

Potential of silica from water treatment sludge modified with chitosan for Pb(II) and color adsorption in sasirangan waste solution

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Abstract

Water treatment sludge (WTS) still contains a lot of silica oxide (SiO_2) as much as 43.12-66.90% by weight and can act as an adsorbent to be applied to the treatment of Sasirangan wastewater. Silica extraction from WTS was carried out by microwave-assisted leaching, which - compared to conventional extraction - had several advantages including high extraction yields, fast, uniform, and more selective processing time. In addition, Sasirangan liquid waste is a by-product of the dyeing process of Sasirangan cloth, which still contains heavy metals in amounts exceeding the quality standard. This study aims to extract silica from WTS by microwave-assisted leaching process to synthesize silica modified by chitosan (Si-Kit) as an adsorbent to reduce Pb(II) from Sasirangan wastewater, and to obtain a kinetic model of the adsorption process. The silica from microwave-assisted leaching process (Si-MaL) and Si-Kit adsorbents were characterized using FTIR and SEM. The results showed that the dominant functional groups of Si-Kit included Si-O-Si, Si-O-C stretching vibrations, and stretching vibration of C=N showing that the condensation between aldehyde groups and amino groups occurred to form base after the addition of glutaraldehyde. The SEM images showed that Si-MaL and Si-Kit adsorbent obviously increased in particle size with the presence of visible particles of homogeneous granules and large pores. The removal efficiency percentage of Pb(II) and color occurred at 6% w/v adsorbent weight and 70 min was 87.20% and 61.87% respectively. Meanwhile, the adsorption kinetics of Pb(II) and color followed the zero order kinetics model at weight variation of 6%-w/v based on the value of R^2 close to one and the adsorption capacity of Pb(II) ion and color were 12.01 mg g⁻¹ and 467 mg g⁻¹, respectively.

Keywords: adsorption; chitosan; silica; Sasirangan waste; water treatment sludge

1. Introduction

The management of the chemicals utilization as coagulants is deemed important as the production of the resulting sludge known as water treatment sludge (WTS) continues to increase every year. WTS in fact comprises a number of main chemical compounds those are silica oxide, aluminum oxide and iron oxide as the results of a coagulation-flocculation process, in which in chemical industry they can be functioned as an adsorbent, coagulant, and catalyst. WTS from the water treatment plant in Banjarmasin, South Kalimantan, Indonesia, as revealed by the results of research by Mirwan et al. [1], covered 49.15% silica oxide (SiO_2), which is not only abundant material in the earth's crust but also valuable as a multipurpose inorganic chemical compound either in gel, crystalline or in amorphous form. Moreover, silica oxide, in consideration to its porous structure with a enormous surface area, becomes one of the most frequently used adsorbents. Silica oxide is extracted using microwave technology because it can increase yield, reduce processing time, and is more selective, uniform, fast and environmentally friendly [2–5].

A linear polysaccharide, chitosan is acquired from chitin by base deacetylation [6] and as a natural biopolymer, it possesses a number of eminencies for being biocompatible, biodegradable, affordable, non-hazardous, simple surface modification, and broadly applied in waste water treatment as a biosorbent for a variety of pollutants such as heavy metals. Chitosan due to the aforementioned eminencies then becomes one of the most preferred and reliable biosorbents to adsorb and remove any metal ions [6–8]. Moreover, for embedding the great amount of crucial amine and hydroxyl groups, it is appropriate to apply chitosan to be modified and form stable compound [7]. Pristine chitosan, nevertheless, has poor mechanical stability and chemical resistance, including being very soluble in any acidic conditions [8]. In order to enhance the adsorption performance process for objective ions, the combination of chitosan and silica might become a proper choice. It combines the beneficial properties of the biopolymer with excellent stability, large surface area and silica porosity. By the use of covalent bonds, the amino and hydroxyl groups on the surface of chitosan can be combined with silica and the amino groups on chitosan could be chemically bound by glutaraldehyde and forming C=N bonds.

