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2 Maret 2021	Submit revised manuscript
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Manuscript submission

2 messages

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January 19, 2021

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Science of Sintering

Institute of Technical Sciences, Serbian Academy of Sciences and Arts

Belgrade, Serbia

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Thank you very much!

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> Modified Fly Ash and Alkali Activated Fly Ash as Zn(II) Ions Adsorbent
> from
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[Quoted text hidden]

Comparison of Alkali Modified Fly Ash and Alkali Activated Fly Ash as Zn(II) Ions Adsorbent from Aqueous Solution

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Abstract. Fly ash which is solid waste can be used as adsorbent for wastewater treatment. Alkali modification and alkali activation on fly ash can increase the adsorption capacity of fly ash. In this study, alkali modified fly ash and alkali activated fly ash were used as Zn(II) ions adsorbents. The effect of adsorption time and initial concentration of Zn(II) ions was studied, as well as the kinetics and isotherm adsorption. The results showed that the removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash. The adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash have reached equilibrium after two hours. The increase of initial concentration of Zn(II) ions would decrease the removal efficiency with both alkali modified fly ash and alkali activated fly ash. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model and Langmuir isotherm model with maximum adsorption capacity of 62.696 mg/g and 66.667 mg/g, respectively.

Keywords: adsorption, alkali modified fly ash, alkali activated fly ash, Zn(II) ions

1. Introduction

The use of coal as energy source by combustion process produces fly ash as solid waste. Fly ash, generally collected by electrostatic precipitator, can be utilized rather than disposed of. Common utilizations of fly ash are for soil amendment, road and pavement construction, concrete and cement production, zeolite and geopolymer production, adsorbent for wastewater treatment, etc. [1-3]. Adsorption is one of the most widely method used in wastewater treatment. Compared to other methods such as chemical precipitation, electrochemical treatment, ion exchange, ultrafiltration, and reverse osmosis, adsorption has advantages namely simple, flexible, efficient, and low cost [4, 5].

In its application as adsorbent, the origin (type of coal, combustion condition) and chemical treatment of fly ash affect its adsorption capacity [6, 7]. Chemical treatment of fly ash by modification with an alkali solution can increase surface area resulting in increased adsorption capacity [8-10]. Meanwhile, activation of fly ash with a mixture of alkali solution and alkali silicate solution, commonly referred to as geopolymerization process, can transform fly ash into an amorphous three-dimensional structure [11]. Alkali activated fly ash has been widely used as adsorbent for heavy metals and dyes [12, 13].

In this study, alkali modification and alkali activation are applied on fly ash before being used as Zn(II) ions adsorbent. The presence of Zn(II) ions at certain level in water can cause health problems, such as gastroenteritis, skin irritations, neurotoxicity, hepatotoxicity, and hemotoxicity [14-16]. The effect of adsorption time and initial concentration of Zn(II) ions on the adsorption process of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash will be studied, as well as the kinetics and isotherm adsorption.

2. Materials and Methods

2.1. Materials

Fly ash containing major oxides Al_2O_3 (22.62%), CaO (14.80%), Fe_2O_3 (9.45%), and SiO_2 (42.38%) from power plants in East Java, Indonesia was used in this study. Fly ash was sieved with 100 mesh standard sieve. Commercial sodium hydroxide flakes (purity of 98%) was used for alkali modification of fly ash and also for alkali activation of fly ash with sodium silicate solution. Sodium silicate solution had SiO_2/Na_2O mole ratio of

3.2 and solid mass fraction of 0.35. Analytical grade $ZnSO_4.7H_2O$ and distilled water were used for preparing aqueous solution of Zn(II) ions.

2.2. Alkali modified fly ash

Fly ash was modified using10 N sodium hydroxide solution with solid to liquid ratio of 1:8 at temperature of 60 ^oC and stirring rate of 200 rpm for 8 hours. Modified fly ash was washed with deionized water then and dried at temperature of 110 ^oC in oven for 12 hours.

2.3. Alkali activated fly ash

Fly ash was activated using alkaline activator consisted of 10 N sodium hydroxide solution and sodium silicate solution in a ratio of 1:1. Fly ash was mixed with alkaline activator in a planetary mixer for 10 minutes (ratio of fly ash to alkaline activator was 2.5:1) and the mixture was then placed in a 5x5x5 cm mold for 24 hours. Alkali activated fly ash was removed from the mold and heated in an oven at temperature of 60 ^oC for 6 hours. After cured for 7 days in room temperature, alkali activated fly ash was crushed and sieved with 60 mesh standard sieve.

2.4. Adsorption of Zn(II) ions

Batch adsorption of Zn(II) ions was carried out on 100 ml solution at pH 6, adsorbent mass of 0.2 g, and stirring rate of 200 rpm. Initial concentration of Zn(II) ions solution was varied, i.e. 10, 25, 50, 75, 100, 125, 150 ppm, respectively. Moreover, adsorption time was also varied, i.e. 15, 30, 45, 60, 75, 90, 105, 120, 150, 180 minutes, respectively. After the adsorption process was complete, the adsorbent was separated from the solution by filtration. The concentration of Zn(II) ions solution was measured by Atomic Absorption Spectroscopy (AAS) with PerkinElmer AAnalyst 400 instruments. The removal efficiency (%) of Zn(II) ions was calculated from the equation:

$$Removal\ efficiency\ of\ Zn(II)\ ions\ (\%) = \frac{C_0 - C_e}{C_0} x100 \quad (1)$$

C_0 is the initial concentration of Zn(II) ions solution (mg/L) and C_e is the concentration of Zn(II) ions solution at equilibrium (mg/L).

2.5. Kinetics and isotherm adsorption studies

Kinetics studies on adsorption of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash were performed with pseudo-first order and pseudo-second order kinetics models. The pseudo-first order kinetics model can be stated by the equation:

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (2)$$

and for the pseudo-second order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t is the adsorption capacity at time t (mg/g) and q_e is the adsorption capacity at equilibrium (mg/g). The adsorption capacity is calculated using equation:

$$q = \frac{(C_0 - C_e)V}{W} \quad (4)$$

where V is volume of solution (L) and W is mass of adsorbent (g) [17, 18].

Isotherm studies were conducted with Langmuir and Freundlich isotherm models. Langmuir isotherm model describes chemical adsorption process with monolayer adsorption, whereas Freundlich isotherm model describes physical adsorption process with multilayer adsorption. Langmuir isotherm model can be expressed by the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where q_m is maximum adsorption capacity and K_L is Langmuir constant related to adsorption capacity. Meanwhile, Freundlich isotherm model can be expressed in equation:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F is Freundlich constant related to adsorption capacity and $1/n$ is related to adsorption intensity [19, 20].

2.6. Characterizations

Characterizations were carried out on fly ash, alkali activated fly ash, and alkali modified fly ash comprising Brunauer-Emmett-Teller (BET) surface area analysis with Quantachrome Instruments, scanning electron microscope (SEM) analysis with JEOL JSM-6510LA instruments, and X-ray diffraction (XRD) with Shimadzu XRD-7000 instrument.

3. Results and Discussion

Characterizations of fly ash, alkali modified fly ash, and alkali activated fly ash cover BET surface area analysis, SEM analysis, and XRD analysis. The results of BET surface area analysis are shown in Tab. I. Both alkali modification and alkali activation have changed the surface area of fly ash to a greater extent. These results are in accordance with the results of SEM analysis with magnification of 1000x in Fig. 1. Surface of alkali modified fly ash looks rougher and porous as obtained by previous research works [9, 21, 22]. Meanwhile, alkali activated fly ash shows continuous phase forming amorphous three-dimensional structure as obtained in previous studies [23-25].

