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Preface

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Preface

The Third International Conference on Green Energy and Environment (The 3rd ICoGEE 2021) was organized by the Faculty of Engineering – Universitas Bangka Belitung together with some co-organized members such as the Faculty of Engineering – Universitas Tadulako, Faculty of Engineering – Universitas Bengkulu, Faculty of Engineering – Universitas Maritim Raja Ali Haji, Faculty of Technology and Science – Universitas Jambi, MIPAnet and Asian Federation of Biotechnology (AFOB). We planned The 3rd ICoGEE 2021 to held on September 29th – 30th, 2021, in Pangkalpinang, Indonesia. However, the COVID-19 pandemic that is still engulfing various countries has hampered diverse gathering and traveling activities. Therefore, The 3rd ICoGEE 2021 has been held virtually using the Zoom Meeting platform.

The 3rd ICoGEE 2021 is a scientific conference involving various disciplines that aims to create innovations related to the development of science and technology to protect energy and the environment. Another goal of ICoGEE is to build a collaborative network between government, practitioners, and academics to solve problems in the energy and environmental sectors. Thus, this year's ICoGEE carries the theme: "Innovation Science and Technology Innovation for Sustainable Development Green Energy and a Cleaner Environment."

Although held online, this conference was attended by about 150 researchers, engineers, and scientists from various institutions. There are more than 60 institutions from nine countries: Indonesia, India, Viet Nam, Japan, Spain, China, Malaysia, Thailand, and Cyprus, participating in The 3rd ICoGEE 2021. The conference consists of two parts: keynote presentation and oral presentation. There were 114 papers (after the review process) divided into three topics: Green Energy and Application, Environmental Science and Technology, and Energy and Environmental Management. During the oral presentation session, the participants were divided into academic groups according to the topic.

We are very grateful because, in 2021, The 3rd ICoGEE has keynote speakers from different countries and institutions who are experts in energy and environmental aspects. Our great honor is that five experts gave excellent keynote speeches: Prof. Misri Gozan as Vice President of Asian Federation of Biotechnology, Associate Prof. Dr. Oki Muraza from King Fahd University of Petroleum and Minerals, Prof Taufik from Cal. Poly. State University, Prof. Ocky Karna Radjasa as Deputy Chairman of Earth Sciences - LIPI, and Prof. Jatna Supriatna as Vice Chairman of the Belantara Foundation.

Although The 3rd ICoGEE was held virtually, the conference can still achieve its primary purpose or benefit. All manuscripts published in the proceeding have been through a rigorous review to meet the requirement of high-quality papers.

The committee wishes to acknowledge speakers and participants who attended this virtual conference. We are beyond glad as this pandemic situation, which has been going on for more than a year, would not let their spirit down to keep participating in this conference. Plenty of thanks are given to all persons who have helped and supported this conference.

Warmest Regards,

Chairman of Organizing Committee

Herman Aldila



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Indonesian hydro energy potential map with run-off river system

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R Hambali and S Wahyuni

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Removal of Congo Red and Procion Red Using Zn/Fe Pillared Bentonite

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Abstract. The process of pillarization of metal oxide Zn/Fe compounds in bentonite has been carried out. The study of adsorbent weight, pH, adsorption time, and initial concentration were investigated to get the optimum reduction of Congo red and Procion red concentration. In addition, the pseudo kinetic also determined to investigate the rate and type of adsorption. From the experiment, the optimum conditions for removal of Congo red for the adsorbent weight, pH, and adsorption time were 0.02 g, 2, 20 minutes, respectively, while for the removal of Procion red was 0.04 g, 2, 20 minutes, respectively and both of adsorbent followed the pseudo-second-order model kinetics with chemisorption mechanism. Although the optimum conditions for removal of the two dyes were similar, in fact the percentage removal of the Congo red dye was greater. In conclusion, the Zn/Fe pillared bentonite was more suitable for the removal of the Congo red than Procion red.