Pb(II) ion, among other various heavy metals, becomes one of the most lethal material that is capable of prompting a toxic

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impact on living creatures [9,10,11]. It is also primarily applied in industries such as pigment, metal plating, textile, painting, battery as well as smelting. As in other textile industries, the manufacture of Sasirangan involves a dyeing process using synthetic dyes such as naphthol, indigosol, and reactive and produces a large amount of concentrated liquid waste and sometimes effluent discharged into the environment directly without any treatment. Even some types of dyes used are suspected to be carcinogenic and harmful to health [2,12].

The treatment of wastewater polluted with detrimental heavy metal ions can be provided through the available techniques/technologies, one of which is through adsorption treatment method that is commonly and widely applied in the treatment of Pb(II) ions contaminated wastewater. Adsorption treatment not only is effective and simple in its operation but also has less secondary pollution, and affordability. A number of studies on the use of silica as an adsorbent for the Pb(II) removal include a study by Peng et al. [13] on the use of magnetically modified silica-xanthan gum composites using magnetite (Fe_3O_4) for the removal and recovery of Pb(II) from aqueous solutions and a study by Anbia et al. [14] investigating the application of magnetically modified MCM-48 mesoporous silica with amine (NH_2) and melamine-based dendrimer amines (MDA) as a novel solid phase adsorbent for the removal of Pb(II) ions. Various silica based adsorbents for Pb (II) ions sorption include Amino-modified mesoporous silica [15], PAMAM-SBA-15 (polyamidoamine-SBA-15) [16], $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{meso-SiO}_2\text{-R}_1\text{-NH}_2$ [17], and Silicon carbide nanoparticle [18].

As found in literature, a number of adsorbents have been used in the removal of Pb(II) ions by means of various materials. The basic silica acquired from WTS, modified with chitosan, so far, has not been studied specifically to remove Pb(II) and the color of Sasirangan wastewater. This study aims to extract silica from WTS by microwave-assisted leaching process, to synthesize silica modified by chitosan as an adsorbent to remove Pb(II) and dyes from Sasirangan wastewater, and to obtain a kinetic model of the adsorption process.

2. Materials and Methods

WTS was obtained from sludge waste from the clarification unit of the IPA Banjarmasin with water content ranging from 70-80%. Any small wood and other impurities were removed by soaking, and washing prior to be dried under direct sunlight within 48 h. After drying, the WTS was grinded and sifted to reduce the size according to the specified particle size parameters. It was then continued to the microwave-assisted leaching process using the optimum parameters from previous studies. Before performing the characterization and leaching process, the WTS was firstly burned using a furnace at a temperature of 700°C for 120 minutes.

Meanwhile, chitosan, sodium hydroxide, sulfuric acid, acetic acid and glutaraldehyde were procured from Aldrich. Sulfuric acid was used to adjust the pH to obtain silica precipitate in sodium sulfate solution. For the microwave leaching process, the experimental device used a microwave oven with 900 W of power at a frequency of 2.45 GHz. It also involved a prior research for best variables [4] including 12 M

sodium hydroxide concentration, 300 mesh particle size, stirring speed of 300 rpm, 0.03 g mL⁻¹ solid to liquid ratio, 90°C temperature, 528 W microwave power, and 20 min of reaction time.

2.1. Synthesis of silica-chitosan

The synthesis of silica-chitosan process was performed by using 85%:15% composition ratio and the modified adsorbent process was carried out by dissolving 1.5 g of chitosan in 80 mL of 2% acetic acid. The chitosan solution was then added with 8.5 g of silica and stirred for 12 hours. Subsequently, it was neutralized with 30 mL of 1mol L⁻¹ NaOH for 30 minutes. The precipitate was decanted and immersed in 40 mL of 0.5% glutaraldehyde (v/v) for 24 hours. The results obtained were filtered and dried at a temperature of 105°C to constant, and cooled. The solid obtained was ground and sieved through 120 mesh and applied as an adsorbent.