Tab. I *Surface area of fly ash, alkali modified fly ash and alkali activated fly ash.*

Fig. 1. *Scanning electron micrographs of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).*

Fig. 2 shows the results of XRD analysis. The major crystalline peaks in all three materials come from quartz and mullite around $2\theta=26^{o}$ [26, 27]. Quartz and mullite originating from fly ash are still found in alkali modified fly ash and alkali activated fly ash. There is a decrease in the intensity of crystalline peaks both in alkali modified fly ash and in alkali activated fly ash.

Fig. 2. *X-ray diffractograms of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).*

Adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash were carried out by varying adsorption time and initial concentration. The increase in adsorption time of up to two hours can increase the removal efficiency of Zn(II) ions but after that the removal efficiency is relatively constant as shown in Fig. 3. This indicates that after two hours the adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash have reached equilibrium. Furthermore, the increase of initial concentration of Zn(II) ions would decrease the removal efficiency with both alkali modified fly ash and alkali activated fly ash as shown in Fig. 4. This can happen because at high initial concentration the surface of adsorbent can no longer adsorb Zn(II) ions. The removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash. In addition to alkali activated fly ash having higher surface area compared to alkali modified fly ash, alkali activated fly ash has negative charge from aluminium sites that can attract positive ions so that more Zn(II) ions will be adsorbed at surface of alkali activated fly ash [13, 28].

Fig. 3. *The effect of adsorption time on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).*

Fig. 4. *The effect of initial concentration on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).*

Kinetic studies on Zn(II) ions adsorption by alkali modified fly ash and by alkali activated fly ash were conducted based on pseudo first order kinetics model and pseudo second order kinetics model. Linear fittings of pseudo first order kinetics model ($ln(q_e-q_t)$ versus t) and pseudo second order kinetics model (t/qt versus t) for adsorption of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash are shown in Fig. 5 and Fig. 6, respectively, with obtained adsorption kinetics parameters are listed in Tab. II. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model based on coefficient of correlations (R^2) which chemical adsorption controls the adsorption process [17, 18].

Fig. 5. *Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali modified fly ash.*

Fig. 6. *Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali activated fly ash.*

Tab. II *Adsorption kinetics parameters for Zn(II) ions adsorption.*

Langmuir isotherm and Freundlich isotherm were used in isotherm studies on Zn(II) ions adsorption by alkali modified fly ash and by alkali activated fly ash. Fig. 7 shows linear fitting of Langmuir isotherm (C_e/q_e versus C_e) and Freundlich isotherm ($log\ q_e$ versus log C_e) for adsorption of Zn(II) ions by alkali modified fly ash, while Fig. 8 for adsorption of Zn(II) ions by alkali activated fly ash. Adsorption isotherm parameters for Zn(II) ions adsorption were listed in Tab. III. Based on coefficient of correlations (R^2) in isotherm model, Langmuir isotherm is better to explain adsorption of Zn(II) ions by both adsorbent. In the Langmuir isotherm, it is assumed that the adsorbent has homogeneous surface so that only one layer of adsorbate is formed on the adsorbent surface (monolayer chemical adsorption) [19, 20]. Furthermore, characteristics of Langmuir isotherm can be expressed in terms of the separation factor, R_L, calculated by the equation:

$$R_L = \frac{1}{1+K_L C_0} \quad (7)$$

From the value of R_L, adsorption process can be classified irreversible (R_L=0), favorable (0< R_L<1), linear (R_L=1), or unfavorable (R_L>1). Adsorption of Zn(II) ions by alkali modified fly ash has R_L value of 0.74-0.16 with initial concentration of 10-150 ppm, while adsorption of Zn(II) ions by alkali activated fly ash has R_L value of 0.54-0.07. Thus, adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash are favorable adsorption.

Fig. 7. *Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali modified fly ash.*

Fig. 8. *Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali activated fly ash.*

Tab. III *Adsorption isotherm parameters for Zn(II) ions adsorption.*

Based on adsorption kinetics and isotherm studies, adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash follow pseudo second order kinetics model and Langmuir isotherm model. Maximum adsorption capacity (q_m) of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash in this study are 62.696 mg/g and 66.667 mg/g, respectively. Similar results were obtained from previous studies using alkali modified fly ash [9] and also using alkali activated slag [15] for adsorption of Zn(II) ions that followed pseudo second order kinetics model and Langmuir isotherm model with q_m of 56.8 mg/g and 86 mg/g, respectively.

4. Conclusions

Alkali modification and alkali activation have been applied on fly ash then used as Zn(II) ions adsorbent. The removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model and Langmuir isotherm model.

Acknowledgements

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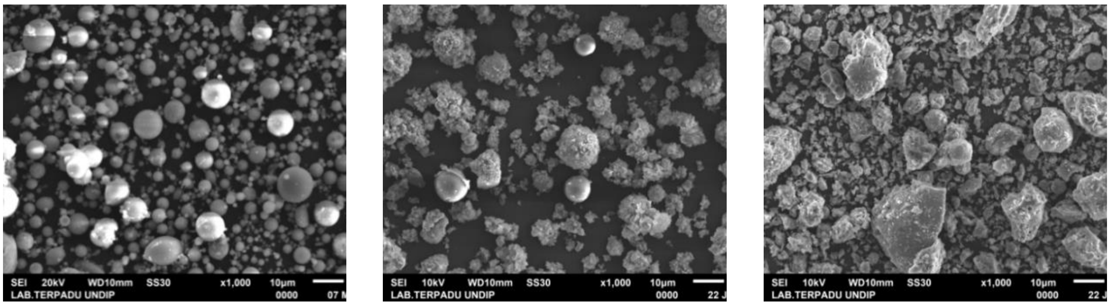
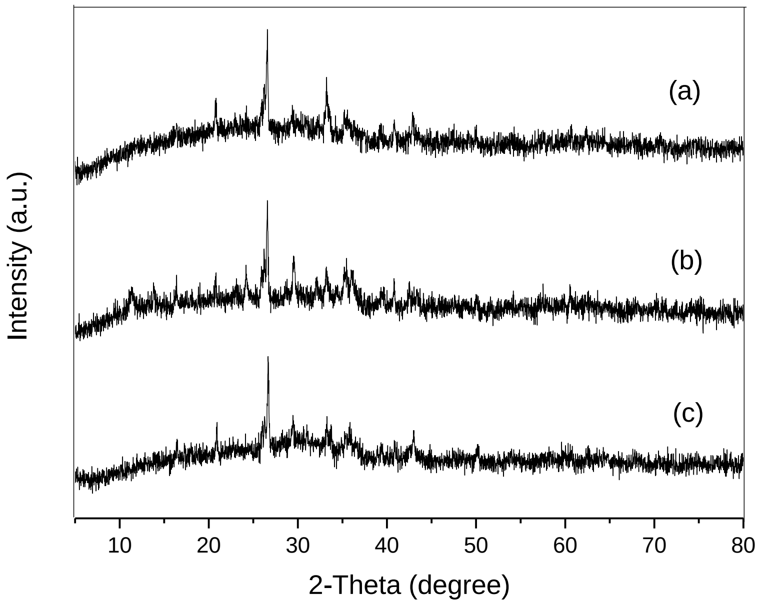
FIGURES



(a) (b) (c)

Fig. 1. Scanning electron micrographs of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).



