Research Article

Utilization of Lapindo Volcanic Mud for Enhanced Sono-sorption Removal of Acid Orange 52

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Abstract

This study applied ultrasonic irradiation technique to remove acid orange 52 (AO52) and in the meantime utilizing the potential adsorbent, Lapindo volcanic mud (LVM). LVM was collected from the erupted mud in Sidoarjo, Indonesia and calcined prior the adsorption process. Previously in another study, Lapindo was proven to be efficient for adsorption of dyes in single adsorption method. In this study, the combination of adsorption with ultrasound, or as known as sono-sorption shows that the adsorptivity increased from 95.54 mg/g to 129.5 mg/g. The isotherm study shows that this process obeyed Langmuir isotherm model with adsorption capacity of 833.33 mg/g. The enhancement of sono-sorption method as compared to conventional method is believed to be resulted from the facilitated mass transfer driven by the ultrasound, along with the adsorption ability of LVM. The kinetic study fit to the pseudo second order equation. Copyright © 2019 BCREC Group. All rights reserved

1. Introduction

Acid orange 52 is widely used in the food industries, dyestuff manufacturing, paper manu-facturing, textile, printing, and also as pH indicator [1]. However, this compound is considerably toxic to the aquatic life as it is being discharged to the water system. There were many research dedicated to the water system concerning the dyestuff toxicity, contributing to the development of various method of treatments. Among them, adsorption method is seen as

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highest potential because of its economic feasibility, flexibility, and efficiency. Meanwhile, the utilization of ultrasound for dyes and pollutants removal from water over the past two decades has received much attention by worldwide researcher owing to their potential to enhance the removal efficiency of dyes and pollutants [3-6]. Ultrasound basically employed acoustic cavitation that formed bubbles that vibrated along the medium [3,7]. In accordance, the mass transfer from adsorbate bulk to the adsorbent surface which typically restrict effectiveness of adsorbent could be improved greatly [8]. From previous studies, there have been several reports utilizing the sono-sorption along with adsorbents for wastewater treatment. Li *et al.* utilized exfoliated graphite to adsorb azo dye, which was enhanced with the presence of ultrasound [9]. In addition, similar trends were observed by M.H. Entezari *et al.*, in which the elimination of Remazol black B from simulated waste solution was greatly enhanced upon the combination ultrasound and adsorption method [10].

Among the researched adsorbents, activated carbon shown outstanding performance of high adsorptivity despite being high cost. Therefore, many study on finding less cost adsorbent had been conducted, which used fly ash [11], sawdust [12], waste sludge [13], waste newspaper [14] and seed husks [15]. Clay minerals such as bentonite [16], montmorillonite [17], kaolin [18] and sepiolite [19] also have drawn much attention in recent years due to their high chemical stabilities, high surface area, functionalizable surfaces and structural properties [20].

Lapindo mud is a type of volcanic mud which erupted in May 2006, located in Sidoarjo, Indonesia that has been in eruption since May 2006. The latest known flow rate of the erupted mud is about 80,000 m³/day and nothing could possibly stop them for more years to come [21]. Therefore, finding a profitable uses for the mud, could be advantageous from the economical and environmental perspective.

Previously, we had investigated the ability of the calcined LVM for the same purpose in conventional method [22]. To date, there were no reports done on using the combination of Lapindo volcanic mud with ultrasound, thus we attempt to identify the synergistic effect of both. This is also due to the assumption that the ultrasound could possibly agglomerate or the LVM that could resulted in reduced surface area. The effects of several parameters on adsorption capacity were also studied along with isotherm and kinetics study.

2. Materials and Methods

2.1 Materials

AO52, with chemical name Sodium *p*-dimethylamino-azobenzesulphonate (Molecular formula $C_{14}H_{14}N_3NaO_3S$; Molecular weight 327.33) was procured from Merck and was used as received. The dye solution was prepared at the desired concentration using Milli-Q water. Adsorbent, Lapindo volcanic mud (LVM), was obtained from Sidoarjo, Indonesia in the form of grey-colored clay. The LVM was treated according to the procedure for washed-calcined LVM described in previous report [22]. It was calcined at 550 ºC prior to use to remove water and hydrocarbons. LVM was sieved by using a sieve set and then was collected in the range of 104 and 150 m. The specific surface area was 45.59 m²/g.