2.2. Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) (Shimadzu, Japan) in the scope of 400 ~ 4000 cm⁻¹ was applied to record the characteristic peaks of the functional groups provided in the samples before and after modification. The microstructures of the sample were characterized by a scanning electron microscope (SEM) (SEM EVO MA 10, Germany). The concentrations of Pb ions in mixture solution were analyzed by atomic absorption spectrophotometry (AAS) (AA-7000, Shimadzu, Japan) and color using UV-Vis spectrophotometry (Cary 100 Conc UV-Vis, Agilent CrossLab, US).

2.3. Adsorption experiments

In the adsorption experiment, 250 mL of Sasirangan waste was added to a shaker flask with the different weights of Si-Kit adsorbent (2, 4, 6 %- w/v) for the evaluation of the determination of silica-chitosan (Si-Kit) adsorbent weight on Pb and color adsorption as a function of time. The shaking flask sealed and positioned in a thermostatic oscillator was shaken at a speed of 100 rpm at 30°C for 10, 15, 20, 30, 40, 50, 60, and 70 min. Afterward, the Pb ions concentration and color of the filter liquor were measured using AAS and UV-Vis. The removal efficiency percentage of Pb(II) and color was calculated on the basis of (1).

$$\text{Removal efficiency percentage} = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (1)$$

where C_i and C_e refer to the initial and equilibrium adsorption concentration of Pb(II) ion and color in the solution, respectively.

3. Results and Discussion

3.1. The adsorbents characterization

The analysis and observation of the surface functional groups of the silica from microwave-assisted leaching process (Si-MaL) and Si-Kit adsorbents were performed by means of

FT-IR spectroscopy as graphically illustrated in Figure 1.

The peak at 3300 cm^{-1} was allotted to the symmetric stretching vibration of N-H and O-H bonds of chitosan and the band at about 2935 cm^{-1} was attributed to C-H bonds stretching. The peaks at 1700 and 1100 cm^{-1} were seen suitable for the incurvature vibrations of Si-O-Si bond. The appearance of the characteristic peaks about 1075 cm^{-1} , in comparison to Si-MaL, was connected with the Si-O-Si and Si-O-C stretching vibrations. Also, amine groups detected on Si-Kit at peak of 3300 cm^{-1} for N-H and O-H stretching vibration and peak of 1631 cm^{-1} for C=N stretching vibration indicating that the condensation between aldehyde groups and amino groups was to form base after the addition of glutaraldehyde.