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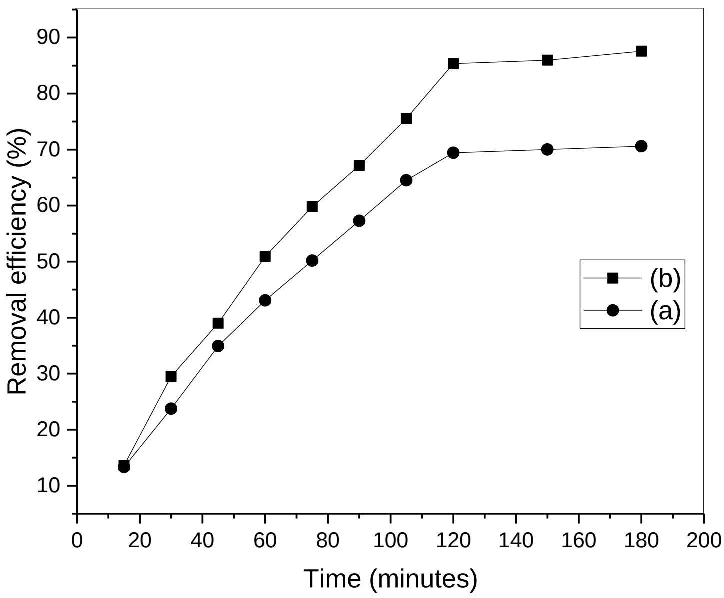


Fig. 3. The effect of adsorption time on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).

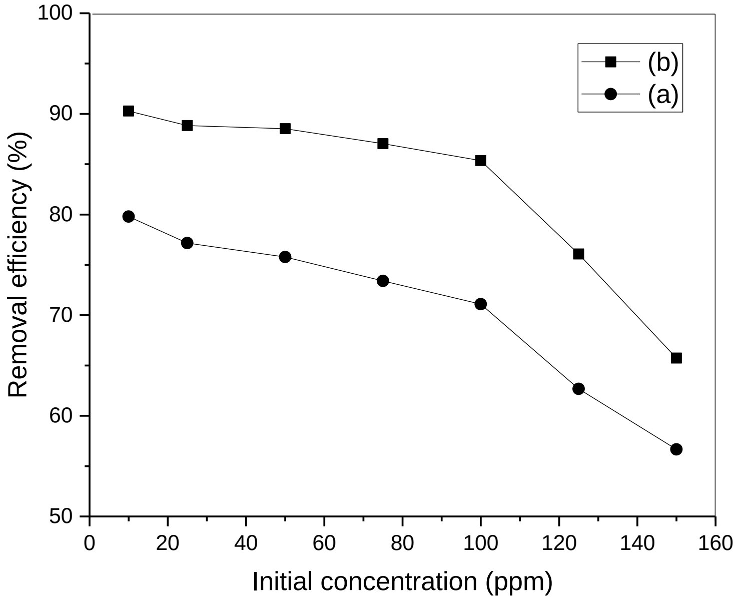
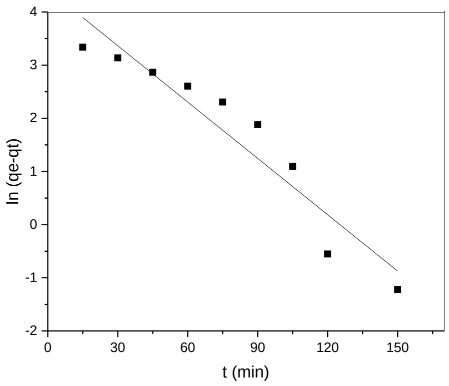
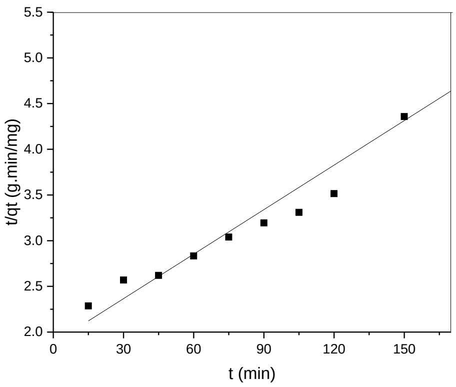


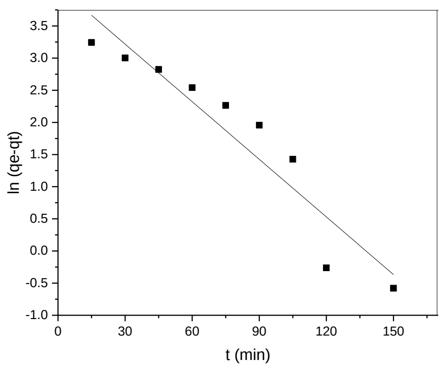
Fig. 4. The effect of initial concentration on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).

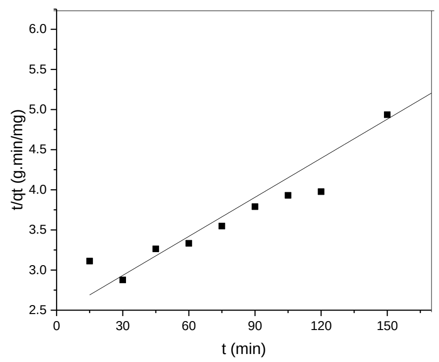




(a) (b)

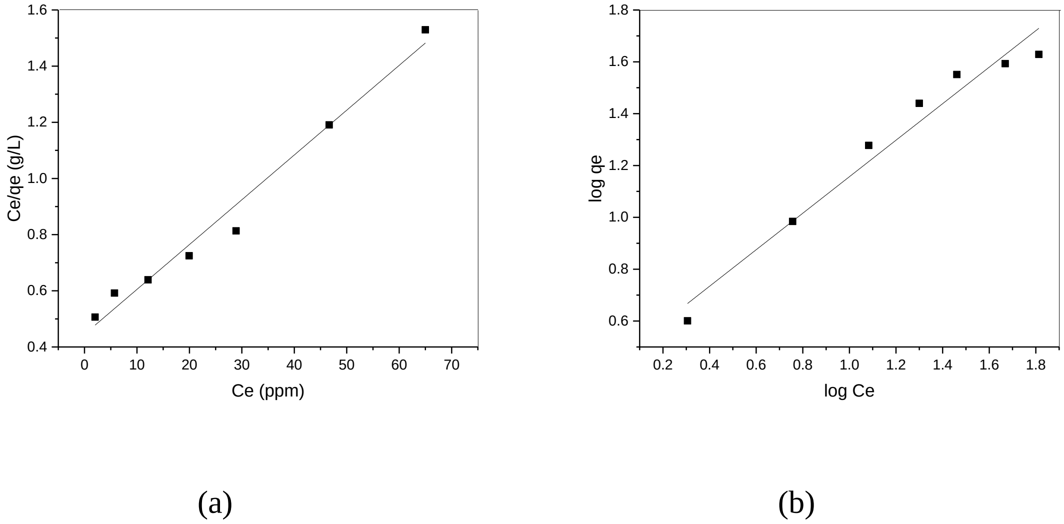
Fig. 5. Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali modified fly ash.





(a) (b)

Fig. 6. Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali activated fly ash.



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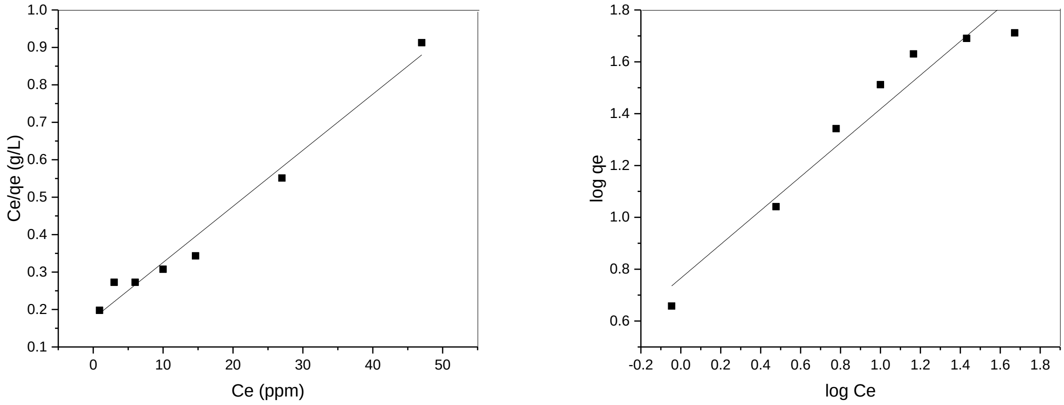

(a) (b)

Fig. 8. Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali activated fly ash.

