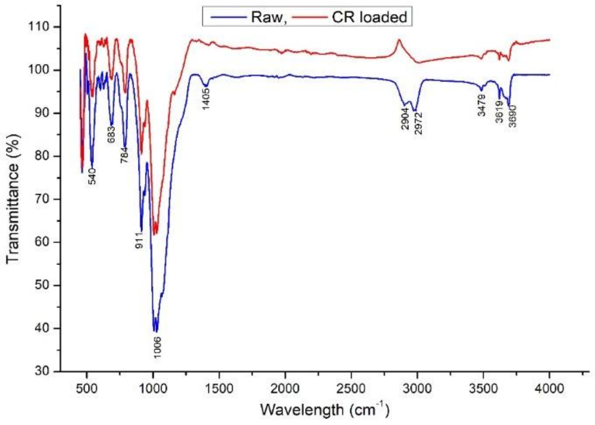

Figure 2. FTIR diagram before and after reaction.

The bands between 3619 cm^{-1}-3690 cm^{-1} correspond to the OH stretching vibrations of Al-OH groups on the surface and inside the kaolin, respectively. The bands between 911 cm^{-1}-1006 cm^{-1} correspond to the Si-O-Si stretching vibrations and silicate groups [26]. The Si-O-Al bond produces a band between 795-748 cm^{-1}, which is also seen at a wavelength of 784 cm^{-1} in this diagram [29]. As seen in Figure 2, bending, shifting or intensity changes at points such as 911 cm^{-1}, 1006 cm^{-1} and 1405^{-1} cm indicate that the adsorbent surface is loaded after adsorption by the adsorbate molecules[30]. The adsorption of CR onto kaolin caused obvious changes, especially in the region of hydroxyl groups (O-H) and C-H stretching vibrations.

3.2. Effect of Environmental Factors

To optimize the variables in the adsorption system, pH, adsorbent amount, contact time and initial CR dye concentration factors were investigated.

3.2.1. Effect of pH

To determine the effect of pH on CR dye removal, kaolin was added to 5 different test tubes with a volume of 10 mL with an initial CR concentration of 3 mg/L at a concentration of 1 g/L and the initial pH values were adjusted between 3-11. At the end of the centrifugation process in the time unit, dye concentrations were measured. The results obtained are presented in Figure 3a. Accordingly, while the q_e value was calculated as 1.4 mg/g at pH 3, this value was calculated as 1.77 mg/g at pH 5. A decrease in the q_e value was observed with the increase in pH. Therefore, since the highest efficiency was obtained at pH 5, the optimum pH value was determined as 5. When similar studies were examined, it was reported that high removal efficiencies were obtained for CR dye between pH 4-6 [31].