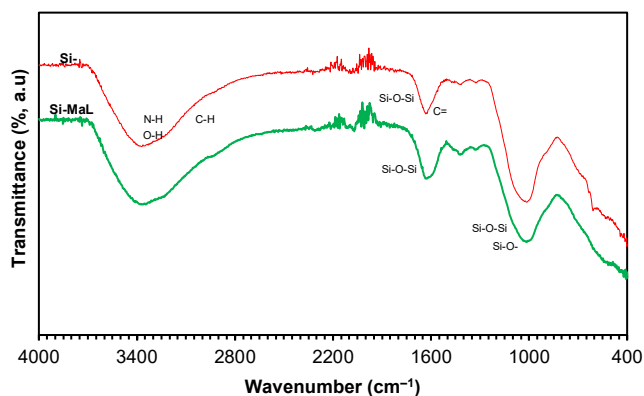


Fig. 1. FT-IR spectra of the Si-MaL and Si-Kit adsorbents

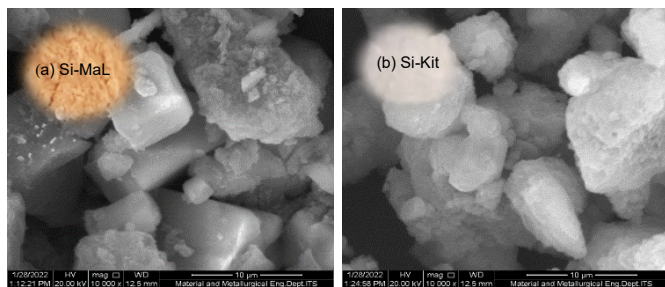


Fig. 2. (a) Si-MaL and (b) Si-Kit adsorbent morphology

As shown in Figure 2, the observation of the morphology of Si-MaL and Si-Kit was conducted by SEM. An obvious difference between Si-MaL and Si-Kit adsorbent, either in obviously increasing particle size or appearing new morphologies was found. After synthesis process, the homogeneous granules and large pores structure were formed (Figure 2(b)). It can be pointed out that the ordered structure of the adsorbents and the mesoporous channels became contrast to Si-MaL. Also, chitosan was well combined with mesoporous silica, and the modification process eliminated the long-range order channels of Si-O-Si system. Here, Si-MaL exhibited coarse, sharp, irregular particle shapes and small pores.

3.2. Behavior of the Si-Kit adsorbents

3.2.1. Effect of Si-Kit adsorbent weights and contact time on adsorption of Pb(II)

Figure 3 overall shows that the percentage of Pb(II) removal increased with the length of time and the adsorption process took various weights of the adsorbent used. This indicated that

the Si-Kit adsorbent used was able to bind Pb(II). Optimum Pb(II) adsorption occurred at 6% w/v adsorbent weight and at 75 minutes at 87.20%. The adsorption process was directly determined by the adsorbent weight. An increase in the adsorbent weight has made the number of active sites available for adsorption process increased as well. Nevertheless, in view of the agglomeration of adsorbent particles at higher amount of weight, therewithal forming unavailable the active sites, this sometimes might not constantly result in the enhanced percentage removal.

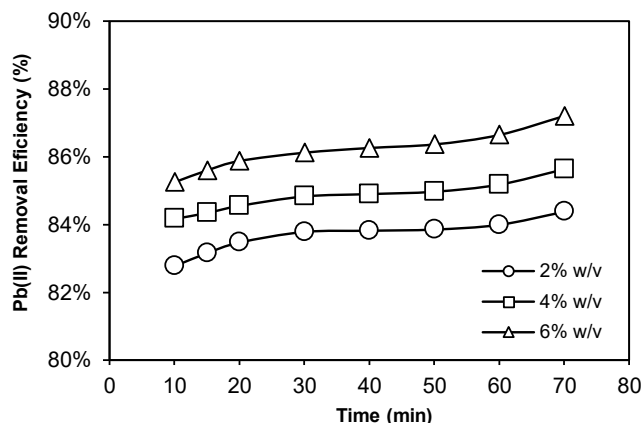


Fig. 3. Effect of Si-Kit adsorbent weights on Pb(II) adsorption

In this study, the largest percentage of Pb(II) removal took place at 6% w/v adsorbent weight, indicating that the adsorbent surface was unsaturated and a second layer formed has enabled the adsorbate to be adsorbed and diffused. Furthermore, since the adsorbent particles had many opportunities to come into contact with metal ions, the longer contact time of the adsorption process has made more metal ions to be adsorbed. Ekinici et al. [19] investigated the removal of Pb(II) ion by means of magnetite nanoparticles mixed with murexide-terminated polyamidoamine dendrimers. The more increasing the adsorbent, the more reducing the adsorbed Pb(II). Mohan et al. [20], in regard to the use of graphene oxide (GO) and magnesium oxide (MgO) nanohybrid (GOMO) for the removal of Pb(II) ions from aqueous solution, figured out that adsorbent uptake capacity increased less when the amount of adsorbent increased from 0.3 to 0.4 g/L; nonetheless, a further increase in weight has made the removal efficiency less. But, in this study, adsorption capacity was proportionate to the adsorbate ratio to active sites, which increased along with the increase in amount of adsorbent. Hence, at high amount of adsorbent, adsorbent uptake capacity increased since Pb(II) ions was able to entirely cover the active sites per mass.

