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Synthesis and Characterization of Nanoparticle Composite CaO/Fe_3O_4 from Duck Egg Shells and Its Application for Congo Red and Procyon Red MX-5b Dyes Adsorption

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Abstract

In order to improve the adsorption performance of CaO prepared from duck egg shells, a 1:1 composite of CaO/Fe_3O_4 were synthesized using a coprecipitation method. This composite was then used to adsorb Congo red and Procyon red MX-5b dyes from an aqueous solution. The adsorption process was studied by investigating the effects of contact time, temperature, and initial concentration of dye. It was found that the optimum conditions for Congo red adsorption are 50 minutes of contact, 50 °C, and 225 mg/L of dye, while for Procyon red MX-5b the conditions are 50 minutes of contact, 60 °C, and 250 mg/L of dye. The behavior of both adsorbents at equilibria follows a pseudo-second-order kinetic model and Langmuir isotherm, with the adsorption capacity at optimum condition for Congo red and Procyon red MX-5b 46.95 mg/g and 47.39 mg/g, respectively. Thermodynamics studies showed that the adsorption process of Congo red was endothermic, while Procyon red MX-5b was exothermic, yet both were found to happen spontaneously.

Keywords: calcium oxide, magnetite, bio sourced material, green adsorbent, wastewater treatment

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Abstrak (Indonesian)

Untuk meningkatkan kinerja CaO yang dipreparasi dari cangkang telur bebek sebagai adsorben, disintesis komposit CaO/Fe_3O_4 (1:1) menggunakan metode kopresipitasi. Komposit ini kemudian digunakan untuk menyerap zat warna Congo red dan Procion red MX-5b dari larutan berair. Proses adsorpsi yang terjadi dipelajari dengan menyelidiki pengaruh beberapa parameter yaitu, waktu kontak, konsentrasi awal zat warna dan suhu. Kondisi optimum adsorpsi waktu kontak, suhu dan konsentrasi awal Congo red masing-masing adalah 50 menit, 50 ˚C dan 225 mg/L. Kondisi optimum adsorpsi waktu kontak, suhu dan konsentrasi awal Procion red MX-5b masing-masing adalah 50 menit, 60 ˚C dan 250 mg/L. Perilaku adsorben pada saat kesetimbangan, keduanya mengikuti model kinetika pseudo-orde-dua dan isoterm Langmuir, dengan kapasitas adsorpsi Congo red dan Procion red MX-5b pada masing-masing kondisi optimum adalah 46,95 mg/g dan 47,39 mg/g. Studi termodinamika menunjukkan bahwa proses adsorpsi Congo red dan Procion red MX-5b keduanya berjalan spontan dan masing-masing bersifat endotermik dan eksotermik.

Kata Kunci: kalsium oksida, magnetit, material bersumber hayati, adsorben hijau, pengelolaan air limbah

INTRODUCTION

Various industries such as textile, plastic production, photography, paint, paper mill, and printing, are typical originators of synthetic dyes contamination in aquatic ecosystem [1]. One of the common dyes used in such industries is Congo red – a toxic, carcinogenic, and difficult-to-degrade aromatic compound. In an aerobic waste treatment process, Congo red needs to be eliminated due to the danger it poses [1,2]. Another routinely-used dye is Procyon red

MX-5b, which is an azo compound that is frequently used in textile industry, especially in Songket production. Procyon red MX-5b is not an easy dye to be degraded and it is known to be able to obstruct the photosynthesis process of aquatic plants by reducing light penetration [3,4]. Hence, a method of treatment to remove such pollutants is critically needed.

Textile wastes are known to be treatable by coagulation, sedimentation, and by using activated clay [5]. An effective and reliable method that can be used to remove metal ions and dyes from waste water is adsorption. Specifically, adsorption of such pollutants by nanoparticle is a green technology that is considered simple, low-cost, efficient, and reversible [6].

Calcium oxide (CaO) nanoparticles have a structure with high surface area. The utilization of CaO nanoparticle as adsorbent is beneficial because it is kinetically fast, effective, inexpensive, highly available, abundant, and safe for human [7,8]. CaO could be synthesized by calcination of calcium carbonate ($CaCO_3$) which could easily be found in duck egg shells. Adsorbent made from bio sourced materials, e.g. duck egg shells, are known to be easily regenerable and have high adsorption capacity due to its larger surface area [9].