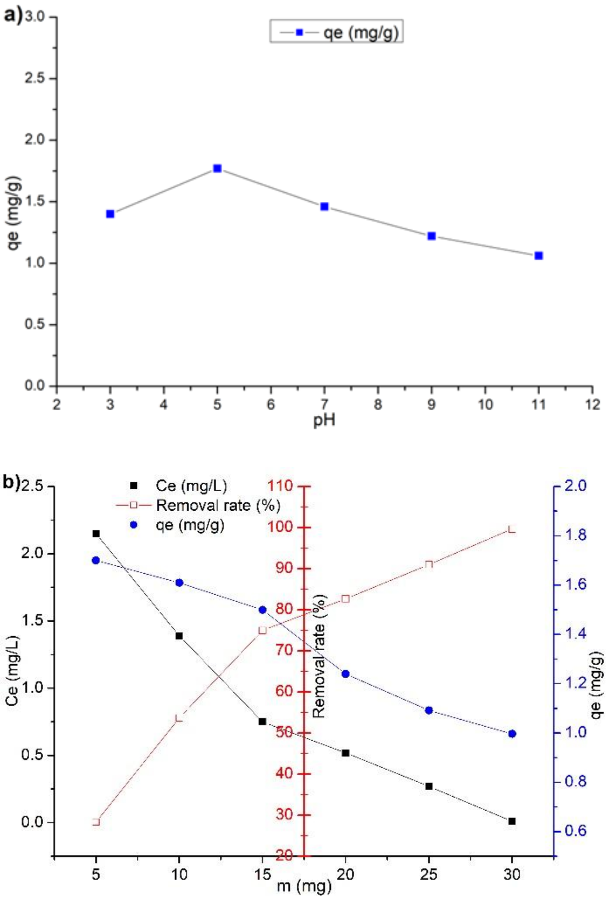

Figure 3. a) Effect of pH (V: 10 mL, C_0: 3.0 g/L, m: 1.0 g/L, time: 30 min, T: 25^{0}C, stirring 250 rpm), b) Effect of adsorbent amount (V: 10 mL, C0: 3.0 g/L, time: 30 min, pH 5.0, T: 25^{0}C, stirring 250 rpm).

3.2.2. Effect of Adsorbent Amount

In the experiments carried out under the same environmental conditions, kaolin was added in amounts ranging from 5 to 30 mg to 6 different test tubes with a pH of 5 and an initial CR concentration of 3 mg/L and a volume of 10 mL, and at the end of the period, centrifugation was performed, and CR dye measurements were made in the upper phase liquid. The results are presented in Figure 3b. According to the figure, while the removal efficiency in the presence of 5 mg kaolin was 28.33%, when the amount of kaolin was increased to 10 mg, the efficiency increased by 53.67%. The efficiency increased gradually with the increase in the amount of kaolin and finally, when the value of 30 mg was reached, the efficiency exceeded 99%. Accordingly, the amount of 30 mg kaolin was accepted as optimum. When the literature was examined, it was stated that there was a gradual increase in the removal efficiency with the increase in the amount of adsorbent in the adsorption of CR dye [32]

3.2.3. Effect of Contact Time

The contact time has an important effect on the adsorption process. A good contact time ensures that the adsorbent is applicable in the treatment of polluted water[33]. In this context, 300 mg of kaolin was added to a 100 mL volume solution with a 3 mg/L CR concentration and samples were taken at certain times to measure the concentration of CR dye. The results obtained are presented in Figure 4a. Accordingly, while the removal efficiency was calculated as 60% in the first 40 seconds at the beginning of the experiment, the efficiency reached 69% at the end of the 1st minute. The efficiency exceeded 90% at the end of the 4th minute and finally, the efficiency exceeded 99% at the end of the 25th minute. On the other hand, while the q_e value was 5.40 mg/g at the 40th second, it reached 6.21 mg/g at the 1st minute and was calculated as 8.13 mg/g at the 4th minute. Similarly, it has been reported in the literature that while high removal efficiency was achieved in short contact time, the efficiency increase continued with the extension of the time, but the increase rate decreased [34].