2.2 Experiments

The adsorption experiments of AO52 on LVM without ultrasonic irradiation were carried out in batch mode according to the method describe in previous report [22]. In short, a 200 ml volume of AO52 solution, previously adjusted to a fixed pH value was added to a 250 mL beaker containing different amount of LVM. The mixture was stirred magnetically at room temperature and 300 rpm.

The sono-sorption (adsorption with ultrasonic irradiation) experiments were accomplished with ultrasonic cleaner bath (Bransonic 5510E-DTH, with a frequency of 40 kHz, and a nominal power of 185 W). 200 ml of AO52 solution (various concentrations) was contained in a 250 mL Erlenmeyer flask and immersed in the bath. The pH of the solution was adjusted with 0.1 M HCl or 0.1M NaOH solution. The temperature was controlled at room temperature by a circulating bath. A desired amount of LVM was added to the AO52 solution and simultaneously the ultrasonic power was turned on.

For both methods, samples were withdrawn from Erlenmeyer flask at pre-determined time intervals until the adsorption equilibrium was reached. Next, samples were centrifuged and filtered according to the method described in the literature [22]. In brief, samples were centrifuged at 13,200 rpm for 20 min and the supernatants were filtered using a Millex-NH filter (Millipore 0.45 mm). Each experiment was replicated three times.

2.3 Dye Concentration and Removal Capacity

The concentration of the dye was measured using a UV-vis spectrophotometer (Genesys 10 UV/Vis Scanning, Thermo Electron, UK). The measurements were made at a wavelength of 478 nm, which corresponds to the maximum absorbance.

The adsorption capacity of the dye (q) was calculated according to Equation (1).

$$q = (C_i - C_e) \times \frac{V}{m} \qquad (1)$$

where C_i is the initial AO52 concentration (mg/L), C_e is the AO52 concentration at the adsorption equilibrium (mg/L), V is the volume of AO52 solution (L), and m is the weight of the LVM (g). The percentage of dye adsorbed (% d) was determined by Equation (2).

$$\% \, d = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (2)$$

2.4 Isotherm Study

The equilibrium isotherms, Langmuir [23] and Freundlich [24] isotherms were applied in this study. The Langmuir model had been linearized as follows:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \qquad (3)$$

where q_e is the amount of AO52 adsorbed per unit of adsorbent at equilibrium (mg/g), C_e is the concentration of dye solution at equilibrium (mg/L), q_m is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g), and K_L is the Langmuir constant, which is related to the energy of adsorption (L/mg). The Langmuir constant q_m
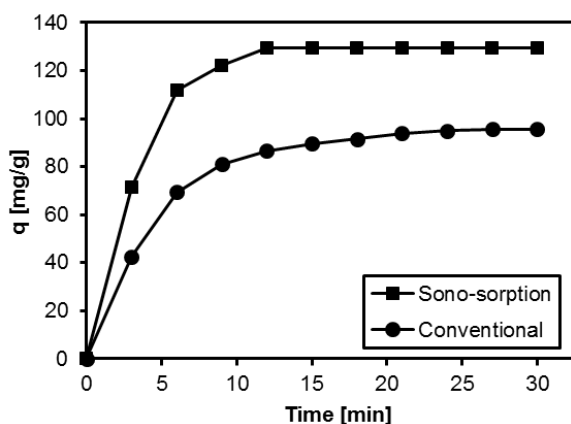

Figure 1. Effect of sono-sorption method on adsorption capacity (initial concentration 100 mg/L, adsorbent dosage 0.5 g/L, initial pH 3).

and K_L can be determined from the intercept and the slope of the linear plot of $1/q_e$ versus $1/C_e$.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous system, and had been simplified in linear form as follows:

$$\log q_e = (1/n) \log C_e + \log K_f \qquad (4)$$

where q_e is the amount of AO52 adsorbed per unit of adsorbent at equilibrium (mg/g), C_e is the concentration of dye solution at equilibrium (mg/L), K_f and n are the Freundlich adsorption isotherm constant, which indicate the extent of the adsorption and the degree of non-linearity between solution concentration and adsorption, respectively. The values of K_f and $1/n$ can be determined from the intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$.

2.5 Kinetics Study

The adsorption kinetics of AO52 onto LVM were analysed by using pseudo-first-order and pseudo-second-order kinetic models. Pseudo-first-order model is based on the assumption that the rate of change of solute uptake over time is directly proportional to the difference in saturation concentration and the amount of solid uptake over time. The pseudo-first order model was presented by Lagergren [25] and had been simplified to the form of:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (5)$$

where q_e and q_t are the amount of AO52 adsorbed per unit of adsorbent (mg/g) at equilibrium, and at time t, respectively and k_1 is the pseudo-first-order rate constant (min⁻¹). The rate constant, k_1 was obtained from slope of the linear plots of $\log (q_e - q_t)$ against t.