One way to enhance the performance of adsorbent in waste water treatment is by incorporating magnetic materials, such as magnetite (Fe_3O_4) – an active, hydrophilic, chemically stable, non-toxic, environmentally friendly, and relatively low cost material [10,11]. To improve its adsorption capabilities, CaO and Fe_3O_4 could be made into a CaO/Fe_3O_4 composite. The addition of magnetite into CaO helps in the process of post-adsorption separation of the adsorbent from the treated waste water, which could be done using an external magnet [11]. Inclusion of Fe_3O_4 also improves the stability, optimizes the adsorption, and prevents agglomeration of the adsorbent [11]. Therefore, we believe that a CaO/Fe_3O_4 composite could be utilized as a good alternative in the treatment of water contaminated by synthetic dyes

MATERIALS AND METHODS

General Methods

Chemicals used in this research were distilled water, duck egg shells, iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), sodium hydroxide (NaOH), sodium chloride (NaCl), hydrochloric acid (HCl), Procyon red MX-5b dye, and Congo red dye. All chemicals were purchased from Merck and used as is, except distilled water and duck egg shells which were locally-sourced.

The measurements of pH were done using a HM Digital PH-80-Original pH meter. Ultraviolet-visible (UV-Vis) spectroscopy analyses were conducted using Thermo Scientific Orion AquaMate 8000 spectrometer. Fourier-transform infrared (FTIR) spectroscopy analyses were performed using a Shimadzu IR-03/17/07 spectrometer. X-ray diffraction (XRD) analyses were done using Panalytical Type X'Pert PR diffractometer (Cu Kα = 1.54 Å, X-ray 40 kV, 30 mA, scan speed 1.74°/min, scan rate 0.02°, scan range 10°–90°). Vibrating-sample magnetometry (VSM) analyses were carried out using Oxford Type 1.2 magnetometer. Brunauer-Emmett-Teller (BET) surface adsorption analyses were conducted using Quadra orb Station 1 Type 7.01 machine

Calcination of CaO from duck egg shells

Calcium oxide was calcinated using a method adapted from Haryono *et al.* [9]. Duck egg shells were washed and then ground into 1–5 millimeter-sized powder. The obtained powder was then washed with distilled water and dried in an oven at 105 °C for 10 hours. The dried egg shell powder was subsequently ground in a mortar and sieved using a 100-mesh sieve. Then, the obtained calcium oxide powder was calcinated in a furnace at 1000 °C for 6 hours. Finally, the synthesized CaO was characterized using XRD analysis.

Synthesis of Fe_3O_4

Magnetite was synthesized using coprecipitation method adapted from Shakerian and Esmaeili [7], and Tamjidi and Esmaeili [8]. 12.0260 g of $FeCl_3{\cdot}6H_2O$ and 4.7244 g of $FeCl_2{\cdot}4H_2O$ were added into 275 mL of distilled water and then heated to 60 °C and then stirred at the speed of 400 rpm for 120 minutes. 1 M of NaOH were added dropwise into the solution until the pH reached 10 and black precipitate formed. The precipitate was then washed with distilled water to neutralize its pH and then vacuum-filtered. The obtained solid was then dried in an oven at 60 °C until its weight became constant, and subsequently ground in a mortar. The ground powder was then sieved using a 100-mesh sieve. In the end, the synthesized Fe_3O_4 was characterized using XRD and VSM analyses.

Preparation of CaO/Fe_3O_4 composite

The CaO/Fe_3O_4 composite was made by coprecipitation method adapted from Shakerian and Esmaeili [7], and Tamjidi and Esmaeili [8]. 1.167 g of $FeCl_3{\cdot}6H_2O$ and 0.429 g of $FeCl_2{\cdot}4H_2O$ were added into 25 mL of distilled water and then the solution's pH was measured. 0.5 g of CaO was then added into the mixture and the pH was measured again.

The mixture was then heated to 60 °C and then stirred at the speed of 400 rpm for 120 minutes. 1 M of NaOH were added dropwise into the solution until the pH reached 10 and black precipitate formed. The obtained solid was left to stand and then dried in an oven at 105 °C until its weight became constant. At last, the synthesized composite was characterized using XRD, VSM, and FTIR analyses.