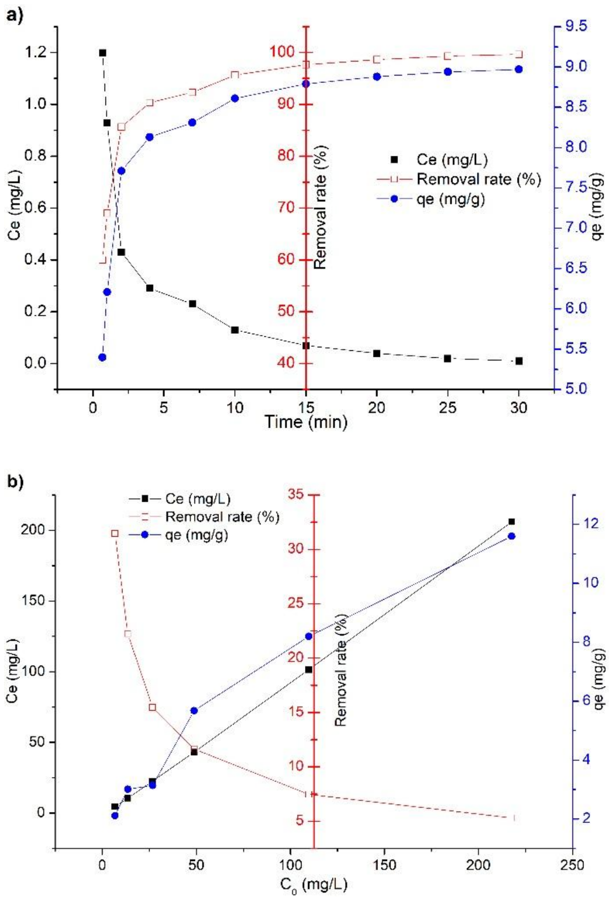

Figure 4. a) Effect of contact time, V: 100 mL, m: 300 mg, C_0: 3.0 mg/L, pH 5.0, T: 25^0C, stirring 250 rpm, b) Effect of initial concentration; C_0: 6.71-217.6 mg/L, V: 10 mL, m: 1.0 g/L, pH 5.0, T: 25^0C, stirring 250 rpm, time: 30 min.

3.2.4. Effect of initial concentration

In the experiments carried out under the same environmental conditions, 1 g/L kaolin was added to each of 6 different test tubes and the initial CR concentrations were changed between 6.71-217.6 mg/L. At the end of the period, CR concentrations were measured, and the obtained results are presented in Figure 4b. Accordingly, in the presence of 6.71 mg/L CR, the removal efficiency was calculated as 31.45% and the q_e value as 2.11 mg/g. When the initial CR concentration was increased to 48.78 mg/L, the efficiency was calculated as 11.64% and the q_e value as 5.68 mg/g. When the CR concentration was increased to 217.6 mg/L, the removal efficiency was calculated as 5.33% and the q_e value as 11.60. Accordingly, the increase in the amount of pollutant caused an increase in efficiency. This situation is that with the increase in the amount of CR, the pushing force of the dye molecules increases, which causes an increase in the efficiency of adsorption on kaolin. Similarly, when studies conducted with dyes are examined, it is reported that the q_e value increases with the increase in the initial dye concentration [35].

3.3. Adsorption kinetics

Estimating the speed of the adsorption process is one of the most important elements in the adsorption system. The adsorption process is affected by the physical and chemical properties of the adsorbent material, which determines the adsorption kinetics [36] In the study, the kinetics of adsorption were investigated to investigate the adsorption mechanism of CR on kaolin. Kinetic studies were carried out using three models, namely pseudo-first order, pseudo-second order and intraparticle diffusion model. In the evaluation carried out for CR dye, R^2 values of Pseudo first order and Intra-particle diffusion models were found as 0.923 and 0.591, respectively. R^2 value of Pseudo second order kinetic model was calculated as 0.999. When 3 kinetic models and error functions were evaluated together, it was seen that the most suitable kinetic model for the adsorption of CR dye onto kaolin clay was pseudo second model. In addition, in the evaluation carried out with SSE, ARE, HYBRID, MPSD and X^2 error functions, it was seen that Pseudo second order kinetic model was the most suitable model. The results obtained were compared with each other and given in Table 4. When the literature is examined, it has been reported that the pseudo-second-order kinetic model is the model that best explains the process in the study of CR dye removal with the environmentally friendly adsorbent obtained from kaolin clay and peanut shell[37].