The pseudo-second-order model is expressed as follows by Ho and McKay [26] and had been simplified in the form as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where k_2 is the pseudo-second-order rate constant (g/mg.min).

3. Results and Discussion

3.1 Combination with Ultrasound

According to Figure 1, presence of ultrasound increased the adsorptivity of AO52 on LVM from 95.54 to 129.5 mg/g. In addition, the time interval to achieve maximum adsorption

capacity became faster in the presence of ultrasound, from 27 min reduced to 12 min of contact time, which is possibly attributed to the rupture of LVM particles due to ultrasonic irradiation which consequently decrease the particle size of LVM and increase the surface area that is accessible for adsorption [27]. Thus, the introduction of ultrasound lead to the increase in adsorption capacity. The similar result was observed for the removal of AO52 with activated aluminas under sonochemical methods reported by Lida *et al.* which mentioned that the action of ultrasound resulted to the enhancement of the mass transfer [8].

3.2 Variation of pH

Figure 2 presented the effect of pH variation on the LVM's adsorptivity under sonochemical method at a pH range of 3-10 is shown. Accordingly, when the pH increased, the adsorption capacity decreased significantly. Based on the
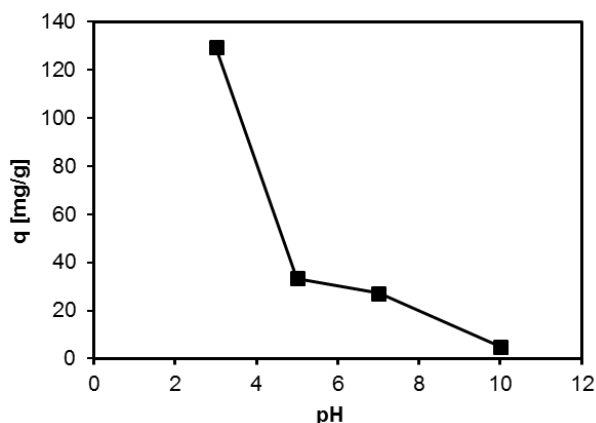

Figure 2. Effect of pH on adsorption capacity (initial concentration 100 mg/L, adsorbent dosage 0.5 g/L).
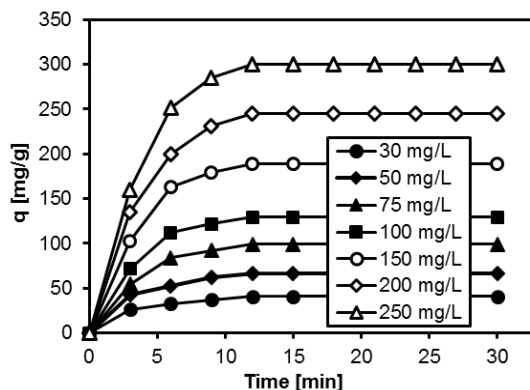
previous report [22], LVM structure consist of mainly SiO_2 and Al_2O_3. At low pH value, silica were protonated to give Si^{4+} and resulting more active LVM surface for adsorption process whereas Al_2O_3 were dissolved in strong acid to form Al^{3+}. This aluminium cation assist the AO52 anion diffusion to the adsorbent surface. In this study, maximum adsorptivity was observed at pH 3 in which the pattern decreased drastically when the pH was increased to 5. This is also in accordance with our previous study using LVM without the ultrasound [22].

3.3 Variation of Initial AO52 Concentration

The effect of various initial concentration is presented in Figure 3. The adsorption capacity of AO52 increased from 40.8 to 300.2 mg/g with the increasing of AO52 initial concentration. As the mass transfer driving force increases, greater amount of AO52 was adsorbed alongwith higher initial dye concentration due the reduced adsorbate uptake resistance. Higher concentration of solution resulted to the higher adsorption. This result is in correspondence with our previous work, which stated that the adsorptivity of AO52 was directly relative to the initial AO52 concentration [22].

