

REMOVAL OF Hg(II) METAL IONS USING KAOLIN ADSORBENTS MODIFIED WITH ANIONIC SURFACTANT AND EFFICIENT ULTRASONIC ASSISTED

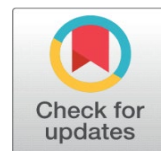


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ABSTRACT

This study reported the reduction of metal Hg (II) from water using natural kaolinite (NK) based adsorbents compared with modified kaolinite adsorbents with Hexadecyl trimethyl ammonium bromide anionic surfactants using ultrasonic technology (SMK). These adsorbent samples were characterized using several different techniques such as FTIR, X-RD and AAS analysis. The adsorption capacity is influenced by variables such as the contact time and adsorbent dosage. The results of the analysis reported that the maximum waste reduction efficiency occurs in modified kaolin (SMK), where adsorption occurs faster than natural kaolin (NK). The maximum persentation is 94.57% for metal removal efficiency using modified kaolin at the contact time of 45 minutes and the dose of adsorbent 1.4 g, while kaolin without modification is 73.83% of efficiency at the contact time of 60 minutes the adsorbent dose was 1.4 g. The use of the adsorption method with the help of ultrasonic technology is proven to be more efficient in accelerating the removal of Hg²⁺ ions by increasing the surface dispersion of the adsorbent with metal ions in water. The adsorption kinetics model that is suitable for calculating the adsorption capacity of the adsorbent in the removal of Hg²⁺ ions using unmodified kaolin is pseudo-second-order models.

Received 10 October 2021
Accepted 01 November 2021
Published 30 November 2021

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DOI
[10.29121/granthaalayah.v9.i11.2021.4379](https://doi.org/10.29121/granthaalayah.v9.i11.2021.4379)

Funding: This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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Keywords: Kaolinite, Adsorbent, Ultrasonic Assisted, Surfactant, Removal of Metal

1. INTRODUCTION

Water pollution is a serious environmental problem that is important for the modern world today, water as an important for all activities of living things on earth, so water and wastewater treatment is a global concern. [Awale and Soubaneh \(2014\)](#), [Mahmoodi and Oveisi \(2019\)](#) Since the industrial revolution in the 18th century, a large increase in industrial activities including metals, dye, battery, printing, mining, engineering metallurgy, electroplating, pigment, PVC stabilizers, electrical equipment manufacturing, semiconductors, and cosmetics produce various types of pollutants in liquid waste which dispose of byproducts in lakes, oceans and rivers, which pollutes water. [Mahmoodi \(2014\)](#).

The largest market share and growth in the Adsorbent Market and is anticipated to reach \$2.3 billion by 2023 at a CAGR of 7.7%. The escalating population in the Asia-Pacific region has triggered the need for different petrochemical and petroleum products that are one of the key drivers for the



adsorbent market. Vietnam, Myanmar and Indonesia are the emerging markets for the adsorbent market as these nations have a developing petroleum industry and comprises of many such plants scheduled to come in the coming years. The key end user markets in the Asia Pacific region are oil refineries, natural gas refineries, waste water treatment plants, refrigeration and air conditioning systems and others. Japan, China, Australia, India and South East nations are the leading manufacturing hubs.

Raw materials such as peat, wood, coir, lignite, coal, coconut, silicate, bauxite and others are procured and further processed by physical and chemical processes. The physical process involves activation processes in the absence of oxygen, and the chemical process involves the treatment of the raw material with an acid or base. By using organic matter as raw materials such as sewage sludge and the remains of plants or animals and others, adsorbents can be manufactured.



Figure 1 Several Kinds of Adsorbents [Mahmoodi and Oveisi \(2019\)](#)

Heavy metals are hazardous pollutants because they are not degraded, are persistent, accumulative and have high and high toxic effects even at low doses so that they can cause damage to human health as well as to the universal ecological system. [Kashi \(2017\)](#) Heavy metals are included in the main group of inorganic polluting materials and pollute large areas of land due to their presence in fertilizer, municipal waste, pesticides, mining industry and smelting. [Ariffin et al. \(2017\)](#) It can be removed by using several conventional methods such as membrane chemical precipitation, filtration, coagulation, chemical extraction, ion exchange etc. However, this conventional technique has several disadvantages such as high energy requirements, sensitive operating conditions and low efficiency. [Tripathi and Ranjan \(2015\)](#)

