Removal of Arsenic(III) from Aqueous Solutions by Adsorption onto Fly Ash

OLUSHOLA S. AYANDA[1,2,*], DOSU MALOMO[2], OYEBAMIJI OYEDELE OKETAYO[3], SIMPHIWE M. NELANA[1] and ELIAZER B. NAIDOO[1]

[1]Department of Chemistry, Vaal University of Technology, Vanderbijlpark 1900, South Africa
[2]Nanoscience Research, Department of Industrial Chemistry, Federal University Oye Ekiti, P.M.B 373, Oye Ekiti, Ekiti State, Nigeria
[3]Department of Physics, Federal University Oye Ekiti, P.M.B 373, Oye Ekiti, Ekiti State, Nigeria

*Corresponding author: E-mail: osayanda@gmail.com

In this work, the ability of fly ash in removing arsenic(III) ions from aqueous solution was considered. The effect of contact time, initial As(III) concentration, fly ash dosage, stirring speed, solution pH and temperature was investigated on the adsorption rate. Experimental studies showed that the adsorption fitted well the pseudo-second order kinetic, while the equilibrium study showed that the sorption of As(III) ions onto fly ash fitted the Langmuir and Freundlich isotherms. The adsorption process is endothermic and spontaneous. Moreover, the maximum percentage removal of As(III) achieved with approx. 2.5 g fly ash mixed with 25 mL of 100 mg/L As(III) solution was 65.4 % at pH 10, 60 min contact time, temperature of 353 K and a stirring speed of 120 rpm.

Keywords: Arsenic, Fly ash, Kinetics, Isotherm, Thermodynamics.

INTRODUCTION

Arsenic is a toxic inorganic pollutant and can be of natural or anthropogenic origin such as mining, smelting, wood preservatives, pesticides, additives, fossil fuels burning, *etc*. It has been described as one of the utmost environmental pollutants threatening the survival of human beings [1]. Exposure to low level of arsenic has been associated with various acute health effect to humans such as diarrhoea, vomiting and abdominal pain, whereas, high exposure to inorganic arsenic can cause long term health effects such as skin lesions, infertility, heart disruptions, brain damage, kidney, bladder and skin cancer, diabetes and lung ailments [2], hence, there is a need for the remediation of water and wastewater pollution caused by arsenic. Several technologies such as adsorption, ion exchange, oxidation, coagulation/flocculation, electrochemical methods, reverse osmosis, biological methods *etc*. have been utilized for the treatment of water pollution. However, some of these treatment techniques are not very effective due to limitation in either the working pH range, operational cost or the production of slag [3]. Owing to these limitations, adsorption method has been widely investigated and utilized by several researchers because it can remove contaminants over a wide pH range and at lower concentrations, with no slag been produced. A number of adsorbents have been reported for the adsorption of heavy metals in literature. The adsorption of arsenic by Fe(III)-Si binary oxide has been reported by Zeng

[4]. Zheng reported that the kinetics of adsorption could be described by the power function model and that the isotherm data satisfactorily fitted the Redlich-Peterson, Freundlich-Langmuir and Langmuir models. Payne and Abdel-Fattah [5] studied the adsorption of arsenate and arsenite by iron-treated activated carbon and zeolites. The adsorption of arsenic by nanoscale zero-valent iron stabilized with starch and carboxymethyl cellulose was assessed by Mosaferi *et al.* [1], while, Liu and Zhang [6] examined the adsorption of arsenic onto magnetic iron-manganese oxide. Furthermore, the adsorption of As(III) on iron oxide coated granular activated charcoal was investigated by Ananta *et al*. [7]. They reported that the equilibrium study fitted well with the Langmuir isotherm model, while adsorption was found to be kinetically pseudo-second order controlled. The adsorption capacities of magnetite nanoparticles composite for As(III) and As(V) has been investigated by Chang *et al*. [8]. They emphasized the effectiveness of magnetite nanoparticles composite for the fast removal of arsenic.