TABLES

Tab. I Surface area of fly ash, alkali modified fly ash and alkali activated fly ash.

Materials	Surface area (m^2/g)
Fly ash	1.745
Alkali modified fly ash	18.693
Alkali activated fly ash	19.567

Tab. II Adsorption kinetics parameters for Zn(II) ions adsorption.

Adsorbent	Pseudo first order kinetics model			Pseudo second order kinetics model		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/(mg.min))	R^2
Alkali modified fly ash	83.513	0.035	0.908	61.576	0.000140	0.941
Alkali activated fly ash	61.191	0.029	0.897	61.652	0.000105	0.910

Tab. III Adsorption isotherm parameters for Zn(II) ions adsorption.

Adsorbent	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	*1/n*	K_F (mg/g.(L/mg)$^{1/n}$)	R^2
Alkali modified fly ash	62.696	0.036	0.980	0.704	2.685	0.965
Alkali activated fly ash	66.667	0.085	0.979	0.652	2.149	0.942

Statement Letter

I am on behalf of all authors of manuscript entitled: "**Comparison of Alkali Modified Fly Ash and Alkali Activated Fly Ash as Zn(II) Ions Adsorbent from Aqueous Solution**" with authors: **Aprilina Purbasari, Dessy Ariyanti, Siswo Sumardiono, Muhammad Anif Shofa, Reinhard Parasian Manullang** state that the manuscript has not been copyrighted or published or submitted for publication in other journals.

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Referee's report-Sci Sint (49)-Aprilina.doc
44K

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id> Tue, Mar 2, 2021 at 8:14 PM
To: ninao <nina.obradovic@itn.sanu.ac.rs>

Dear Dr. Nina Obradovic,

Hereby I send my revised manuscript and also answers to reviewer"s comments.
Thank you.

Regards,
Aprilina Purbasari
[Quoted text hidden]

---

2 attachments

Manuscript_SciSinter_Purbasari_etal_rev.docx
1005K

Answers to Reviewer's Comments.docx
580K

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id> Tue, May 4, 2021 at 5:24 PM
To: ninao <nina.obradovic@itn.sanu.ac.rs>

Dear Dr. Nina Obradovic,

I have submitted my revised manuscript on March 2 2021. I would be grateful if you could let me know whether there has been any further progress on my submission.
Thank you very much for your cooperation.

Best regards,
Aprilina Purbasari
[Quoted text hidden]

---

ninao <nina.obradovic@itn.sanu.ac.rs> Tue, May 4, 2021 at 10:44 PM
To: Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id>

Dear Dr. Aprilina,

your paper is accepted and will be published in the 1st volume 2022.

Best regards,

Nina

[Quoted text hidden]

Aprilina Purbasari <aprilina.purbasari@che.undip.ac.id>
To: ninao <nina.obradovic@itn.sanu.ac.rs>

Wed, May 5, 2021 at 8:50 AM

Dear Dr. Nina Obradovic,

Thank you very much for your information.

Best regards,
Aprilina Purbasari

[Quoted text hidden]

REFEREE'S REPORT

Journal:	Science of Sintering
Title of paper	Comparison of Alkali Modified Fly Ash and Alkali Activated Fly Ash as Zn(II) Ions Adsorbent from Aqueous Solution
Reviewer's Name	

Points for Evaluation of the paper

1. Is the paper of sufficient scientific interest and has originality in its technical content to merit publication?

The paper satisfies the scientific criteria and possesses originality in technical and scientific content related to using chemical modification methods for improving the adsorption characteristics of waste material (fly ash). However, there is need to improve same parts of the manuscript which will be presented in Reviewer's specific comments.

2. If the paper is generally acceptable, are there any errors of fact, logic or interpretation which need correction(s)?

The paper is generally acceptable and there are no fact, logic or interpretation errors.

3. Is the paper well written and the presentation clear and concise? If not, which portions or parts including tables and figures, need deletion, recasting or condensation.

The paper is well written with clear and concise presentation of the aim of work. However, it is need to improve same experimental data and results interpretation.

4. (i) Have the authors cited the relevant literature?

The authors cited relevant literature, but some new literature should be cited.

(ii) Is there any cited document, which, in your opinion, is superfluous or irrelevant?

There is no cited irrelevant document.

5. Is the abstract sufficiently informative, concise, and clear?

Abstract is well written, concise and clear.

6. Is the paper written according to Instructions for Authors?

The paper is written in accordance with the Journal instructions.

7. Is there a clear and concise correlation between experimental work and results and discussion?

Experimental work, results and discussion are in clear correlation.

8. Recommendation: Does the paper deserve to be published

(i) as it is
(ii) with minor modifications
(iii) with major modifications
(iv) rejected

Specific comments, if any:

Authors investigate using of alkali treated fly ash as adsorbent for wastewater treatment. It is confirmed that alkali modification/activation of fly ash increases the adsorption capacity of Zn(II) ions. The effect of adsorption time and initial concentration of Zn(II) ions is studied, and kinetics and isotherm adsorption parameters are determined. The subject of research is very much interesting since it explores conversion of waste (fly ash) to novel high effective sorption material. The paper is well written in terms of technical contents. However, there is need to improve same parts of the manuscript related to experimental data and results interpretation and reviewer would like to bring the following points to the author's attention.

Specific Comments:

Introduction

1. Authors should describe more in detail literature review of the using of modified fly ach in adsoprtion processes. See refences https://doi.org/10.1016/j.wasman.2018.05.052, 10.1016/j.jenvman.2018.07.051

Experimental part

1. Authors select pH 6 Zn adsorption. What was criteria for selection? It is important to determine point of zero change (pHpzc) and Zn ionic distribution related to the pH of the solution. Please provide the determination of the pHpzc) and Zn ionic distribution (see reference https://doi.org/10.1016/j.ijbiomac.2019.11.152.).

Results and discussion

1. Please provide more detail textural characteristics from BET analysis e.g. pore volume, volume of mesopores, average pore diameter, and pore diameter.
2. Please provide SEM images at higher magnification to evaluate porous structure.
3. Please provide more detailed XRD analysis (see references https://doi.org/10.1016/j.wasman.2018.05.052, 10.1016/j.jenvman.2018.07.051)
4. Describe the mechanisms of the Zn ions removal, e.g. complexation/electrostatically interaction with modified/activate fly ash surface groups. Also, it would be useful to use FTIR analysis for proving the interaction (differences in peaks position of adsorbents before and after Zn removal)
5. It would be useful to provide Overview of adsorption capacities of fly ash-based adsorbents

Introduction

1. Authors should describe more in detail literature review of the using of modified fly ach in adsoprtion processes. See refences https://doi.org/10.1016/j.wasman.2018.05.052, 10.1016/j.jenvman.2018.07.051

Answer:
Revisions had been made in manuscript.

"In its application as adsorbent, the origin (type of coal, combustion condition) and chemical treatment of fly ash affect its adsorption capacity [6, 7]. Chemical treatment of fly ash can be done by modification using an alkali solution, lime or magnetite. These modifications can increase surface area resulting in increased adsorption capacity of heavy metals [8-12]. Meanwhile, activation of fly ash with a mixture of alkali solution and alkali silicate solution, commonly referred to as geopolymerization process, can transform fly ash into an amorphous three-dimensional structure [13]. Alkali activated fly ash has been widely used as adsorbent for heavy metals and dyes [14, 15]."

Experimental part

1. Authors select pH 6 Zn adsorption. What was criteria for selection? It is important to determine point of zero change (pHpzc) and Zn ionic distribution related to the pH of the solution. Please provide the determination of the pHpzc) and Zn ionic distribution (see reference https://doi.org/10.1016/j.ijbiomac.2019.11.152.).