3.4 Effect of LVM Dosage

According to Figure 4, percentage removal of AO52 increased with the LVM dosage, whereas the adsorption capacity was decreased. In fact, a greater number of possible binding sites for adsorption process should be increase as the adsorbent dosage increased. In contrast, adsorption capacity decreased since the unit of the adsorption capacity was milligram of adsorbate per mass (g) of LVM. In accordance, a higher absorbent dosage exposed
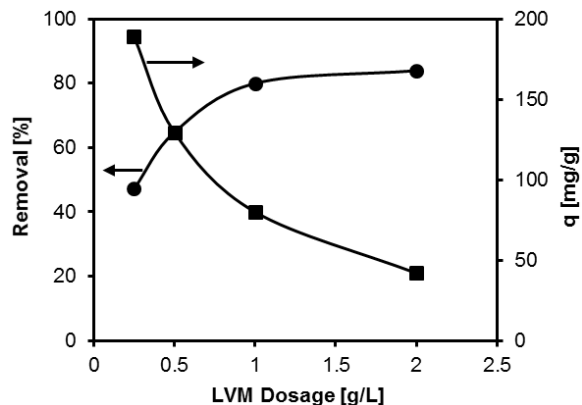

Figure 3. Effect of initial concentration on adsorption capacity (adsorbent dosage 0.5 g/L, initial pH 3).

Figure 4. Effect of LVM dosage on adsorption capacity and removal percentage (initial concentration 100 mg/L, initial pH 3).

more surface site for adsorption. For the same amount of adsorbate with higher adsorbent dosage, more surface site is offered thus more adsorption sites remain unoccupied, thus resulted to lower adsorption capacity [22]. By considering the values of percentage removal

and adsorption capacity, optimum adsorption dosage was observed at 0.5 g/L. Thus, all further studies were carried out at this adsorbent dosage.

3.5 Adsorption isotherms

The adsorption isotherm was calculated and plotted accordingly as in Section 2.4 (Figure 5 and Table 1). It's appeared that the adsorption of AO52 obeyed the Langmuir model, based on the R^2 values. This result demonstrated that the adsorption of AO52 formed monoloyer process on the surface of LVM. This result is in correspondence with our previous work, for the adsorption onto LVM without the ultrasound [22]. However, the values of adsorption capacity (q_m) in current study is higher (833.33 mg/g) than prior method (333.33 mg/g) as discussed in the previous section. As it was explained, the presence of ultrasound increased the surface area available for reaction and facilitated the contact between LVM and AO52 molecule.

Table 1. Isotherm parameters for adsorption of AO52 on LVM under sono-sorption method at 30 °C.

Isotherm	Parameters
Langmuir	
q_m (mg/g)	833.33
K_L (L/mg)	0.00534
R^2	0.9997
R_L range	0.4284-0.8620
Freundlich	
K_f	6.1306
$1/n$	0.8506
R^2	0.9990

Table 2. Adsorption kinetic parameters for the adsorption of AO52 on LVM under sono-sorption method at different initial temperatures.