Determination of Point of Zero Charge

Point of zero charge (pHpzc) of CaO/Fe_3O_4 composite was determined using pH drift method adapted from Nasiruddin Khan and Sarwar [12]. 50 mL of 1 M NaCl were added into several Erlenmeyer flasks. To set the pH into 1–11, 1 M of HCl or 1 M of NaOH were subsequently added dropwise into each flask. Then, 0.1 g of CaO/Fe_3O_4 composite were added into the mixture and then stirred at room temperature for 24 hours. After that, the composites were removed by filtration, and the pH of the filtrates were measured using pH meter.

Dye adsorption test

The adsorption of Congo red and Procion red MX-5b to CaO/Fe_3O_4 composite was studied using UV-Vis spectroscopy adapted from Purwaningrum *et al.* [13]. Three parameters were set as variables in this study: contact time, dye concentration, and temperature. CaO/Fe_3O_4 composite were added into a 25–300 mg/L solution of dye and then heated to 30–70 °C while being stirred at 120 rpm for 5–120 minutes. After that, the composite was removed from the mixture using an external magnet. Then, the concentration of dye was measured using UV-Vis spectrometer by comparing its absorption against a calibration curve. The adsorption capacity and adsorption efficiency could be calculation using Equation 1 and 2, respectively.

$$Q_e = \frac{C_0 - C_e}{w} \times V \quad \text{..... (1)}$$

$$\%R = \frac{C_0 - C_e}{C_0} \times 100\% \quad \text{..... ..(2)}$$

Where: Q_e (Adsorption capacity (mg/g)), %R (Adsorption efficiency (%)), C_0 (Initial concentration of dye (mg/L)), C_e (Final concentration of dye (mg/L)), w (Weight of adsorbent (g)), and V (Volume of adsorbate (L))

RESULTS AND DISCUSSION

Synthesis and characterization of adsorbent

Calcium oxide was successfully synthesized through calcination of duck egg shells. Figure 1 shows the condition of ground duck egg shells pre- (**Figure** 1a) and post-calcination (**Figure** 1b). The color of the obtained synthesized calcium oxide was visibly whiter after the calcination process, which indicates the increase in its CaO content [14]. The synthesis of magnetite and CaO/Fe_3O_4 composite via coprecipitation were also successful as proven by a simple test using an external magnet (**Figure** 1c, d).

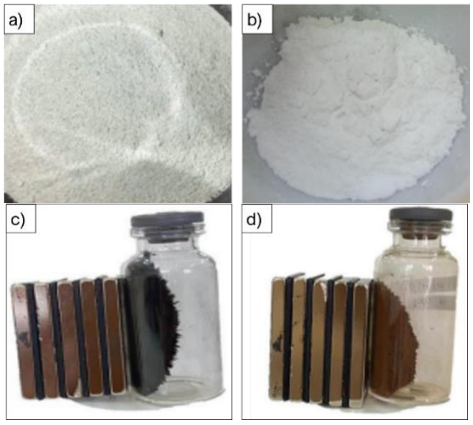

Figure 1. Ground duck shells a) before and b) after calcination; Synthesized c) Fe_3O_4 and d) CaO/Fe_3O_4 composite under the influence of external magnet

X-ray diffractogram of CaO, Fe_3O_4, and the composite also proven the success of the syntheses (**Figure** 2, **Table** 1) as the peaks showed by CaO correlates to the patterns of JCPDS No. 82-1690 and Fe_3O_4 were similar to the patterns of JCPDS No. 65-3107. According to the JCPDS data, CaO has a cubic structure while Fe_3O_4 has a spinel cubic crystal. Using the Debye-Scherrer equation, the calculated crystal size of CaO and Fe_3O_4 were 28.53 nm and 28.23 nm, respectively. The peaks of CaO/Fe_3O_4 composite (Fig. 2c) were strikingly similar to Fe_3O_4 with a distinguishable 2θ peak at 35.62°, indicating that magnetite was more dominant in the composite structure than CaO.

Table 1. Diffraction data of CaO, Fe_3O_4, and CaO/Fe_3O_4 composite compared to JCPDS data.