Nonetheless, researchers have now focused on cost implication; this has resulted to the use of adsorbents that are readily available and low cost. Examples of low cost adsorbents that have been investigated on environmental remediation include soils *e.g.* clay [9], rice husk carbon [10], peat [11], wood fly ash [12], nut carbon [13], seaweeds [14], fly ash [15], *etc*. The use of waste materials is currently gaining importance in pollution control and environmental remediation. Fly

ash is a waste generated during the combustion of coal for energy production. Fly ash is a mixture of oxides with unburned carbon, it is readily available and inexpensive. The use of fly ash in the manufacture of bricks and other construction activities has received major attention, likewise, the synthesis of zeolite with fly ash, extraction of metals from fly ash and the removal of toxic pollutants from wastewaters by treatment with fly ash. Thus, the use of fly ash as a low-cost adsorbent to remove copper ions from aqueous solutions has been described by Luo *et al.* [16]. It was described that the removal rate of copper ions reached a maximum of 99.60 % when the pH of the solution is 6. Similarly, fly ash has been used as adsorbent to remove dyes [13,17] and other toxic organic pollutants. Ayanda *et al.* [18] investigated the kinetics, equilibrium and thermodynamics of the adsorption of lead(II) ions onto fly ash. The adsorption process was reported to be endothermic and spontaneous and the maximum percentage removal of lead(II) ions achieved was around 98.94 % at pH = 7.

Reports on the adsorption of arsenic ions onto fly ash from aqueous solution are limited. Consequently, the study is aimed at the assessment of the adsorption of As(III) from aqueous solution by fly ash. Moreover, the study will comprise of the investigation of the kinetic and equilibrium studies of As(III) adsorption onto fly ash. The adsorption equilibrium was fitted by the Langmuir and Freundlich isotherms and the adsorption kinetic was explained by the pseudo-first order and pseudo-second order models.

EXPERIMENTAL

Stock solution of As(III) (1000 mg/L) was bought from Sigma Aldrich, USA. Fly ash was obtained from Matla power station, Mpumalanga, South Africa. HCl and NaOH were purchased from Merck. Deionized water was used for all analytical preparations. The concentration of As(III) before and after adsorption was determined by the inductively coupled plasma-optical emission spectroscopy (ICP-OES). The surface area, point of zero charge (pzc), elemental composition, X-ray diffraction (XRD) and scanning and transmission electron micrographs of fly ash have been reported elsewhere [19].

Adsorption experiment: The effect of contact time was performed at 20 °C in Erlenmeyer flasks containing 2.5602 g of fly ash and 25 mL of 100 mg/L As(III) aqueous solution. The flasks were stirred at contact time of 10 min to 120 min. The effect of initial As(III) concentration was performed by preparing 10-100 mg/L As(III) from the stock solution. 25 mL of each solution were poured in Erlenmeyer flasks and mixed for 60 min with 2.5602 g fly ash. This was conducted at 20 °C and pH 8. The effect of fly ash dosage was conducted at 20 °C. Different masses of fly ash (0.0489-2.5602 g) were thoroughly mixed with 25 mL As(III) solution on an orbital shaker (Orbita Shake Labotec) for 60 min. The effect of stirring speed was achieved at 20 °C in Erlenmeyer flasks containing 2.5602 g of fly ash and 25 mL of the 100 mg/L As(III) solution. The flasks were stirred at 120-200 rpm. The pH of the As(III) aqueous solution was maintained at desired value (pH 1.09-11) by the addition of 0.1 M NaOH and/or 0.1 M HCl solution. The aqueous solutions containing 2.5602 g of fly ash were shaken for 60 min. Lastly, the thermodynamic study was conducted at 293-

353 K. After each of the experiments, the reaction mixtures were filtered and the concentration of As(III) in the filtrate was analyzed by ICP-OES.

Adsorption capacity of fly ash: The amount of As(III) adsorbed (mg As per g fly ash) was determined according to eqn. 1.

$$q = \frac{(C_o - C_{aq}) \times V}{m} \tag{1}$$

where C_o and C_{eq} are As(III) concentration (mg/L) at time 0 and t, respectively. m is the mass of fly ash (g), V is the volume of the As(III) aqueous solution (mL) and q is the amount of As(III) uptake by the fly ash in mg/g.