1. Introduction

Dyes can harmfully affect waters and can restrain the action of living organic entities due to their nature. The Congo red and Procion red, as well known dyes, additionally have a significant degree of poisonousness and are difficult to remove naturally. Based on the character, it is really needed to use a suitable method to reduce the pollutant. Among the methods, adsorption is still the best and cheap method to treat the dyes in waste water [1]. A few past investigations have consistently utilized activated carbon as an adsorbent, though enacted carbon has the hindrance that it required high energy of activation method and costly [2]. Along these lines, we need another kind of adsorbent that is cheap, simple to get and reusable.

Bentonite is one of famous natural adsorbent. Bentonite has a layered structure and exchangeable inorganic cations that make it suitable for adsorption process [3]. Since bentonite has a small distance between layers, it needed an addition action to increase the basal spacing. To overcome this, the researcher has been investigated the use of large molecules to increase the distance between layers [4].

Bentonite modification is done by inserting and intercalation material on the surface and inside bentonite as known as doping and pillarization [5]. Metal ions such as Al^{3+} , Co^{2+} , Cu^{+2} , Al^{3+} , Fe^{+3} , Cr^{3+} , and so on have been used to increase the adsorption capacity of bentonite via pillarization [6]. Furthermore, the use of a combination of two metal ions, such as Zr/Al [7], Cr/Al [8] and so on, is fascinating because it provides an increased adsorption capacity compared to the single metal [9]. The combination of Zn/Fe metals is getting more attention because these metals are reported to have a high



surface area to volume ratio, high density of reactive surface sites and are environmentally friendly [10-11].

The combination of Zn/Fe metal oxide may have a synergic effect on increasing the ability of bentonite to adsorb dyes. Adsorption studies of congo red and procion red dyes using Zn/Fe pillared bentonite have not yet been reported. Therefore, this research will focus on studying the effect of adsorbent weight, pH, adsorption time, and pseudo kinetic parameters of Zn/Fe pillared bentonite on the percentage removal of congo red and procion red dyes also will compare to natural bentonite as a control.

2. Materials and method

2.1. Materials

Bentonite clay was supplied from bentonite deposit located in Lampung Province, Indonesia. The Congo red and Procion red dye were obtained from the local market in Palembang, Indonesia. Materials used in research these are: ZnCl_2 , FeCl_2 , NaOH, and HCl that purchased from Merck Millipore and used as received without further purification.

2.2. Pillarization of Bentonite with Metal Oxides Zn/Fe

Pillarization of Zn/Fe was synthesized by adding 12 g of bentonite to 120 mL of distilled water and stirred for 2 hours. The prepared suspension was then added with the Zn/Fe solution. The mixture was stirred and distilled for 24 hours. After 24 hours, the solution was filtered and the solid was dried at 100°C and followed calcined for 2 hours at 400°C .

2.3. Effects of Adsorbent Weight

50 mL of Congo red and Procion dye solution with concentration of 100 mg/L in interaction with bentonite polarized Zn/Fe metal oxide and natural bentonite (control) with variation of weight of adsorbent 0.01; 0.02; 0.03; 0.04 and 0.05 g. The mixture was stirred using a horizontal shaker for 60 minutes, then the dyestuff solution having been centrifuged and measured using UV-Vis Spectrophotometer at λ max of 498 nm and 537 nm for congo red and procion red, respectively.

2.4. Effect of pH

The effect of pH was studied by interaction of 0.05 g bentonite which had been polarized by Zn/Fe metal oxide and natural bentonite (control) and then added to 50 mL of Congo red and Procion dye with concentration of 100 mg/L while stirring in a horizontally using shaker within 1 hour. pH was adjusted by 0.01 M HCl or 0.01 M. NaOH. The pH variations used were 1, 2, 3, 4, 5 and 6. Then we observed the stability using UV-Vis spectrophotometer.

2.5. Effect of Adsorption Time and Kinetic Parameters

A total of 0.05 g of natural bentonite (control) was added to 5 mL of dye with a concentration of 100 mg/L. The mixture is stirred with a horizontal shaker at predetermined intervals. Adsorption time variation starts from 20, 30, 40, 50, 60, 70, 80, 90, and 100 minutes. Pigment, which has gone through the adsorption process, is separated and measured its absorbance using a UV-Vis spectrophotometer. The same procedure is performed for the pillarized bentonite adsorbent. The amount of residual concentration (C_e) and the amount of adsorbed dye ($C_0 - C_e$) was calculated using the standard solution calibration curve equation, while the kinetic model can be calculated using pseudo first order and second order pseudo equation.