JCPDS 82-1690	Synth. CaO	JCPDS 65-3107	Synth. Fe_3O_4	Composite
32.59°	28.65°	30.50°	30.19°	30.19°
37.75°	34.06°	35.51°	35.58°	35.62°
53.54°	47.09°	43.32°	43.21°	43.19°
64.10°	50.77°	53.71°	53.73°	53.72°
67.76°	64.28°	57.21°	57.17°	57.18°
		62.94°	62.81°	62.80°

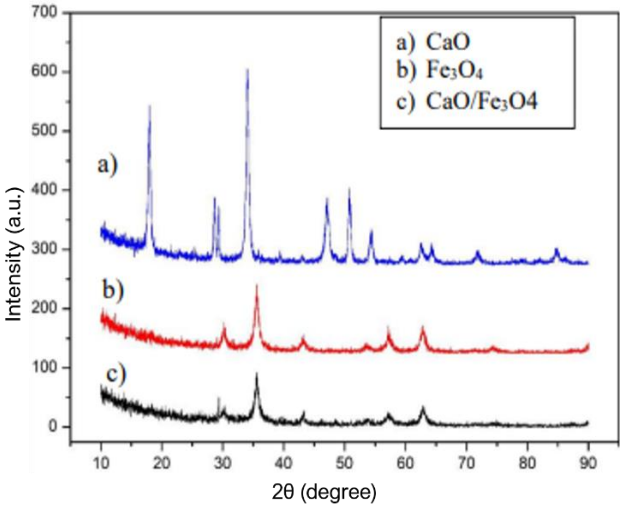

Figure 2. X-ray diffractogram of a) CaO, b) Fe_3O_4, and c) CaO/Fe_3O_4 composite

VSM analyses of Fe_3O_4 and CaO/Fe_3O_4 composite (**Figure** 3) were conducted to explore their magnetism. From the hysteresis curve, it was found that the magnetization value of the CaO/Fe_3O_4 composite (65 emu/g) was noticeably lower than Fe_3O_4 (91 emu/g). This result is expected, as calcium oxide is not magnetic, thus making the composite less magnetic overall compared to pure magnetite.

Surface area analysis for CaO/Fe_3O_4 composite using Brunauer-Emmett-Teller (BET) method reveals that the composite has a surface area of 110.55 m^2/g. This result was remarkably higher than 71.23 m^2/g reported by Shakerian and Esmaeili for CaO/Fe_3O_4 composite, in which the CaO was synthesized from hen egg shells [7]. When compared to non-bio sourced material, the difference is much more prominent. Previously, Tamjidi and Esmaeili reported that CaO/Fe_3O_4/SDS had a surface area of 36.47 m^2/g, which is 3 times smaller than our findings [8].

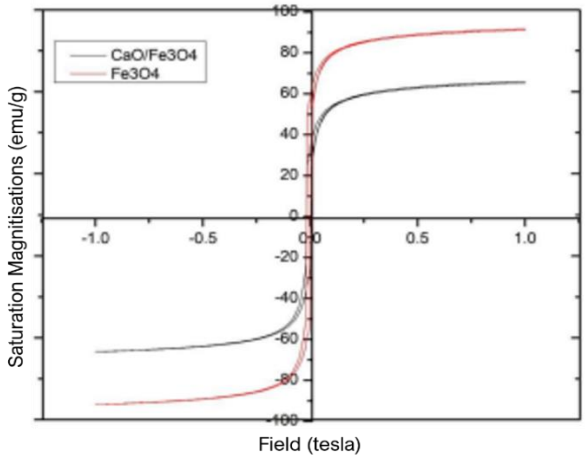

Figure 3. VSM hysteresis curve of Fe_3O_4 and CaO/Fe_3O_4 composite

Point of zero charge of the CaO/Fe_3O_4 was determined in order to know the pH at which the composite would have neutral surface charge. This analysis is necessary to decide whether the pH of adsorption system needs to be tuned to ensure that the adsorbent have opposite surface charge compared to the adsorbate. At pH below pHpzc, the adsorbent would have a positive surface charge. Conversely, if the pH is above pHpzc, the surface charge would be negative [15]. It was found that the pHpzc of CaO/Fe_3O_4 composite is 6.8 (**Figure** 4). As Congo red and Procion red MX-5b are anionic dyes with pH of 6.1 and 5.88, adjustment of pH is therefore not necessary because the adsorbent is expected to have opposite charge to the dyes at that pH.