Table 1 MCL standard and ill effect of hazardus heavy metals. [Singh and Gupta \(2016\)](#)

Heavy Metal	Ill Effect	MCL, mg/L
As	Skin and vascular diseases, visceral cancer	0.05
Cr	Headache, Diarrhea, Nausea, Carsiogenic	0.05
Hg	Rheumatoid arthritis, circulatoru & Nervous disorder	3.0 x 10-5
Cu	Liver damage, Insomnia, Wilson's disease	0.25
Cd	Renal disorders and damage, Carsiogenic	0.01
Ni	Dermatitis, Chronic, Asthma, Carsiogenic	0.20
Pb	Renal, Cerebal Disorder, Nervous disorder & Circulatory	6.0 x 10-5

To overcome this weakness, the adsorption method is considered to be one of the most economical and efficient processes in removing harmful metal ions, due to

its availability, low cost and operation. [Leal et al. \(2017\)](#), [Santhosh et al. \(2016\)](#) This process involves separating a substance from one phase and accumulating it on another surface. This method is effective in removing toxic pollutants, even at low concentrations and is easy to operate. [Rao et al. \(2014\)](#) Adsorption is often accompanied by an inversion-desorption process, which represents the transfer of adsorbate ions to solution from the adsorbent surface. The adsorption reversibility can depend on the amount of adsorbate adsorbed from the adsorbent, the more adsorbate is adsorbed, the more reversible the adsorption process. [Rao et al. \(2014\)](#), [Mishra \(2014\)](#) Kaolin is one of the adsorbents that is often used in the metal ion adsorption process.

Kaolin is a fine particle composed of one layer of tetrahedral oxygen silicate (SiO_4) and one layer of octahedral alumina in a ratio of 1: 1. Kaolin has low expansion, high chemical stability and cation exchange capacity. Kaolin is classified into trioctahedral and dioctahedral minerals. Kaolin has the potential to be an adsorbent because it is cheap, safe, and easy to obtain, which is available throughout the world in rock as a crystalline structure. [Emam et al. \(2017\)](#), [Mustapha et al. \(2019\)](#) However, the absorption ability of kaolin as an adsorbent is still low when compared to zeolites, activated charcoal, and bentonite. [Teuku et al. \(2019\)](#) It has to be an effort to increase the ability of adsorption of kaolin, which is by using surfactant as agent to modification.

The weathering process in the formation of kaolin occurs at or near the soil surface which mostly occurs in igneous rocks. Meanwhile, the hydrothermal alteration process occurs because the hydrothermal solution flows through fractures, faults, and other permeable areas while converting limestone into kaolin deposits. [Safitri et al. \(2020\)](#), [Mudzielwana et al. \(2019\)](#), [Sodeifian and Ali \(2018\)](#) Kaolin deposits consist of two kinds, namely residual and sediment. Residual kaolin, this type is found where it was formed with the parent rock, has not undergone displacement, crystals are regular, and ion substitution is rare. Kaolin sedimentary, has undergone displacement by water, wind, glaciers, deposited in basins, and irregular crystals. The structure of kaolin can be seen in [Figure 2](#).

The surface of the kaolinite crystal has a constant negative charge and does not depend on pH (permanent charge). The negative charge comes from atomic substitution in the crystal structure which does not affect the crystal structure, for example, the presence of an Al atom with a charge of $+3$ replacing a Si atom with a charge of $+4$ causes the kaolinite framework to lack a positive charge or an excess of negative charge. [Sodeifian and Ali \(2018\)](#)

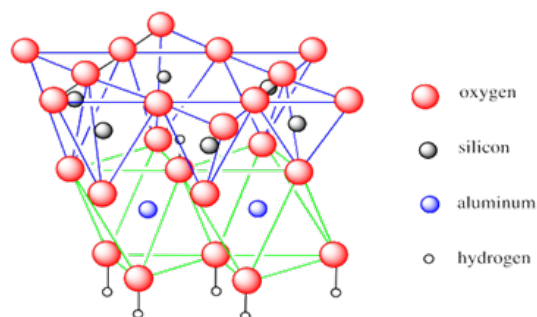


Figure 2 Kaolinite structure [Coelho et al. \(2014\)](#)