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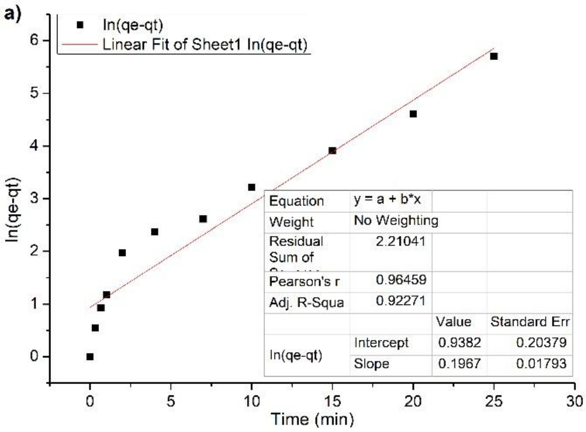
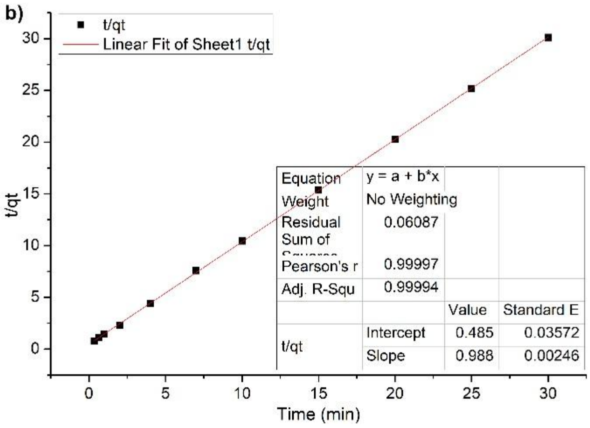
Table 4. Summary of the Calculated Kinetic Models for the Adsorption of CR onto Kaolin.

Kinetic models	Pseudo first order	Pseudo second order	Intra-Particle Diffusion
Parameters	k_1 = 0.052	k_2 = 2.014 q_e = 1.011	k_i =0.091 a = 0.573
R^2	0.923	0.999	0.591
SSE	1.07	0.003	0.124
ARE	53.60	2.25	19.33
HYBRID	75.04	1.780	0.340
MPSD	0.997	0.96	0.945
X^2	1.58	0.004	0.194

In addition, the graphs obtained from the linearized forms of each kinetic model equation are given in Figure 5.





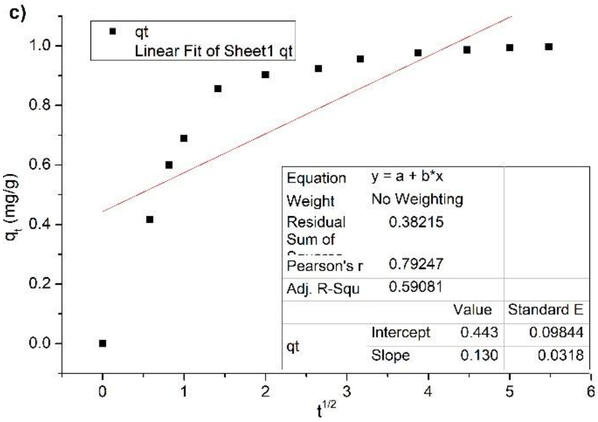


Figure 5. Regression curves, a) Pseudo first order, b) Pseudo second order, c) Intra-Particle Diffusion

In addition, the change graph comparing the numerical values obtained from the kinetic models applied with the amount of pollutants removed by the unit adsorbent obtained in the experimental studies with *qt* is given in Figure 6.

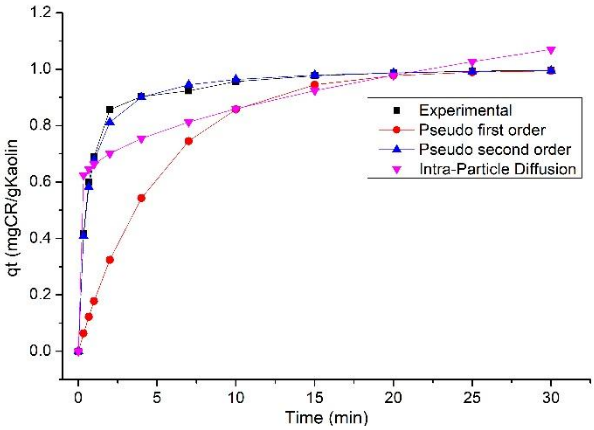


Figure 6. Plot of q_t values versus time.