Commonly, in the plot of the amount of the adsorbent adsorbed toward time, the typical feature of the plot comprises three stages: very rapid adsorption, slow adsorption, and the adsorption process reaching an equilibrium state [21]. As investigated by Pelalak et al. [22] the adsorption time effect for Cd(II) and Pb(II) adsorption on Ash/GO/Fe₃O₄ nanocomposite at reaction time was in the range of 5 to 150 min. Meanwhile, biocomposite alginate/treated biomass, as reported by Mohammadabadi and Javanbakht [23], adsorbed a large part of Pb(II) ions less than 2 h. Over time, when the adsorbent becomes saturated with adsorbate, the adsorption rate of, as a consequence, stabilizes in order to reach equilibrium state.

3.2.2. Effect of Si-Kit adsorbent weights and contact time on adsorption of color

The ratio of adsorbent had a greater influence in adsorption of naphthol compared to the stirring time. The significant decrease in color concentration was due to the higher ratio of adsorbent to waste. As depicted in Figure 4, the percentage of color removal overall increased along with the increase in adsorbent weight and the length of contact time for the adsorption process. Contact time was required for the stirring process between the adsorbent and the adsorbate. The contact time affected the removal efficiency in which the longer the contact between the adsorbent and the adsorbate, the more adsorbate to diffuse into the adsorbent. The increase in the adsorption percentage was also determined by the adsorption equilibrium factor of the adsorbent on metal ions and organic substances.

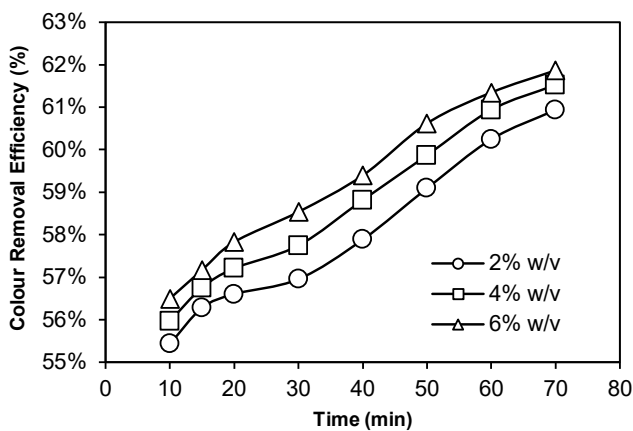


Fig. 4. Effect of Si-Kit adsorbent weights on colour adsorption

Table 1. Adsorption capacities of silica-based, chitosan based, modified-silica, modified-chitosan adsorbents for Pb (II) ions sorption

Adsorbents	Parameters	Adsorption capacity (mg/g)	References
chitosan-modified silica	70 min; pH 7	12.10	Present study
Chitosan-pyromellitic dianhydride modified biochar	-	13.32	Deng et al. [24]
Amino-modified mesoporous silica	120 min; pH 5.07; 298 K	593	Hao et al. [15]
Modified magnetic mesoporous silica MCM-48	90 min; pH 4	127.24	Anbia et al. [14]
Hydroxypropyl chitosan/oxidized multiwalled carbon nanotubes composites	pH 5.0; 120 min	116.3	Wang et al. [25]
Polyaniline grafted chitosan	pH 6	16.1	Karthik and Meenakshi [26]
Chitosan and Chitosan-glutaraldehyde	100 min; pH 4.5	14.24	Ngah and Fatinathan [27]

Table 1 presents the lists of the adsorption capacities of various silica-based adsorbents from other references and this study. The adsorption capacity was relatively comparable to the literature results. The higher adsorption capacity was related to

the type of kinetic model and adsorbents [14,26]. The highest adsorption capacity that belonged to the work [14] was due to the Langmuir kinetic model as the adsorption capacity was obtained with the value of 41.64 mg/g [14].

3.2.3. Kinetic study of Pb(II) ion adsorption onto silica modified by chitosan

The adsorption kinetics became a key to express the possible mechanism for Pb(II) and color adsorption. Pb(II) ion and color kinetic adsorption were investigated with the initial concentration of 2.87 mg L⁻¹ and 153 mg L⁻¹, respectively. The adsorption capacity of Pb(II) ion and color increased up to 4.07 mg g⁻¹ and 12.01 mg g⁻¹; 144 mg g⁻¹ and 467 mg g⁻¹, respectively.