This modification increases the absorption of anions through ion exchange. Based on research [Leal et al. \(2017\)](#), natural kaolin was successfully modified through the intercalation of the surfactant Hexadecyltrimonium bromide (HDTMA-Br) to the interlayers. The adsorbents modified showed a maximum

adsorption capacity of 2.3 and 2.88 m²/g. This means that the aid of ultrasonic technology can significantly improve the adsorption ability of the adsorbent. Ultrasonic has proven to be a very useful tool in severing the relationship between adsorbents and adsorbates and intensifying the process of mass transfer. [Mudzielwana et al. \(2019\)](#), [Sodeifian and Ali \(2018\)](#)

Ultrasonic technology has the advantage of being low in operating costs and has no negative impact on the environment. This technique has the effect of increasing the absorption capacity of the adsorbent up to two times with the help of ultrasonic speed which in the process increases the surface area of the adsorbent. [Roosta et al. \(2017\)](#) This research focused in investigation and study of optimization of kaolinite adsorbent by modifying with hexadecyltrimethylammonium (HDTMA) surfactants and ultrasonic irradiation in adsorbing Hg (II) metal in water. It is hoped that the ultrasonic technology can become one of the environmentally friendly alternatives in an effort to increase adsorbent absorption, especially kaolin.

2. MATERIALS AND METHODS

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Natural kaolin is collected from Nisam, North Aceh. Natural kaolin is activated using 1N HCl for one hour, then washed and dried in an oven at 85 °C, filtered through a 110-mesh filter and then stored in a desiccator before use. All chemicals used in this study are analytical reagent class. The surfactant used is hexadecyltrimethylammonium (HDTMA) purchased from Merck. The metals and HCl used in this study were purchased from Rudang Jaya, North Sumatra.

2.2. METHODS

2.2.1. SYNTHESIS OF SURFACTANT MODIFIED KAOLIN CLAY (SMK)

To synthesize a modified kaolin surfactant, activated kaolin is added 10 g to a hexadecyltrimethylammonium (HDTMA) (50 mL) surfactant solution known and the mixture is maintained in a shaker incubator at 30 °C and 150 rpm for 24 hours. The residue is washed with distilled water several times to remove excess surfactants. The residue obtained was then dried in an oven at 60 °C for 12 hours and then ground using mortar and pestle to pass through a 110-mesh sieve. The experiment was repeated until adequate adsorbents were synthesized. [Suryani et al. \(2020\)](#)

2.2.2. CHARACTERIZATION OF SAMPLES

The physicochemical properties of the sample are determined by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and AAS. Shimadzu-8400S spectrometer was used for recorded of spectrum in the range of 400-4000 cm⁻¹ at room temperature using KBr pellets. [Raya and Zakir \(2014\)](#) X-ray diffraction pattern recorded by the STOE powder diffraction system using CuK radiation with wavelength of 1.54060 Å. The level of Hg²⁺ ions is determined by the Shimadzu AAS model AA-6300. The pH is measured using a pH meter. Ultrasonic bath with heating system (Elmasonic, Italy) at a frequency of 60 Hz and a power of 130 W is used for ultrasound-assisted adsorption procedures. The adsorption of metal ions Hg (II) from water with modified kaolin using ultrasonic technique was studied to find the optimal adsorbent dose, pH and sonication time as well as initial

Hg²⁺ concentration. The solution containing the metal ion Hg²⁺ was mixed with natural kaolin and modified kaolin adsorbent at a certain pH (adjusted with acetate buffer) in an ultrasonic bath for a variable time. Then the adsorbent was immediately separated from the solution and the remaining Hg²⁺ ion concentration was measured by atomic absorption spectrophotometer. Mathematically the number of Hg²⁺ ions adsorbed at equilibrium conditions (Q_e , mg g⁻¹) is obtained by using Equation (1):

$$Q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

Where, C_o , C_e is the initial concentration and equilibrium of Hg (II) (mg L⁻¹), and V and M are the volume of solution (ml) and mass of adsorbent (g). [Jeeva et al. \(2019\)](#)