3. Results and Discussion

3.1. Effect of Adsorbent weight

Variation of adsorbent dosage was conducted in order to know the influence of adsorption weight between natural and pillared bentonite on the percentage of dye removal that can be seen in Figure 1.

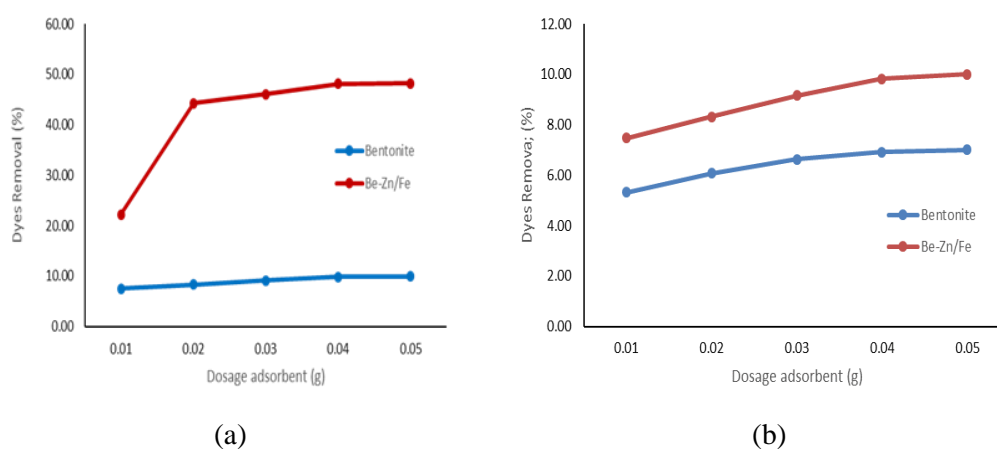


Figure 1. Effect of adsorbent weight on: (a) Congo red and (b) Procyon red

Figure 1 shows that the percentage of dye removal increased with increasing adsorbent dosage. Along with the increase in the adsorbent dosage, the number of active sites also increases. Therefore the adsorption process is more facilitated, leading to an increase in the percentage of dye removal [12]. This trend consistent with similar adsorption studies of Procion Red MX-5B and Crystal Violet using activated carbon from corn cobs reported by Nazifa et al. [13].

Figure 1 also shows that The percentage of dye removal over Zn/Fe pillared bentonite is greater than natural bentonite, indicating that the pillarization is positively correlated with the increasing ability of bentonite as an adsorbent; this is probably due to the availability of Zn/Fe active sites on the bentonite surface, thus making the percentage of dye removal more effective [6-7]. Similar conditions have been reported by Issaoui et al. [5] using Al pillared bentonite. Furthermore, the increase in the percentage of dye removal in bentonite is relatively insignificant compared to Zn/Fe pillared bentonite. This is probably due to the agglomeration of adsorbent particles and saturation of the active site, thus giving a relatively constant dye removal percentage [16].

The adsorbent dosage effect on the percentage removal of dyes has been reported using other adsorbents. Jumadi et al. [17] using chitosan, Fe_3O_4 , and magnetic chitosan nanocomposite (MCN) reported that almost 100 % of dyes removed with an optimum dosage of 50 mg. Stjepanovi et al. [18] using waste wood biomass Euroamerican Poplar with an adsorbent dosage range of 1-10 mg dm^{-3} , reported that the optimum dosage for Congo red dye removal was 8 mg dm^{-3} with a dye removal percentage of 69.4 %. Ghorai et al. [19] used polyacrylamide grafted xanthan gum/silica nanocomposite, reported that the optimum dosage for congo red dye removal was 50 mg with a dye removal percentage of 96.37 %. Georgin et al. [20] using avocado shells- H_2SO_4 and HNO_3 , reported that the optimum adsorbent dosage for Procyon red dye removal was 0.3 g L^{-1} with a dye removal percentage of 96%. Nazifa et al. [13] using activated charcoal from corn cobs, reported that the optimum dosage for Procyon red dye removal was 0.5 g/50 mL with dye removal percentage of 98.9 %. Generally, it can be concluded that Zn/Al pillared bentonite is quite effective in increasing the percentage of dye removal compare to bentonite because of its active site that plays a role in adsorption of dyes.