   Answer:
   We selected pH 6 and also adsorbent mass of 0.2 g for adsorption of 100 ml Zn(II) ions solution based on preliminary experiment that gave the highest removal of Zn(II) ions. At this time, we're sorry that we are unable to perform additional experiment to determine pH_{ZPC}.

Results and discussion

1. Please provide more detail textural characteristics from BET analysis e.g. pore volume, volume of mesopores, average pore diameter, and pore diameter.

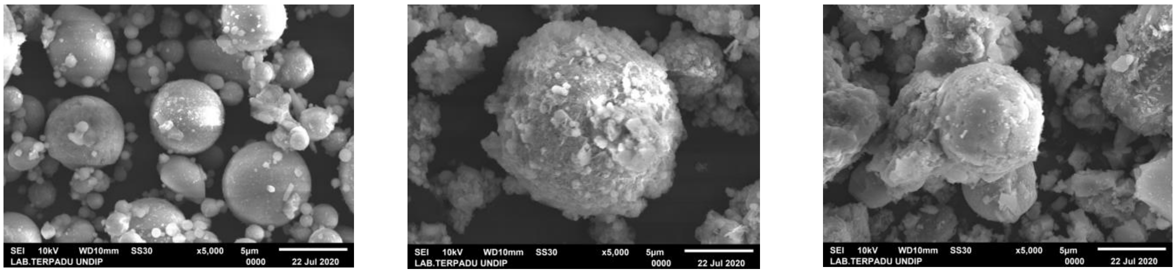
   Answer:
   Detailed characteristics from BET analysis had been added in manuscript.

Tab. I Physical properties of fly ash, alkali modified fly ash and alkali activated fly ash.

Materials	Surface area (m^2/g)	Average pore radius (nm)	Total pore volume (cc/g)
Fly ash	1.745	7.270	0.006
Alkali modified fly ash	18.693	12.892	0.120
Alkali activated fly ash	19.567	9.098	0.097

2. Please provide SEM images at higher magnification to evaluate porous structure.

   Answer:
   SEM images with higher magnification (5000x) had been added in manuscript.



(a) (b) (c)

Fig. 1. Scanning electron micrographs of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).

3. Please provide more detailed XRD analysis (see references https://doi.org/10.1016/j.wasman.2018.05.052, 10.1016/j.jenvman.2018.07.051)

   Answer:
   Detailed XRD analysis had been added in manuscript.

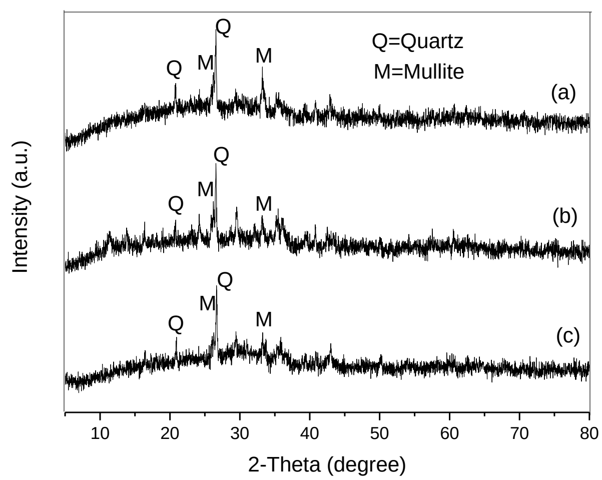


Fig. 2. X-ray diffractograms of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).

4. Describe the mechanisms of the Zn ions removal, e.g. complexation/electrostatically interaction with modified/activate fly ash surface groups. Also, it would be useful to use

FTIR analysis for proving the interaction (differences in peaks position of adsorbents before and after Zn removal)

Answer:
The mechanism of Zn(II) ions removal with modified fly ash and activated fly ash had been added in manuscript. Unfortunately, we did not do the FTIR analysis so we could not include it in manuscript.

"Zn(II) ions can be adsorbed by both alkali modified fly ash and alkali activated fly ash. Alkali modified fly ash will be negatively charged at pH 6 solution because alkali modified fly ash has low pH value at zero point charge (pH_{ZPC}), i.e. about 3.7 [8]. This condition supports adsorption of positive ions on alkali modifief fly ash. On alkali activated fly ash, the surface is also negatively charged from aluminium sites that can attract positive ions [15, 30]. The removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash due to alkali activated fly ash has higher surface area compared to alkali modified fly ash."

5. It would be useful to provide Overview of adsorption capacities of fly ash-based adsorbents.

Answer:
At last paragraph in Results and Discussion section, we compared the adsorption capacities of alkali modified fly ash and alkali activated fly ash with unmodified fly ash, also alkali modified fly ash and alkali activated fly ash from other studies.

"Based on adsorption kinetics and isotherm studies, adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash follow pseudo second order kinetics model and Langmuir isotherm model. Maximum adsorption capacity (q_m) of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash in this study are 62.696 mg/g and 66.667 mg/g, respectively. These values are higher than maximum adsorption capacity of unmodified fly ash for Zn(II) ions, i.e. 6.5-13.3 mg/g at temperature of 30-60 ^{o}C [18]. Meanwhile, similar results were obtained from previous studies using alkali modified fly ash [9] and also using alkali activated fly ash [31] for adsorption of Zn(II) ions that followed pseudo second order kinetics model and Langmuir isotherm model with q_m of 56.8 mg/g and 47.1 mg/g, respectively."

Comparison of Alkali Modified Fly Ash and Alkali Activated Fly Ash as Zn(II) Ions Adsorbent from Aqueous Solution

Aprilina Purbasari*, Dessy Ariyanti, Siswo Sumardiono, Muhammad Anif Shofa, Reinhard Parasian Manullang

Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Jl. Prof. Soedarto, Kampus Tembalang, Semarang 50275, Indonesia

*Corresponding author: aprilina.purbasari@che.undip.ac.id

Abstract. Fly ash which is solid waste can be used as adsorbent for wastewater treatment. Alkali modification and alkali activation on fly ash can increase the adsorption capacity of fly ash. In this study, alkali modified fly ash and alkali activated fly ash were used as Zn(II) ions adsorbents. The effect of adsorption time and initial concentration of Zn(II) ions was studied, as well as the kinetics and isotherm adsorption. The results showed that the removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash. The adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash have reached equilibrium after two hours. The increase of initial concentration of Zn(II) ions would decrease the removal efficiency with both alkali modified fly ash and alkali activated fly ash. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model and Langmuir isotherm model with maximum adsorption capacity of 62.696 mg/g and 66.667 mg/g, respectively.

Keywords: adsorption, alkali modified fly ash, alkali activated fly ash, Zn(II) ions

1. Introduction

The use of coal as energy source by combustion process produces fly ash as solid waste. Fly ash, generally collected by electrostatic precipitator, can be utilized rather than disposed of. Common utilizations of fly ash are for soil amendment, road and pavement construction, concrete and cement production, zeolite and geopolymer production, adsorbent for wastewater treatment, etc. [1-3]. Adsorption is one of the most widely method used in wastewater treatment. Compared to other methods such as chemical precipitation, electrochemical treatment, ion exchange, ultrafiltration, and reverse osmosis, adsorption has advantages namely simple, flexible, efficient, and low cost [4, 5].

In its application as adsorbent, the origin (type of coal, combustion condition) and chemical treatment of fly ash affect its adsorption capacity [6, 7]. Chemical treatment of fly ash can be done by modification using an alkali solution, lime or magnetite. These modifications can increase surface area resulting in increased adsorption capacity of heavy metals [8-12]. Meanwhile, activation of fly ash with a mixture of alkali solution and alkali silicate solution, commonly referred to as geopolymerization process, can transform fly ash into an amorphous three-dimensional structure [13]. Alkali activated fly ash has been widely used as adsorbent for heavy metals and dyes [14, 15].