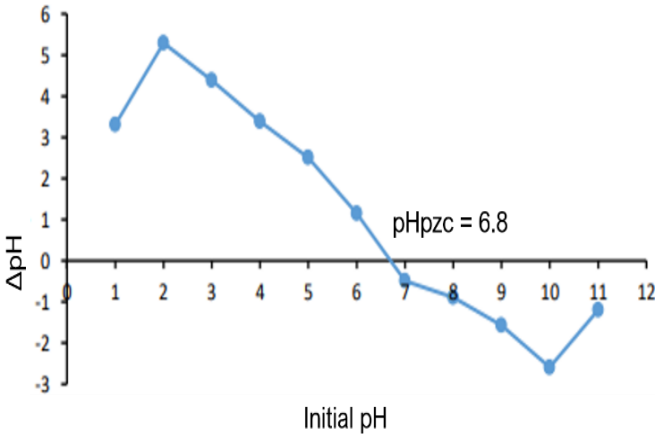

Figure 4. Initial pH vs. ΔpH graph to determine pHpzc.

Adsorption of Congo red and Procyon red MX-5b into CaO/Fe_3O_4 composite were studied through three variables: contact time, dye concentration, and temperature. The data from the contact time variation experiments could be derived to determine its adsorption kinetics, while the data from the dye concentration variation experiments could be used to deduce its adsorption isotherm, and the data from the temperature variation experiments could be applied to calculate its adsorption thermodynamics.

The effects of contact time on adsorption capacity could be seen on **Figure** 5. It was found that the optimum contact time for both Congo red and Procyon red MX-5b is 50 minutes, with adsorption capacity of 12.14 and 24.60 mg/g and adsorption efficiency of 98.0% and 98.4%, respectively. As contact time increases, the adsorption capacity tends to slightly increase up until the optimum time where it either plateaued or slightly decreased afterwards due to adsorbent saturation [16].

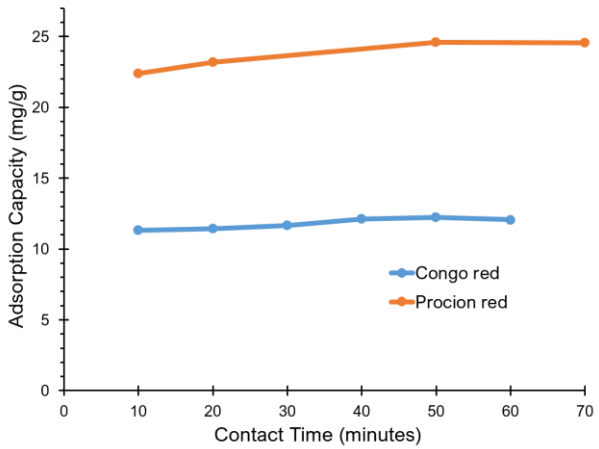

Figure 5. Adsorption capacity of CaO/Fe_3O_4 composite in relation to contact time.

Adsorption kinetics could be derived by plotting the data into either the pseudo-first-order (Equation 3) or pseudo-second-order (Equation 4) equation, and then checking its correlation coefficient (R^2) to see which model fits better mathematically. It was found that the adsorption kinetics of both Congo red and Procyon red MX-5b follows a pseudo-second-order model with adsorption rate of 0.12 and 0.053 $g \cdot mg^{-1} \cdot minute^{-1}$, and R^2 of 0.9992 and 0.9996, respectively. By using pseudo-second-order model, the calculated adsorption capacity fits well with the values observed in the experiments (**Table** 2).

$$\log(Q_e - Q_t) = \log Q_e - k_1 \cdot \log e \cdot t \quad \text{.....(3)}$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad \text{.....(4)}$$

Table 2. Kinetics of the adsorption of Congo red and Procion red MX-5b into CaO/Fe_3O_4 composite.

Adsorbate	Model	Parameter	Value
Congo red	Pseudo First Order	Q_e obs.	12.24
		Q_e calc.	1.07
		k_1	0.02
		R^2	0.661
	Pseudo Second Order	Q_e obs.	12.24
		Q_e calc.	12.24
		k_2	0.12
		R^2	0.9992
Procyon red MX-5b	Pseudo First Order	Q_e obs.	24.60
		Q_e calc.	10.03
		k_1	0.075
		R^2	0.8154
	Pseudo Second Order	Q_e obs.	24.60
		Q_e calc.	24.80
		k_2	0.053
		R^2	0.9996

The unit for Q_e is mg/g; k_1 is $minute^{-1}$; k_2 is $g \cdot mg^{-1} \cdot minute^{-1}$. R^2 is unitless.