3.2. Effect of Initial pH

Effect of pH on natural and pillared bentonite to Congo red and Procyon red removal are presented in Figure 2 and show that the percentage of dye removal decreased as the pH value increased. This is due to the electrostatic attraction between the anionic dye Congo red which has a negatively charged sulfonate group (SO_3^-Na^+), and the surface of the adsorbent, which has a positively charged Xylanol group. When the pH is close to neutral, the percentage of dyes removal relatively constant. This is caused by the interaction only involve the physical forces. Furthermore, as the pH increases from neutral to

basic, the amount of negative charge on the surface of the adsorbent increased due to deprotonation leading to electrostatic repulsion with the anionic dye, thus decreasing the percentage of dye removal [10-11]. Similar results have been reported by Etemadinia et al. [23] using $\text{ZnFe}_2\text{O}_4/\text{SiO}_2/\text{Tragacanth}$ gum magnetic nanocomposite with a pH interval study of 5-11.

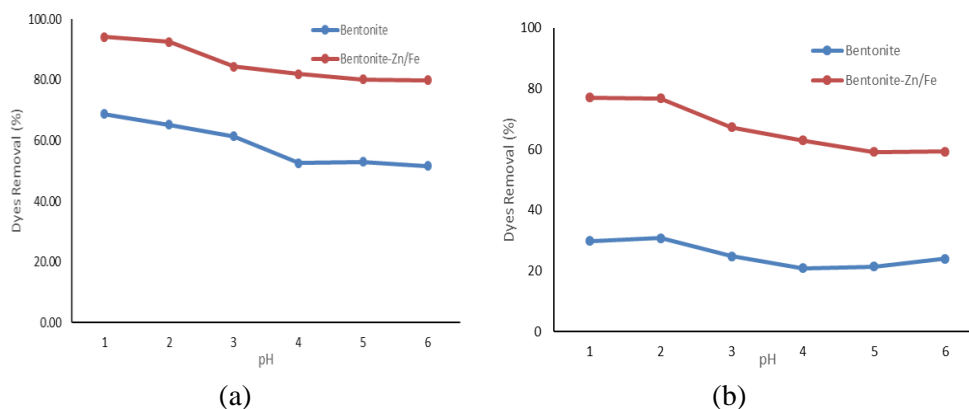


Figure 2. Effect of pH on: (a) Congo red and (b) Procyon red

Ribas et al. [24] reported that the maximum dye removal percentage of Procyon Red MX-5B obtained at pH 2 was 84 % using activated carbon from peaches, and this is consistent with the data obtained using bentonite and Zn/Fe pillared bentonite. The percentage affinity for the removal of Congo red and Procyon red relatively different. This difference in affinity is because specific dyes have different electrostatic and physical forces according to their structure, size, and functional groups [15].

3.3. Effect of Adsorption Time

The effect of adsorption on the removal of Congo red and Procyon using natural and pillared bentonite are shown in Figure 3.