In this study, alkali modification and alkali activation are applied on fly ash before being used as Zn(II) ions adsorbent. The presence of Zn(II) ions at certain level in water can cause health problems, such as gastroenteritis, skin irritations, neurotoxicity, hepatotoxicity, and hemotoxicity [16-18]. The effect of adsorption time and initial concentration of Zn(II) ions on the adsorption process of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash will be studied, as well as the kinetics and isotherm adsorption.

2. Materials and Methods

2.1. Materials

Fly ash containing major oxides Al_2O_3 (22.62%), CaO (14.80%), Fe_2O_3 (9.45%), and SiO_2 (42.38%) from power plants in East Java, Indonesia was used in this study. Fly ash was sieved with 100 mesh standard sieve. Commercial sodium hydroxide flakes (purity of 98%) was used for alkali modification of fly ash and also for alkali activation of fly ash with sodium silicate solution. Sodium silicate solution had SiO_2/Na_2O mole ratio of

3.2 and solid mass fraction of 0.35. Analytical grade $ZnSO_4.7H_2O$ and distilled water were used for preparing aqueous solution of Zn(II) ions.

2.2. Alkali modified fly ash

Fly ash was modified using10 N sodium hydroxide solution with solid to liquid ratio of 1:8 at temperature of 60 ^oC and stirring rate of 200 rpm for 8 hours. Modified fly ash was washed with deionized water then and dried at temperature of 110 ^oC in oven for 12 hours.

2.3. Alkali activated fly ash

Fly ash was activated using alkaline activator consisted of 10 N sodium hydroxide solution and sodium silicate solution in a ratio of 1:1. Fly ash was mixed with alkaline activator in a planetary mixer for 10 minutes (ratio of fly ash to alkaline activator was 2.5:1) and the mixture was then placed in a 5x5x5 cm mold for 24 hours. Alkali activated fly ash was removed from the mold and heated in an oven at temperature of 60 ^oC for 6 hours. After cured for 7 days in room temperature, alkali activated fly ash was crushed and sieved with 60 mesh standard sieve.

2.4. Adsorption of Zn(II) ions

Batch adsorption of Zn(II) ions was carried out on 100 ml solution at pH 6, adsorbent mass of 0.2 g, and stirring rate of 200 rpm. Initial concentration of Zn(II) ions solution was varied, i.e. 10, 25, 50, 75, 100, 125, 150 ppm, respectively. Moreover, adsorption time was also varied, i.e. 15, 30, 45, 60, 75, 90, 105, 120, 150, 180 minutes, respectively. After the adsorption process was complete, the adsorbent was separated from the solution by filtration. The concentration of Zn(II) ions solution was measured by Atomic Absorption Spectroscopy (AAS) with PerkinElmer AAnalyst 400 instruments. The removal efficiency (%) of Zn(II) ions was calculated from the equation:

$$Removal\ efficiency\ of\ Zn(II)\ ions\ (\%) = \frac{C_0 - C_e}{C_0} x100 \qquad (1)$$

C_0 is the initial concentration of Zn(II) ions solution (mg/L) and C_e is the concentration of Zn(II) ions solution at equilibrium (mg/L).

2.5. Kinetics and isotherm adsorption studies

Kinetics studies on adsorption of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash were performed with pseudo-first order and pseudo-second order kinetics models. The pseudo-first order kinetics model can be stated by the equation:

$$\ln(q_e - q_t) = ln q_e - k_1 t \qquad (2)$$

and for the pseudo-second order kinetics model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_t is the adsorption capacity at time t (mg/g) and q_e is the adsorption capacity at equilibrium (mg/g). The adsorption capacity is calculated using equation:

$$q = \frac{(C_0 - C_e)V}{W} \qquad (4)$$

where V is volume of solution (L) and W is mass of adsorbent (g) [19, 20].

Isotherm studies were conducted with Langmuir and Freundlich isotherm models. Langmuir isotherm model describes chemical adsorption process with monolayer adsorption, whereas Freundlich isotherm model describes physical adsorption process with multilayer adsorption. Langmuir isotherm model can be expressed by the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (5)$$

where q_m is maximum adsorption capacity and K_L is Langmuir constant related to adsorption capacity. Meanwhile, Freundlich isotherm model can be expressed in equation:

$$q_e = K_F C_e^{1/n} \qquad (6)$$

where K_F is Freundlich constant related to adsorption capacity and $1/n$ is related to adsorption intensity [21, 22].

2.6. Characterizations

Characterizations were carried out on fly ash, alkali activated fly ash, and alkali modified fly ash comprising Brunauer-Emmett-Teller (BET) surface area and pore size analysis with Quantachrome Instruments, scanning electron microscope (SEM) analysis with JEOL JSM-6510LA instruments, and X-ray diffraction (XRD) with Shimadzu XRD-7000 instrument.

3. Results and Discussion

Characterizations of fly ash, alkali modified fly ash, and alkali activated fly ash cover BET surface area and pore size analysis, SEM analysis, and XRD analysis. Physical properties from the results of BET surface area and pore size analysis are shown in Tab. I. Both alkali modification and alkali activation have changed the surface area, average pore radius, and total pore volume of fly ash to a greater extent. These results are in accordance with the results of SEM analysis with magnification of 5000x in Fig. 1. Surface of alkali modified fly ash looks rougher and porous as obtained by previous research works [9, 23, 24]. Meanwhile, alkali activated fly ash shows continuous phase forming amorphous three-dimensional structure as obtained in previous studies [25-27].

Tab. I *Physical properties of fly ash, alkali modified fly ash and alkali activated fly ash.*

Fig. 1. *Scanning electron micrographs of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).*

Fig. 2 shows the results of XRD analysis. The major crystalline peaks in all three materials come from quartz and mullite [28, 29]. Quartz and mullite originating from fly ash are still found in alkali modified fly ash and alkali activated fly ash. There is a decrease in the intensity of crystalline peaks both in alkali modified fly ash and in alkali activated fly ash.

Fig. 2. *X-ray diffractograms of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).*

Adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash were carried out by varying adsorption time and initial concentration. The increase in adsorption time of up to two hours can increase the removal efficiency of Zn(II) ions but after that the removal efficiency is relatively constant as shown in Fig. 3. This indicates that after two hours the adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash have reached equilibrium. Furthermore, the increase of initial concentration of Zn(II) ions would decrease the removal efficiency with both alkali modified fly ash and alkali activated fly ash as shown in Fig. 4. This can happen because at high initial concentration the surface of adsorbent can no longer adsorb Zn(II) ions.

Zn(II) ions can be adsorbed by both alkali modified fly ash and alkali activated fly ash. Alkali modified fly ash will be negatively charged at pH 6 solution because alkali modified fly ash has low pH value at zero point charge (pH_{ZPC}), i.e. about 3.7 [8]. This condition supports adsorption of positive ions on alkali modifief fly ash. On alkali activated fly ash, the surface is also negatively charged from aluminium sites that can attract positive ions [15, 30]. The removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash due to alkali activated fly ash has higher surface area compared to alkali modified fly ash.

Fig. 3. *The effect of adsorption time on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).*

Fig. 4. *The effect of initial concentration on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).*

Kinetic studies on Zn(II) ions adsorption by alkali modified fly ash and by alkali activated fly ash were conducted based on pseudo first order kinetics model and pseudo second order kinetics model. Linear fittings of pseudo first order kinetics model ($ln(q_e-q_t)$ versus t) and pseudo second order kinetics model (t/qt versus t) for adsorption of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash are shown in Fig. 5 and Fig. 6, respectively, with obtained adsorption kinetics parameters are listed in Tab. II. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model based on coefficient of correlations (R^2) which chemical adsorption controls the adsorption process [19, 20].