3. RESULTS AND DISCUSSIONS

3.1. CHARACTERIZATION OF KAOLINITE ADSORBENT

The FTIR spectrum of the material was used to determine the composition and pattern of functional groups. The FTIR spectrum of natural kaolin (NK) and kaolin modified surfactant (SMK) is presented in [Figure 3](#). For NK, the absorption band at 3663.23 cm⁻¹ and 1626.17 cm⁻¹ shows the -OH stretching vibration in water adsorbed by physis. Bands at 1012.50 cm⁻¹ and 961.54 cm⁻¹ were associated with vibrations of Si-OH and Al-OH bonds. The band at 1509.46 cm⁻¹ shows the vibrations of the C-C-C flex vibrations associated with the methylene group. Bands at lower wavelengths indicate Al-O-Si and Si-O-Si network vibrations.

Hexadecyl trimethyl ammonium bromide (HDMTA) spectrum indicated stronger absorption bands in the region of 2893.51 and 2944.05 cm⁻¹, which are assigned to the C-H stretching bond in the -CH₃ and -CH₂ groups. Bands at 925.72 cm⁻¹ and 946.4 cm⁻¹ are associated with vibrations of C-N bonds. It was confirmed by bands at 2847.25 and 2975.31 cm⁻¹ that kaolinite adsorbent successfully modified which were ascribed to the vibrations of the C-H bond. After mercury adsorption, no changes were observed in the modified kaolin spectrum. However, there is an increase in the intensity of the band transmittance. This could be an indication that Hg (II) can produce a higher adsorption affinity for contaminants. [Ridwan et al. \(2018\)](#)

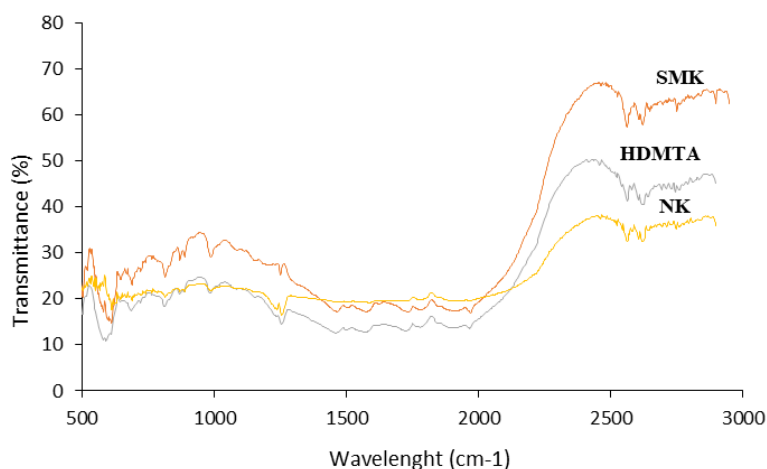


Figure 3 FTIR spectrum of NK, HDTMA and SMK

The crystal structure and purity of the prepared sample is determined by X-ray diffraction analysis. In Figure 4, presents the XRD pattern of natural kaolin (NK) and modified kaolin with surfactant (SMK). The results reported that the main kaolinite consisted of quartz and kaolin as the main minerals. After modification with HDTMA, no changes were observed in the kaolin XRD pattern. This could indicate that the absorption of HDTMA surfactants to the surface of the kaolin mineral does not affect the clay layer. The same observation was also reported by Wu et al. (2015), during the modification of bentonite clay using hexadecyltrimethylammonium chloride.