When Table 3 and Figure 5 are examined together, the R^2 values of the Pseudo first order and Intra-particle diffusion models are calculated as 0.923 and 0.591, respectively, while the R^2 value of the Pseudo second order model is calculated as 0.999. Accordingly, it was determined that the most suitable kinetic model for the adsorption of CR dye onto kaolin clay is the Pseudo second order model. When different literature studies are examined, it is stated that the adsorption kinetics in the study of the adsorption of CR dye from aqueous medium with NaOH modified phengite clay is best represented by the Pseudo second order model [38]. In another similar study, the removal of CR dye from wastewater with chitosan waste and biobased composite material obtained from clay was aimed. As a result of the study, it was reported that CR removal was similarly controlled by the pseudo-second order model [39].

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3.4. Adsorption Isotherms

Isotherm studies conducted in adsorption experiments are one of the steps that provide important ideas about the process. It will reveal the mechanism of interaction of the adsorbate with the surface of the solid adsorbent and provide information about how the adsorbent particle works with the adsorbate molecules and how it reaches equilibrium [40]. In the study conducted, Freundlich, Langmuir and Temkin isotherm models were used to determine the most suitable isotherm model for the adsorption of CR dye onto kaolin clay. The results obtained from the models are presented in Table 5. When Table 5 is examined, the R^2 value of the Langmuir and Temkin models for CR dye is calculated as 0.964 and 0.917, respectively, while the R^2 value of the Freundlich isotherm model is calculated as 0.999. Again, in the evaluation made with the error functions given in Table 5, the SSE value is 0.063, while the Langmuir and Temkin models are calculated as 3.51 and 4.212, respectively. When the other error functions, ARE, HYBRID, MPSD and X^2, are examined, it is seen that the Freundlich isotherm model is the most suitable model. When similar studies were examined, it was reported that the isotherm that best represents the adsorption process in the study of removal of CR dye by adsorption on phyrophyllite was Freundlich[41].

Table 5. Summary of the Calculated Isotherm Models for the Adsorption of CR Dye onto Kaolin Clay.

Isotherms	**Freundlich**	**Langmuir**	**Temkin**
Parameters	k_F = 1.05 $1/n$ = 0.447	k_L = 0.023 R_L = 0.768 q_{max}=7.984	B_T =1.001 k_T =0.342
R^2	0.999	0.964	0.917
SSE	0.063	3.51	4.212
ARE	1.45	19.82	20.58
HYBRID	0.016	5.190	3.53
MPSD	0.916	0.971	0.967
X^2	0.008	0.774	0.945

The graph obtained from the regression curves of each model is displayed in Figure 7.