Adsorption kinetic models: The linearized form of the pseudo-first and pseudo-second order kinetic models is given by eqns. 2 and 3, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_t} t \tag{3}$$

q_t and q_e are the adsorption capacities at time t (mg/g) and at equilibrium, respectively. k_{ad} (min⁻¹) in eqn. 2 is the pseudo-first order rate constant of the adsorption. $h = kq_e^2$ (mg/g/min) in eqn. 3 and k is the rate constant for pseudo-second order adsorption (g/mg/min). The plot that gave a straight line graph indicates the relevant model that best describe the kinetic of adsorption.

Adsorption isotherms: The linearized Langmuir and Freundlich isotherms used in this study are given by eqns. 4 and 5, respectively.

$$\frac{1}{q} = \frac{1}{q_m K_L} \frac{1}{C_{eq}} + \frac{1}{q_m} \tag{4}$$

$$\log q = \log K_F + \frac{1}{n} \log C \tag{5}$$

K_L in eqn. 4 is the Langmuir equilibrium constant and q_m is the maximum monolayer sorption capacity. In eqn. 5, q is the quantity of As(III) ions adsorbed per unit weight of the fly ash, C is the equilibrium concentration of As(III) ion and K_F is the adsorption capacity when As(III) equilibrium concentration equals to 1. n denotes the degree of dependence of adsorption on the As(III) equilibrium concentration.

Thermodynamic equations: The standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption were evaluated by the use of eqns. 6-8.

$$K_c = \frac{C_{Ae}}{C_e} \tag{6}$$

$$\Delta G° = -RT \ln K_c \tag{7}$$

$$\log K_c = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{8}$$

K_c is the equilibrium constant, C_{Ae} is the solid-phase concentration at equilibrium, C_e is the equilibrium concentration in solution, R is the gas constant (8.314 J/mol/K) and T is the temperature in Kelvin.

RESULTS AND DISCUSSION

Effect of contact time: Fig. 1 shows that as the contact time increases, there is enhancement in the adsorption of As(III) in both cases in percentage as well as amount adsorbed. This may be explained with the fact that the larger surface area of fly ash is made readily available with time for the adsorption of As(III) ions.
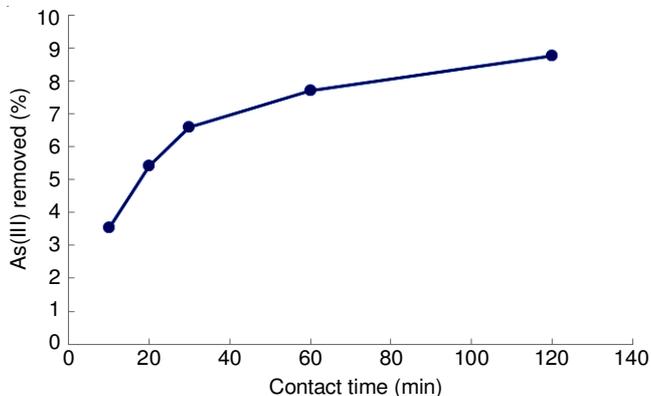

Fig. 1. Effect of contact time on the adsorption of As(III) ions onto fly ash

The plots of the pseudo-first order and pseudo-second order kinetic models are shown in Figs. 2 and 3. The R^2 value of the pseudo-first order kinetic model is low (0.7901), whereas, the pseudo-second order plot (Fig. 3) is linear with high R^2 value (0.9659). This suggests that As(III) adsorption onto fly ash followed the pseudo-second order kinetic model. Therefore, it could be affirmed that the adsorption of As(III) ions onto the fly ash surface is through chemical interaction. Table-1 presents the evaluated parameters of the kinetics models.
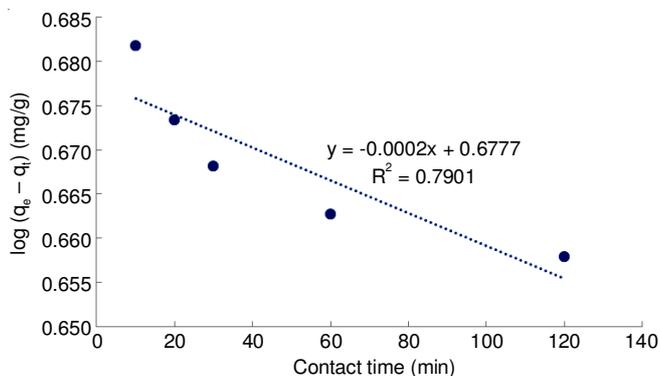