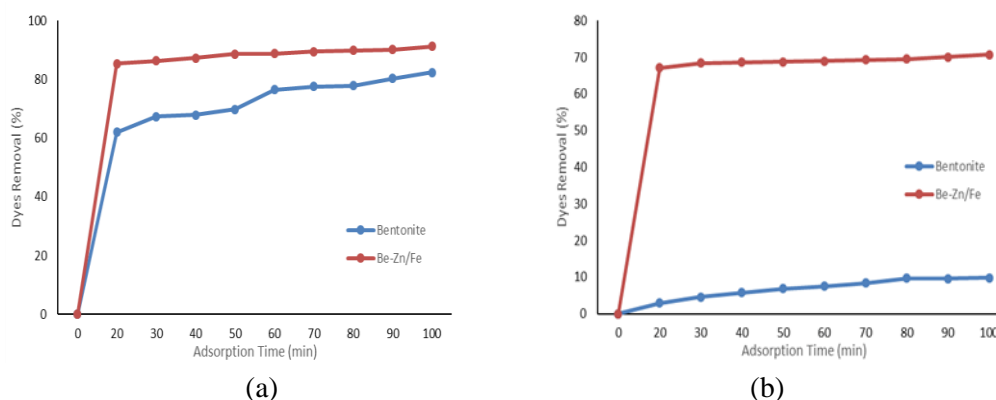


Figure 3. Effect of adsorption time on: (a) the Congo red and (b) Procyon red

From Figure 3, it can be seen that the dye removal process in bentonite and Zn/Fe pillared bentonite is relatively fast in the initial time interval. However, with increasing contact time, the percentage of dye removal increases slowly and gradually reaches equilibrium. A similar condition has been reported by Huang et al. [25] in the study of the adsorption of Rhodamine B and Acid red 1 using CTAB-bentonite with an interval time of 10-130 minutes. The high percentage of dye removal in the early stages was due to the availability of adsorption sites on the surface of the adsorbent. After rapid adsorption, a phase transition occurs where the percentage rate of dye removal is slow and reaches a constant value [15].

The rapid adsorption in the early stages can be attributed to external surface adsorption. While at a slower stage, it occurs through internal surface adsorption [26].

Yulizar et al. [6] reported that the optimum adsorption time occurred at 45 minutes with the percentage of sodium dodecyl benzene-sulfonate adsorption of 99.30% using Al-pillared bentonite/PDDA. Ayati et al. [27] reported that the adsorption of Congo red was achieved in 30 minutes with Na-bentonite and more quickly using Ti, HDTMA, and Al/Fe modified clay, which was less than 20 minutes.

The adsorption kinetics study is an important factor to evaluate the rate of dye removed by the adsorbent. The adsorption process generally occurs through a process that starts from the external mass transfer of adsorbate molecules from the solution to the external adsorbent surface, followed by the transfer of the adsorbed molecules to the adsorption site and finally, the absorption itself [28]. Experimental data can be described by pseudo-first-order and pseudo-second-order and can be seen in equations 1 and 2, respectively.

$$\log (q_e - q_t) = \log q_e \frac{k_1}{2.303} t \quad (1)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

Where q_e and q_t are adsorption capacity (mg/g) at equilibrium and any time t (min), also k_1 (min^{-1}) and k_2 ($\text{g/mg} \cdot \text{min}$) are pseudo-first order and pseudo-second order constant, respectively.

The natural bentonite has a smaller adsorption rate than pillared. It is caused the Zn/Fe metal oxide give a greater reactive rate as listed in Table 1.

Table 1. Constant of kinetic adsorption model of Congo red and Procion red

Type of Adsorbate (Adsorbent)	Experimental	Pseudo-first-order (PFO)		Pseudo-Seconds-order (PSO)	
	Q_e	Q_e	R^2	Q_e	R^2
CR (N)	75.76	77.08	0.966	85.83	0.995
CR (P)	80.14	88.16	0.936	90.61	0.988
PR (N)	24.831	52.461	0.906	60.431	0.904
PR (P)	54.761	65.760	0.905	60.666	0.908

From the Table 1 shows the adsorption of Congo red on bentonite and Zn/Fe pillared bentonite match with the PSO kinetic adsorption model with coefficient of determination (R^2) 0.995 and 0.988, respectively which higher than PFO. This result indicates that the adsorption process follows PSO kinetics with the chemisorption mechanism [23]. Similar results have been reported by Kadeche et al. [29] in the Coomassie blue dye adsorption study using Na-bentonite and Fe pillared bentonite, and Huang et al. [25] in the study of the adsorption of Rhodamine B and Acid red 1 using organobentonite.

4. Conclusion

The adsorption capacity of bentonite was successfully enhanced by modification using Zn/Fe metal to pillar the inner layer of bentonite. Congo red and Procion red dye can be adsorbed by natural bentonite and Zn/Fe pillared bentonite. The results showed that the adsorption of Congo red and Procion on raw natural and pillared bentonite followed the pseudo-second-order kinetic with chemisorption mechanism.

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CERTIFICATE

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