Fig. 5. *Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali modified fly ash.*

Fig. 6. *Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali activated fly ash.*

Tab. II *Adsorption kinetics parameters for Zn(II) ions adsorption.*

Langmuir isotherm and Freundlich isotherm were used in isotherm studies on Zn(II) ions adsorption by alkali modified fly ash and by alkali activated fly ash. Fig. 7 shows linear fitting of Langmuir isotherm (C_e/q_e versus C_e) and Freundlich isotherm ($log\ q_e$ versus log C_e) for adsorption of Zn(II) ions by alkali modified fly ash, while Fig. 8 for adsorption of Zn(II) ions by alkali activated fly ash. Adsorption isotherm parameters for Zn(II) ions adsorption were listed in Tab. III. Based on coefficient of correlations (R^2) in isotherm model, Langmuir isotherm is better to explain adsorption of Zn(II) ions by both adsorbent. In the Langmuir isotherm, it is assumed that the adsorbent has homogeneous surface so that only one layer of adsorbate is formed on the adsorbent surface (monolayer chemical adsorption) [21, 22]. Furthermore, characteristics of Langmuir isotherm can be expressed in terms of the separation factor, R_L, calculated by the equation:

$$R_L = \frac{1}{1+K_L C_0} \qquad (7)$$

From the value of R_L, adsorption process can be classified irreversible (R_L=0), favorable (0< R_L<1), linear (R_L=1), or unfavorable (R_L>1). Adsorption of Zn(II) ions by alkali modified fly ash has R_L value of 0.74-0.16 with initial concentration of 10-150 ppm, while adsorption of Zn(II) ions by alkali activated fly ash has R_L value of 0.54-0.07. Thus, adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash are favorable adsorption.

Fig. 7. *Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali modified fly ash.*

Fig. 8. *Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali activated fly ash.*

Tab. III *Adsorption isotherm parameters for Zn(II) ions adsorption.*

Based on adsorption kinetics and isotherm studies, adsorptions of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash follow pseudo second order kinetics model and Langmuir isotherm model. Maximum adsorption capacity (q_m) of Zn(II) ions by alkali modified fly ash and by alkali activated fly ash in this study are 62.696 mg/g and 66.667 mg/g, respectively. These values are higher than maximum adsorption capacity of unmodified fly ash for Zn(II) ions, i.e. 6.5-13.3 mg/g at temperature of 30-60 °C [18]. Meanwhile, similar results were obtained from previous studies using alkali modified fly ash [9] and also using alkali activated fly ash [31] for adsorption of Zn(II) ions that followed pseudo second order kinetics model and Langmuir isotherm model with q_m of 56.8 mg/g and 47.1 mg/g, respectively.

4. Conclusions

Alkali modification and alkali activation have been applied on fly ash then used as Zn(II) ions adsorbent. The removal efficiency of Zn(II) ions by alkali activated fly ash is higher than that by alkali modified fly ash. Adsorptions of Zn(II) ions by both alkali modified fly ash and alkali activated fly ash tend to follow pseudo second order kinetics model and Langmuir isotherm model.

Acknowledgements

The authors are grateful to *DRPM Deputi Bidang Penguatan Riset dan Pengembangan Kemenristek/Badan Riset dan Inovasi Nasional Indonesia* for supporting financially through *PDUPT 2020*.

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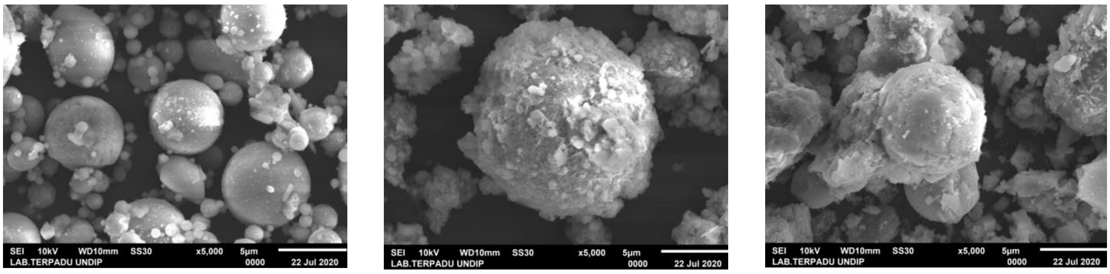
FIGURES



(a) (b) (c)

Fig. 1. Scanning electron micrographs of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).

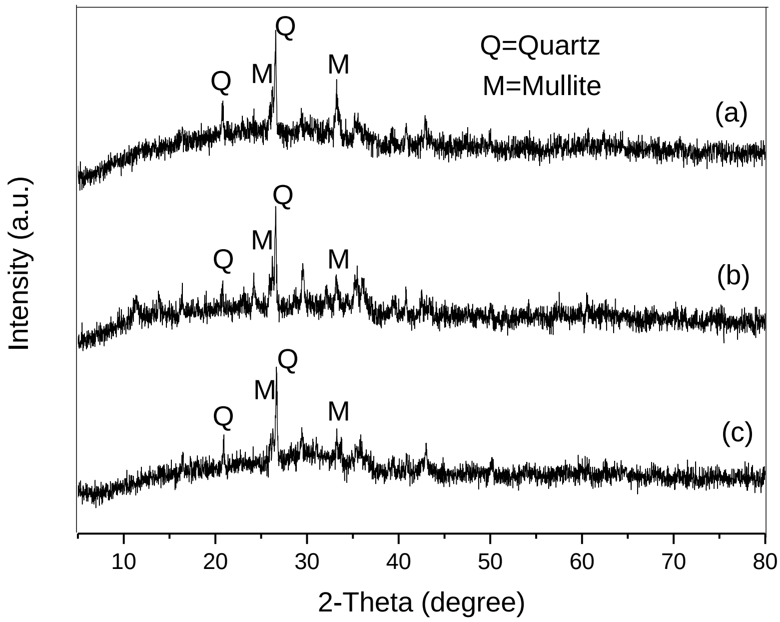


Fig. 2. X-ray diffractograms of fly ash (a), alkali modified fly ash (b) and alkali activated fly ash (c).

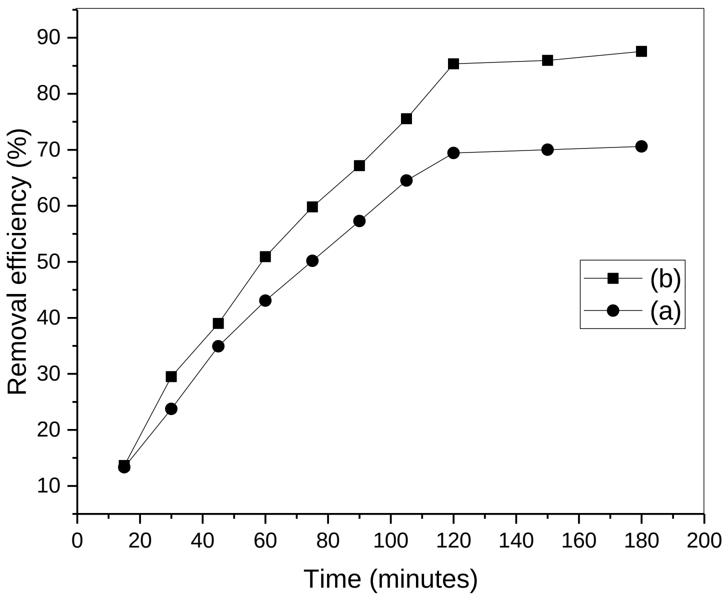


Fig. 3. The effect of adsorption time on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).