To study the adsorption behavior of Si-Kit under pH 7 at various weights and times, the zero-order, first-order, and second-order (Eq. 2–4) were used.

$$C_A = C_{A0} - kt \tag{2}$$

$$\ln C_A = \ln C_{A0} - kt \tag{3}$$

$$1/C_A - 1/C_{A0} = kt \tag{4}$$

where C_A (mg/L⁻¹) refers to the concentration of A at time $t = t$, C_{A0} (mg/L⁻¹) is the concentration of A at $t = 0$, and k is the rate constant of adsorption (min⁻¹).

The calculation of the parameters of kinetic models was done by using non-linear regression, the results of which are shown in Table 2. Regarding the higher number of coefficient correlation (R^2), the zero order, 1st order and 2nd order kinetic model fitted well for both Pb(II) and color.

Table 2. The kinetic parameter of Pb(II) ion and color adsorption onto Si-Kit at several of adsorbent weights

Parameter	Adsorbent weight	Kinetic model	Parameter constant	Value
Pb(II)	5 g	zero order	q_e (mg/g)	11.865
			k (min)	0.0006
			R^2	0.8632
		1 st order	q_e (mg/g)	11.920
			k (min)	0.0013
			R^2	0.8695
	2 nd order	q_e (mg/g)	11.965	
		k (min)	0.0028	
		R^2	0.8754	
	10 g	zero order	q_e (mg/g)	12.010
			k (min)	0.0006
			R^2	0.9450
1 st order		q_e (mg/g)	12.015	
		k (min)	0.0014	
		R^2	0.9441	
2 nd order	q_e (mg/g)	12.020		
	k (min)	0.0032		
	R^2	0.9427		
15 g	zero order	q_e (mg/g)	12.095	
		k (min)	0.0008	
		R^2	0.9442	
	1 st order	q_e (mg/g)	12.040	
		k (min)	0.0020	
		R^2	0.9425	
2 nd order	q_e (mg/g)	12.021		
	k (min)	0.0050		
	R^2	0.9415		

Continued Table 2. The kinetic parameter of Pb(II) ion and color adsorption onto Si-Kit at several of adsorbent weights

Parameter	Adsorbent weight	Kinetic model	Parameter constant	Value
Color	5 g	zero order	q_e (mg/g)	144.33
			k (min)	0.1378
			R^2	0.9843
		1 st order	q_e (mg/g)	151.73
			k (min)	0.0022
			R^2	0.9826
	10 g	zero order	q_e (mg/g)	158.05
			k (min)	0.0003
			R^2	0.9803
		1 st order	q_e (mg/g)	214.46
			k (min)	0.1415
			R^2	0.9932
	15 g	zero order	q_e (mg/g)	225.37
			k (min)	0.0022
			R^2	0.9932
		1 st order	q_e (mg/g)	235.76
			k (min)	0.0004
			R^2	0.9926
15 g	zero order	q_e (mg/g)	467.02	
		k (min)	0.1415	
		R^2	0.9932	
	1 st order	q_e (mg/g)	443.62	
		k (min)	0.0022	
		R^2	0.9932	
2 nd order	q_e (mg/g)	424.79		
	k (min)	0.0004		
	R^2	0.9926		

The appearance of adsorption of Si-Kit at adsorbent weight of 15 g showed the higher adsorption capacity compared to Si-Kit at adsorbent weight of 5 and 10 g. This indicated the contribution of amine group in chitosan to increase Pb(II) ion adsorption capacity. The adsorption kinetics of Pb(II) ions and color with Si-Kit from WTS at 15 g adsorbent weight followed a zero order kinetics model. This was based on the value of R^2 i.e. close to one.

4. Conclusion

The synthesis of chitosan functionalized on silica from WTS with glutaraldehyde was successfully synthesized by a conventional method. The silica-chitosan adsorbent has well on Pb(II) ion adsorption, and dye in Sasirangan wastewater. The effects of silica-chitosan adsorbent on wastewater contaminants leads to be a postulant material to be developed and applied in various wastewater treatment applications.

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