Fig. 2. Pseudo-first order reactions of As(III) ions adsorption onto fly ash
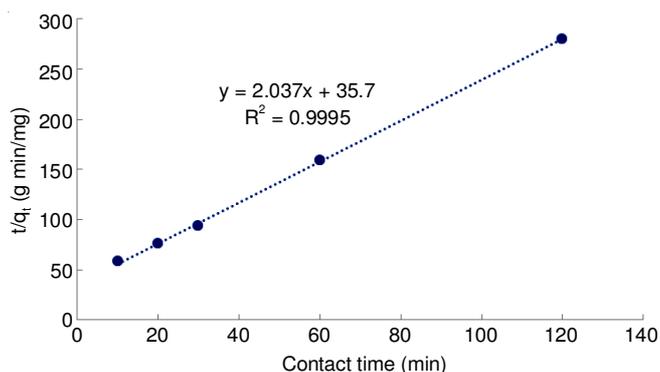

Fig. 3. Pseudo-second order reactions of As(III) ions adsorption onto fly ash

TABLE-1
KINETIC PARAMETERS

Pseudo-first order	Pseudo-second order
	k (g/mg/min) 0.12
k_{ad} (min^{-1}) 4.61 × 10^{-4}	q_e (mg/g) 0.49
q_e (mg/g) 4.76	h (mg/g/min) 0.028
R^2 0.7901	R^2 0.9659

Jeong [20] affirmed that the kinetic data obtained on the adsorption of arsenic onto Fe_2O_3 and Al_2O_3 oxides could be described by the pseudo-second order kinetic equation. Jeong [20] further explained that this model assumes that the rate limiting step is chemisorption. In chemisorption, the As(III) ions stick to the fly ash surfaces by forming a chemical bond commonly covalent.

Effect of initial As(III) concentration: The plot (Fig. 4) shows that the As(III) adsorption efficiency decreases with increasing As(III) concentration. Such occurrence could be explained with the fact that at higher As(III) concentration, the vacant sites of adsorption becomes fewer and hence the percentage removal of As(III) decreases.
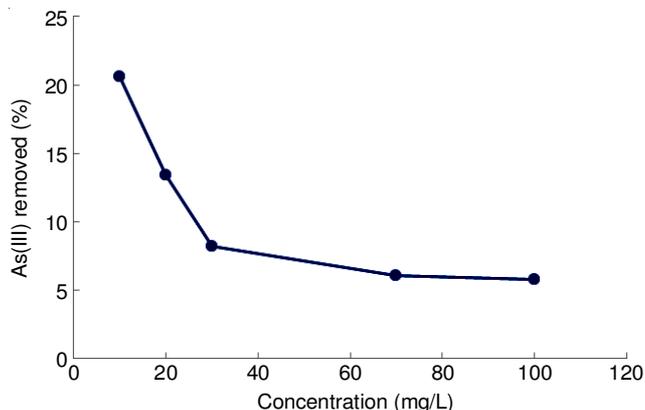

Fig. 4. Effect of initial concentration on As(III) ions adsorption onto fly ash

To estimate the equilibrium of adsorption, the Langmuir and Freundlich models were verified on the results obtained on the effect of initial As(III) concentration. Figs. 5 and 6 present the Langmuir and Freundlich plots, respectively, the two figures showed that R^2 value of the Langmuir isotherm (0.7560) is slightly lower than the Freundlich isotherm (0.8459). However, since R^2 value obtained for the two models is very close (*i.e.* apprrox. equal to 0.8), the adsorption of As(III) ions onto fly ash may be said to have satisfied both Langmuir and Freundlich isotherms. This finding is supported by Yao *et al.* [21] and Vaishya and Gupta [22]. Table-2 presents the calculated parameters obtained from the equilibrium models.