The effects of initial dye concentration on adsorption capacity could be seen on **Figure** 6. It was observed that the optimum concentration for Congo red was 225 mg/L, with adsorption capacity of 45.16 mg/g and adsorption efficiency of 80.25%. On the other hand, the optimum concentration for Procyon red MX-5b was 250 mg/L, with adsorption capacity of 44.34 mg/g and adsorption efficiency of 71.58%. It was also found that the adsorption capacity tends to increase along with the increase of initial dye concentration before optimum concentration is reached. Beyond the optimum point, the adsorption capacity decreases due to saturation.

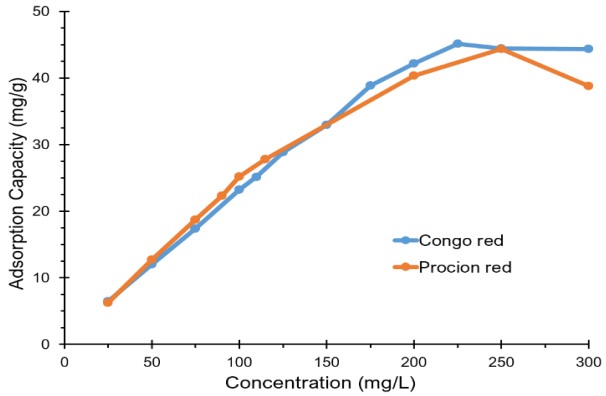

Figure 6. Adsorption capacity of CaO/Fe_3O_4 composite in relation to initial dye concentration

Adsorption isotherm could be determined by plotting the data into either the Langmuir (Equation 5) or Freundlich (Equation 6) isotherm model, and then comparing their correlation coefficient (R^2) to see which model fits better mathematically. It was found that the adsorption of both Congo red and Procion red MX-5b could be well described with a Langmuir isotherm model with the values of R^2 of 0.9942 and 0.9962, respectively (**Table** 3). Therefore, it is expected that the adsorption process happens on the homogeneous monolayer of the adsorbent [17].

$$\frac{C_e}{Q_e} = \frac{1}{k_L \cdot Q_m} + \frac{1}{Q_m} \cdot C_e \quad \text{.....(5)}$$

$$\log Q_e = \log k_F + \frac{1}{n} \cdot \log C_e \text{.....(6)}$$

Table 3. Isotherm of the adsorption of Congo red and Procion red MX-5b into CaO/Fe_3O_4 composite.

Adsorbate	Model	Parameter	Value
Congo red	Langmuir	Q_m	46.95
		k_L	0.16
		R^2	0.9942
	Freundlich	n	3.43
		1/n	0.29
		k_F	13.36
		R^2	0.9443
Procyon red MX-5b	Langmuir	Q_m	39.84
		k_L	83.67
		R^2	0.9962
	Freundlich	n	4.114
		1/n	0.243
		k_F	15.070
		R^2	0.6087

The unit for Q_m and k_F are mg/g; k_L is L/mg. R^2 is unitless.

The effect of temperature on adsorption capacity can be seen on **Figure** 7. The observed optimum temperature for the adsorption of Congo red was 50 °C, while the adsorption of Procyon red MX-6b reached optimum at 60 °C. It was found that the adsorption capacity increases as the temperature increases up to the optimum temperature. Above the optimum temperature, the adsorption of Congo red noticeably reduced, while Procyon red MX-5b only reduced slightly.

Thermodynamics of the adsorption could be deduced by calculating the free energy (Equation 7), then plotting the data into the rearranged Gibbs Free Energy equation (Equation 9), and then calculating the ΔH° and ΔS° from the obtained graph, assuming both ΔH° and ΔS° is unchanged within the temperature range of the experiment [18]. It was calculated that the adsorption of Congo red was endothermic with the enthalpy value of 39.77 kJ/mol and entropy of 0.15 J/mol·K, while Procyon red MX-5b was exothermic with the enthalpy value of –10.772 kJ/mol and entropy of 0.0308 J/mol·K. The adsorption of both dyes was spontaneous with the Gibbs free energy in the range of –4.72 to –10.59 kJ/mol for Congo red and between –20.105 to –21.029 kJ/mol for Procyon red MX-5b (Table 4).