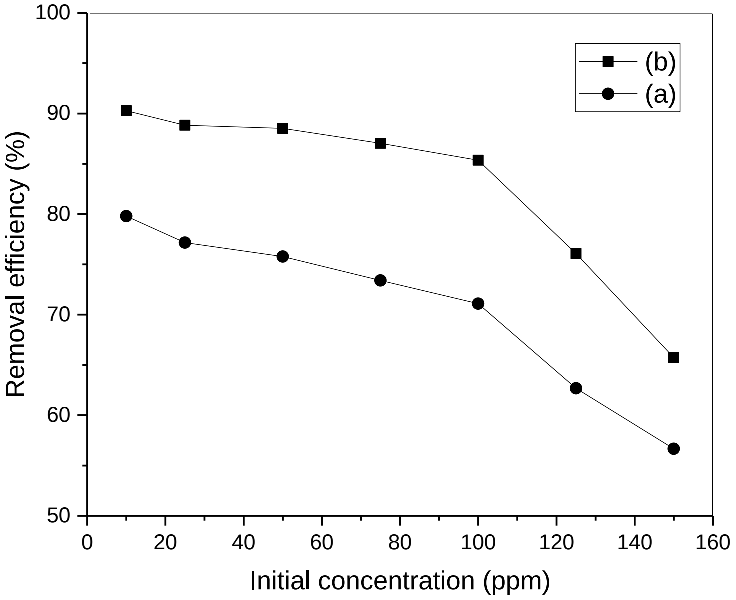
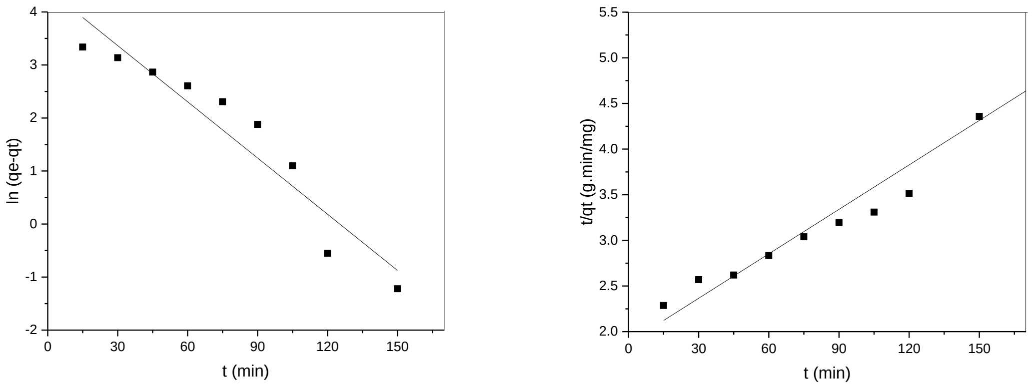
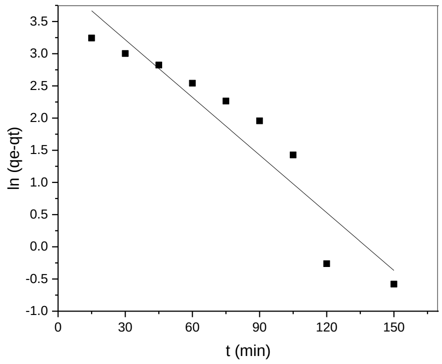


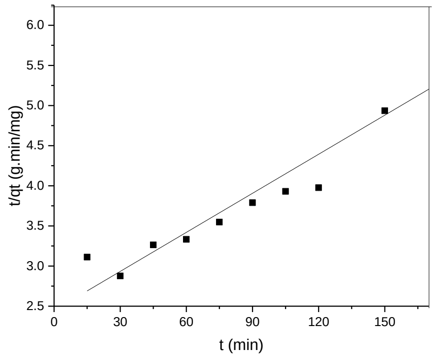
Fig. 4. The effect of initial concentration on Zn(II) ions removal efficiency by alkali modified fly ash (a) and by alkali activated fly ash (b).



(a) (b)

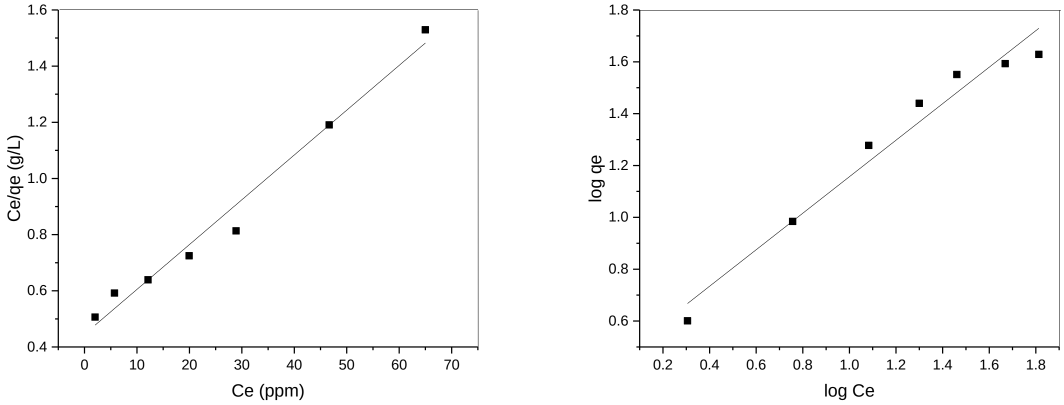
Fig. 5. Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali modified fly ash.





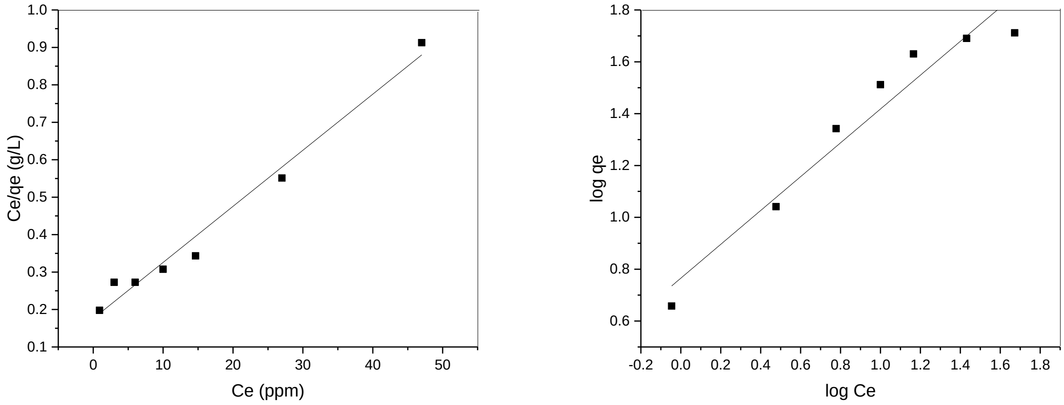
(a) (b)

Fig. 6. Linear fittings of pseudo first order kinetics model (a) and pseudo second order kinetics model (b) for adsorption of Zn(II) ions by alkali activated fly ash.



(a) (b)

Fig. 7. Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali modified fly ash.



(a) (b)

Fig. 8. Linear fitting of Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of Zn(II) ions by alkali activated fly ash.

TABLES

Tab. I Physical properties of fly ash, alkali modified fly ash and alkali activated fly ash.

Materials	Surface area (m^2/g)	Average pore radius (nm)	Total pore volume (cc/g)
Fly ash	1.745	7.270	0.006
Alkali modified fly ash	18.693	12.892	0.120
Alkali activated fly ash	19.567	9.098	0.097

Tab. II Adsorption kinetics parameters for Zn(II) ions adsorption.

Adsorbent	Pseudo first order kinetics model			Pseudo second order kinetics model		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/(mg.min))	R^2
Alkali modified fly ash	83.513	0.035	0.908	61.576	0.000140	0.941
Alkali activated fly ash	61.191	0.029	0.897	61.652	0.000105	0.910

Tab. III Adsorption isotherm parameters for Zn(II) ions adsorption.

Adsorbent	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	*1/n*	K_F (mg/g.(L/mg)$^{1/n}$)	R^2
Alkali modified fly ash	62.696	0.036	0.980	0.704	2.685	0.965
Alkali activated fly ash	66.667	0.085	0.979	0.652	2.149	0.942