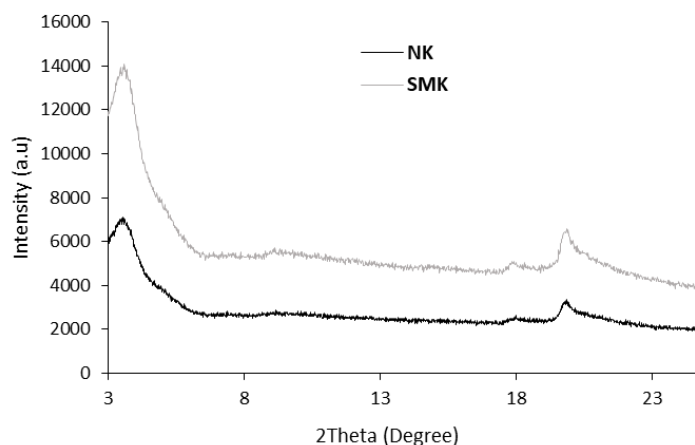


Figure 4 XRD pattern (Quartz) of NK and HMK

3.2. EFFECT OF CONTACT TIME

A batch experiment was carried out to investigate the adsorption efficiency and ultrasonic-assisted adsorption process to remove Hg ions. The contact time needed to effectively remove metal by the adsorbent is important to determine when the equilibrium time is reached. The effect of contact time on metal adsorption to kaolin clay SMK and NK is shown in Figure 4. The results showed a very significant difference between the adsorbent SMK and NK adsorbents, SMK was more efficient in adsorbing Hg²⁺ than in NK adsorbents.

The adsorption efficiency of NK results obtained the best results at 60 minutes contact time by 73.83%, while at SMK the best results at 45 minutes contact time were 94.57%. This is because the Hg²⁺ has been adsorbed in the pores of SMK adsorbents because of the molecules in wastewater that move faster, so interactions between SMK adsorbents and metal ions occur more frequently, the longer the ultrasonic contact time the absorption efficiency decreases due by the saturation of the adsorbent in adsorbing the metal Hg²⁺. Sun et al. (2015)

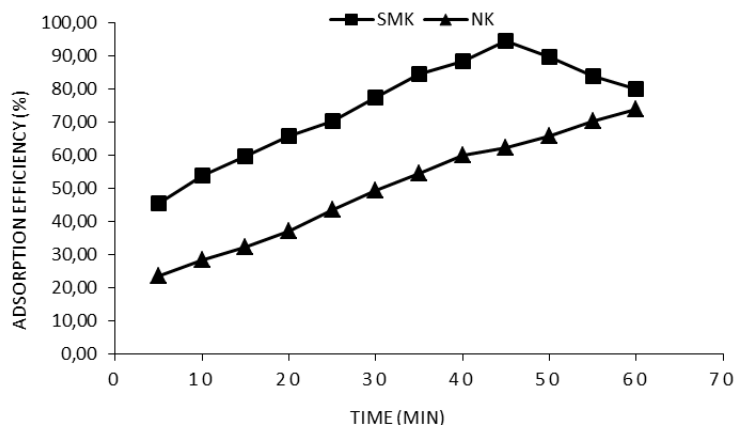


Figure 5 Effect of contact times on the adsorption of Hg²⁺ on SMK and NK.

The mechanism for increasing the adsorption of kaolin adsorbents with the addition of surfactants is because it attaches to the kaolin surface forming interactions between molecules on the kaolin and surfactants. Interaction causes the formation of a new layer, thus forming a collection of bilayers which results in many metal ions being adsorbed. In addition, the presence of surfactants also increases the number of ions that are on the surface of the surfactant, so that more modified adsorbents capture the ions around them in wastewater. [Lee et al. \(2015\)](#)

According to research conducted by [Fainerman et al. \(2020\)](#), adsorbing Cr (IV) metal using anionic surfactant modified kaolin and obtaining an adsorption efficiency of 95.08% at an optimal contact time of 180 minutes, The difference in optimal adsorption time that occurs due to adsorption using ultrasonic can adsorb metals quickly because the effect of using high-speed ultrasonic techniques in the adsorption process increases the surface area. This accelerates the movement of molecules so that the adsorption process occurs faster. [Suryani et al. \(2018\)](#) This phenomenon is caused by cavitation (nucleation, growth, and collapse of small gas bubbles) and high-pressure variations induced during ultrasonic irradiation. [Soltani et al. \(2016\)](#)

3.3. EFFECT OF ADSORBENT DOSAGE

The effect of the adsorbent dose was investigated by experimenting on adsorbent doses that differed from 0.4 to 1.4 g/L at pH 8 and an initial concentration of 50 mg/l. [Figure 6](#). Shows an increase in the amount of adsorbent in adsorbing Hg²⁺ in SMK and NK. At lower doses, the adsorption rate is influenced by competition between ions among metal ions caused by the presence of a small surface area. At higher doses, the adsorption process in NK and SMK increases. This is due to the increased availability of active binding sites and a greater surface area of the adsorbent. Thus, this affects the removal efficiency of the Hg²⁺ metal from the solution by the adsorbent. This can also be concluded because of the availability of sites which can be exchanged for adsorption. [Saleh et al. \(2016\)](#), [Haroon \(2016\)](#)