| C_o (mg/L)	$q_{e, exp}$ (mg/g)	Pseudo-first order			Pseudo-second order			
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2	h (mg/g.min)
30	40.80	36.50	0.2579	0.9860	42.37	0.0245	0.9972	44.0529
50	66.82	65.46	0.2909	0.9790	69.44	0.0148	0.9968	71.4286
75	99.03	101.02	0.3005	0.9954	103.09	0.0090	0.9955	95.2381
100	129.50	135.83	0.3247	0.9942	135.14	0.0073	0.9956	133.3333
150	189.50	202.95	0.3280	0.9942	196.08	0.0049	0.9952	188.6792
200	244.90	266.62	0.3169	0.9920	256.41	0.0035	0.9952	227.2727
250	300.20	334.81	0.3339	0.9919	312.50	0.0029	0.9947	285.7143
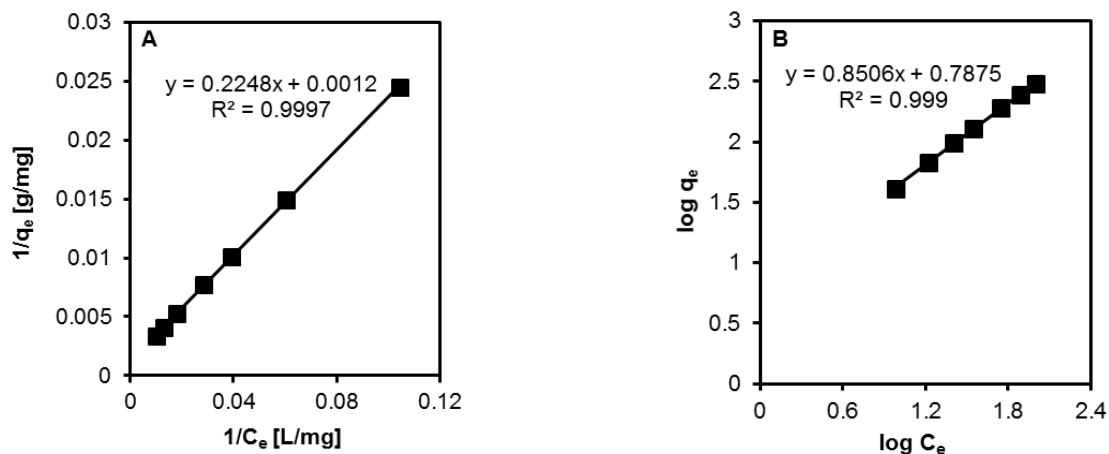
Figure 5. Adsorption isotherm (A) Langmuir and (B) Freundlich for adsorption of AO52 on LVM under sono-sorption method (initial concentration 100 mg/L, adsorbent dosage 0.5 g/L, initial pH 3).
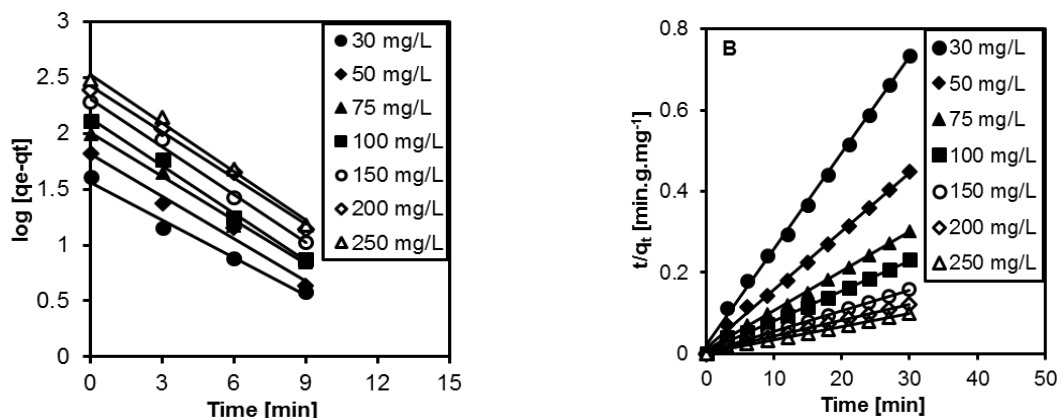
Figure 6. (A) Pseudo-first-order and (B) Pseudo-second-order kinetics for adsorption of AO52 on LVM under sono-sorption method (initial concentration 100 mg/L, adsorbent dosage 0.5 g/L, initial pH 3).

Since the values of $0 < R_L < 1$, the adsorption of AO52 on the surface of LVM is favourable at the temperature studied.

Enhancement in the adsorption process caused by the introduction of ultrasound was also observed on the adsorption of methyl-thioninium chloride (Swiss Blue) [14] in which the introduction of ultrasound increased the adsorptivity from 59 to 611 mg/g.

3.7 Adsorption Kinetics

Table 2 presented the kinetic data, whereas, Figure 6 elucidates the linear plots for both models, of pseudo first-order and pseudo second-order kinetics for adsorption of AO52 on LVM under sono-sorption method. The linear plots of pseudo second-order kinetic model displayed the equivalent values of calculated and experimental q_e. Since the R^2 value is more than 0.9947, the adsorption process of AO52 on LVM under sono-sorption method is indicated to obey this kinetic model. This result is in correspondence with our previous work, for the adsorption of AO52 on LVM under conventional method [22]. However, the rate constants were higher in sono-sorption (0.0029-0.0245 g/mg.min) than conventional method (0.0014-0.0094 g/mg.min).

4. Conclusion

The current work investigated the elimination of AO52 by LVM in synergistic condition of sono-sorption. Sono-sorption condition increased the adsorption capacity of AO52 by 35.5% which is initially 95.54 mg/g, to 129.5 mg/g, due to the enhancement of mass transfer which assist the adsorption of AO52. The adsorption isotherm followed the Langmuir mod-els, demonstrating that the adsorption of AO52 on LVM occurs as a monolayer process. Kinetic studies showed that the adsorption of AO52 onto LVM followed the pseudo-second-order model. The higher adsorption capacity and faster removal of AO52 by the sono-sorption method by using an adsorbent of LVM could be employed as a method to remove pollutants, especially dyestuff in industrial water treatment due to the abundance and efficiencies of LVM.

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