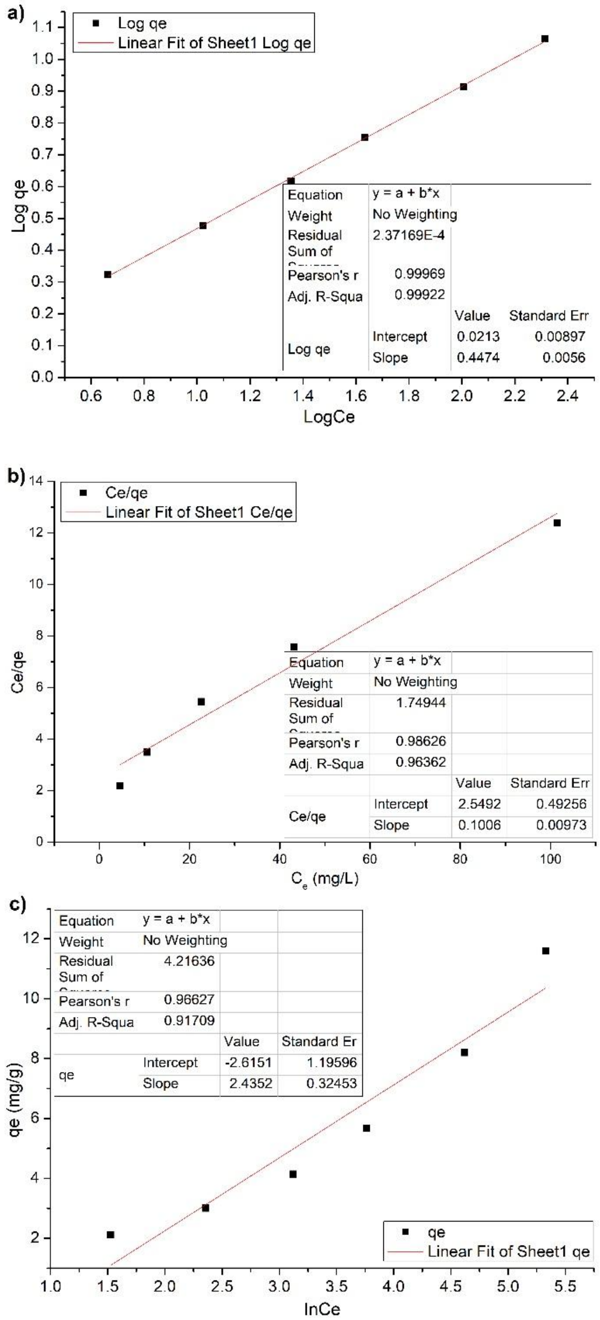

Figure 7. Regression Curves (a) Freundlich, b) Langmuir, c) Temkin.

In addition, the comparison graph of q_t values against C_e values, in which the isotherm models used are compared, is given in Figure 8.

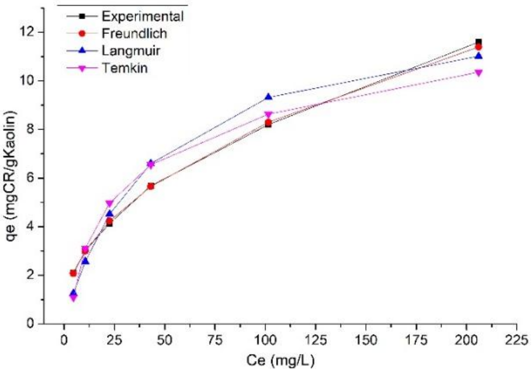

Figure 8. Graph of the changes in q_t values against C_e values.

3.5. Comparison of the Study and the Results Obtained with the Literature

When the studies in the literature (Table 6) are examined, the maximum adsorption capacity was reported as 1.896 mg/g in the study where basic yellow dye was removed with Ethiopian kaolin. In the study where CR was removed with kaolin clay functionalized with cellulose extract obtained from peanut shells, the maximum adsorption capacity was reported as 130.7 mg/g and the adsorption kinetics and isotherm were reported as pseudo-second order and Freundlich, respectively. In the study where methylene blue was removed from aqueous solutions by adsorption onto kaolin, which is a similar adsorbent, the maximum adsorption capacity was reported as 52.76 mg/g. In the study where crystal violet and brilliant green dyes were removed from aqueous solutions by adsorption onto kaolinite and acid-treated kaolinite, the maximum adsorption capacities were reported as 50.51 mg/g and 26.88 mg/g, respectively.

Table 6. Comparison of the Obtained Values with the Literature.

Type of pollutant	Adsorbent	q_m(mg/g)	Reference
Basic yellow dye	Ethiopian Kaolin	1.896	[30]
CR	Kaolin clay/cellulose composite	130.7	[37]
Methylene blue	Kaolin	52.76	[26]
Crystal violet - Brilliant green	Kaolin	50.51-26.88	[42]
CR	Kaolin clay	7.984	This study

4. Conclusion

The effects of pH, adsorbent amount, initial concentration, and time were investigated in this adsorption where kaolin clay was used in the removal of CR dye in aqueous solution. The obtained results were examined with 3 different kinetic and isotherm models. FTIR and SEM images of raw and CR loaded states of kaolin clay were examined to support the adsorption mechanism. According to the data obtained from batch adsorption studies, the most suitable kinetic and isotherm models were found as Pseudo second order (R^2: 0.999) and Freundlich (R^2: 0.999), respectively. In addition, the amount of CR dye removed per unit kaolin was calculated as 7.984 mg/g. With this study, it can be said that CR dye, which has ecotoxicological effects for flora and fauna, was successfully removed with kaolin clay.

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Ethics

There are no ethical issues after the publication of this manuscript.

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