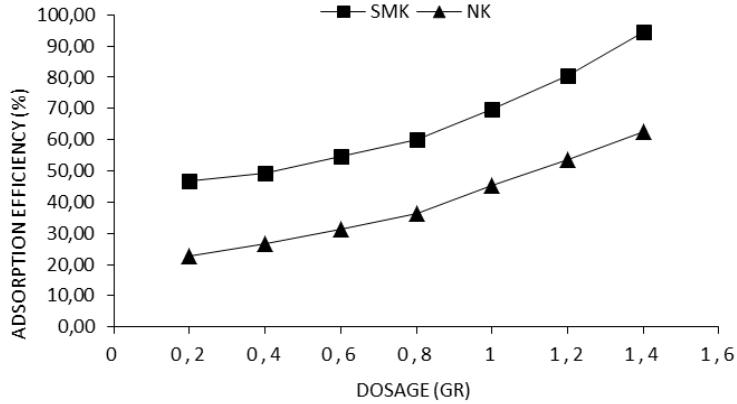


Figure 6 Effect of dosage on the adsorption of Hg²⁺ on SMK and NK.

3.4. ADSORPTION KINETIC STUDY

Examination of reaction kinetics is an important factor in the design of adsorption systems. The adsorption process will depend on the condition of the system and the physical or chemical characteristics of the adsorbent system. Both the first and second pseudo models were investigated to study the rate and mechanism of the adsorption process. Zhou et al. (2018) In 1898, for the first time, Lagergren had proposed a pseudo-first order model. Vargas et al. (2011) The pseudo-first and pseudo-second sequence models are applied to check the adsorption rate based on equilibrium time data. Vargas et al. (2011) The second-order pseudo-kinetic model can anticipate adsorption behavior in the entire adsorption range. Intra-particle diffusion models are mostly applied to distinguish pathways and mechanisms as well as the driving forces involved in adsorption. Vargas et al. (2011)

Table 2 Constant parameters for pseudo-first-order and pseudo-second-order models of reaction kinetics (initial concentration of 5 mg/L, adsorbent dosage of 1.4 g)

Model	Equation	Parameter	Value of parameter	
			SMK	NK
First-order kinetic	Log(qe-qt)=log(qe)-k1/2.303t	k ₁	1.879	1.067
		q _e (calc)	142.87	128.56
		R ²	0.8921	0.8364
Second-order kinetic	(t/qt)= 1/(k ₂ q _e ²) + 1/q _e (t)	K ₂	0.052	0.023
		q _e (calc)	142.65	132.44
		R ²	0.9994	0.9921

Apart from the first-order model, the plot of t/qt vs t for the second-order kinetic model gives a straight line with a high correlation coefficient which is k₂ and the equilibrium adsorption capacity (q_e) is calculated from the intercept and slope of this line, respectively. The value of R² and the proximity of experimental and theoretical adsorption capacity values (q_e) indicate the application of a second-order model to explain and interpret experimental data. The R² value for the second-order pseudo-kinetic model was found to be higher, namely for SMK 0.9994 and for NK which was 0.9921 and the q_e value calculated was especially close to the experimental adsorption capacity value under different physicochemical conditions.

4. CONCLUSIONS AND RECOMMENDATIONS

In this study, the natural kaolin clay mineral (NK) was successfully modified through the intercalation of HDTMA surfactant (SMK) to interlayers and ultrasonic assistance to remove Hg²⁺ metal ions in water. The synthesized adsorbents showed the maximum adsorption efficiency of SMK and NK 94.57% and 73.57%, respectively. In this study it was also proven that the ultrasonic adsorption method became a very useful tool in intensifying the mass transfer process and severing the relationship between adsorbate and adsorbent. For the sake of comparison, ultrasonic adsorption is higher and faster than the adsorption process. Also, kinetic studies show that the adsorption process follows the pseudo-second order.

ACKNOWLEDGEMENTS

The authors express their gratitude and thanks to the Education, Culture, Research and Technology Ministry of the Republic of Indonesia for the financial support through grant Nomor: 256/E4.1/AK.04.PT/2021.

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