$$\Delta G^o = -RT \cdot \ln K \text{.....(7)}$$

$$\Delta G^o = \Delta H^o - T \cdot \Delta S^o \text{.....(8)}$$

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \text{.....(9)}$$

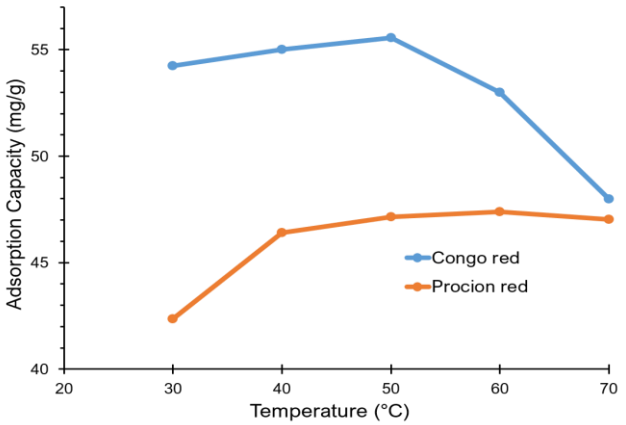

Figure 7. Adsorption capacity of CaO/Fe_3O_4 composite in relation to reaction temperature.

Table 4. Thermodynamics of the adsorption of Congo red and Procyon red MX-5b into CaO/Fe_3O_4 composite.

T	Congo red ΔG°	Procyon red MX-5b ΔG°
303 K	–4.72	–20.105
313 K	–6.19	–20.413
323 K	–7.65	–20.721
333 K	–9.12	–21.029
343 K	–10.59	
ΔH°	**39.77**	**–10.772**
ΔS°	**0.15**	**–0.0308**

The unit for ΔG° and ΔH° are kJ/mol; ΔS° is J/mol·K.

FTIR analyses was conducted on the CaO/Fe_3O_4 composite before and after adsorption process to see whether adsorption changes the chemical bonds inside the composite. The FTIR spectra could be seen on Figure 8. Peaks of Fe–O bonds at around 561 and 584 cm^{-1} and also Ca–O bond at 874 cm^{-1} was observed in the composite. After adsorption with Congo red, additional peaks at around 1175 cm^{-1} and 1227 cm^{-1}

were observed, which corresponds to the S–O and C–N groups, respectively. On the other hand, after adsorption with Procyon red MX-5b, additional peaks were observed at around 1174 cm^{-1} which corresponds to the S–O group and at around 740 cm^{-1} which corresponds to the C–Cl group [8].

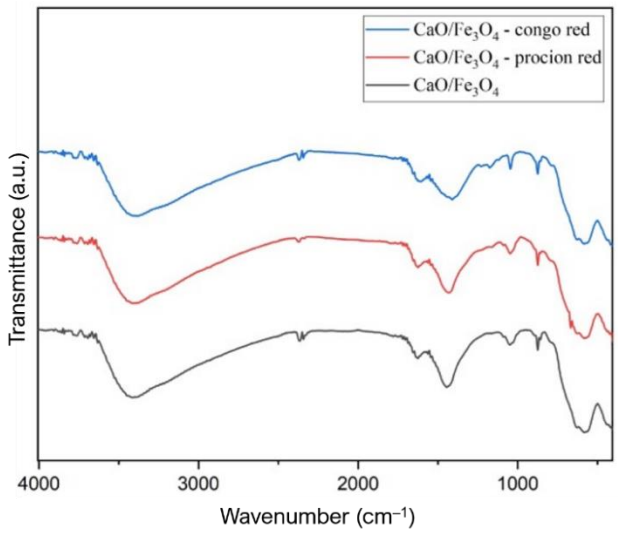

Figure 8. FTIR spectra of CaO/Fe_3O_4 composite before and after adsorption of Congo red and Procyon red MX-5b.

CONCLUSION

CaO/Fe_3O_4 composite was successfully synthesized as proven by its X-ray diffractogram, VSM hysteresis curve, FTIR spectra. Optimum conditions for the adsorption of Congo red are 50 minutes of contact, 50 °C, and 225 mg/L of dye, while the optimum conditions for Procyon red MX-5b are 50 minutes of contact, 60 °C, and 250 mg/L of dye. The adsorption of both dyes follows the pseudo-second-order kinetic model, adheres to the Langmuir isotherm, and happens spontaneously. The difference between Congo red and Procyon red MX-5b is that the adsorption of Congo red is endothermic, while Procyon red MX-5b is exothermic.

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