Effect of fly ash dosage: The results (Fig. 7) obtained showed that as the amount of fly ash was increased from 0.0489 to 2.5602 g, the amount of As(III) adsorbed and the percentage of As(III) ions removed was respectively improved from 2.8

TABLE-2
EQUILIBRIUM MODEL PARAMETERS

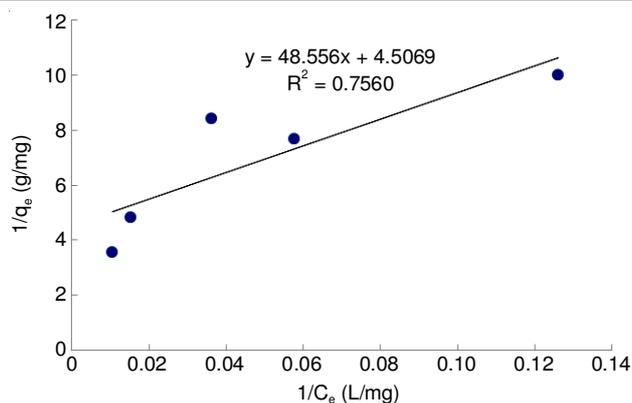| Langmuir isotherm	Freundlich isotherm
K_L (L/mg) 0.09	K_F (mg/g(L/mg)$^{1/n}$) 0.039
q_m (mg/g) 0.22	n (g/L) 2.48
R^2 0.7560	R^2 0.8459

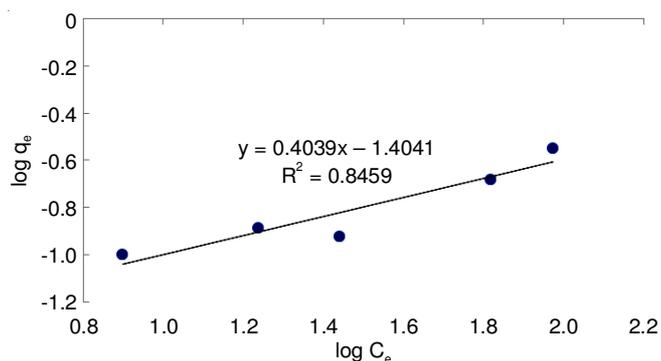Fig. 5. Langmuir isotherm for the adsorption on As(III) ions onto fly ash

Fig. 6. Freundlich isotherm of As(III) ions adsorption onto fly ash

to 29.4 %. The fly ash dosage positively affects the adsorption capacity; this is because as the fly ash dosage increases, more active sites become available for the As(III) ions and hence, the increase in the amount of As(III) adsorbed.
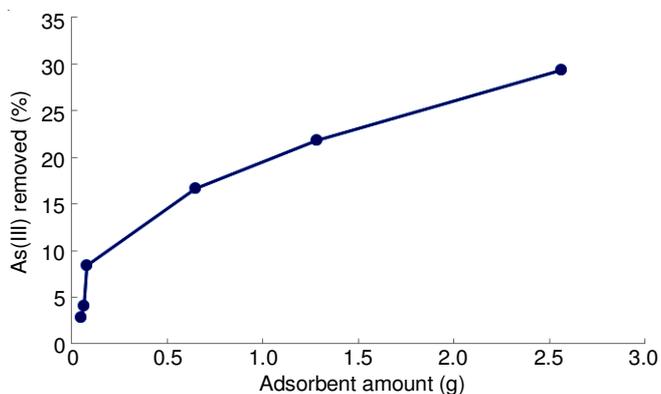

Fig. 7. Effect of fly ash dosage on the adsorption of As(III) ions

This is in support of the work by Yao *et al.* [21], Shugi *et al.* [23] and Yean *et al.* [24], they reported that the removal efficiency of arsenic onto oxides and composites increases with increasing adsorbent dosage.

Effect of stirring speed: Fig. 8 showed that the interaction between As(III) and fly ash was not effective at high speed. That is, there is a reduction in the amount of As(III) ions adsorbed with respect to speed. The As(III) ions may have fallen back into solution as the stirring speed increases from 120-200 rpm, thereby, bringing the amount of As(III) adsorbed down to about 9.3 from 21.7 %.
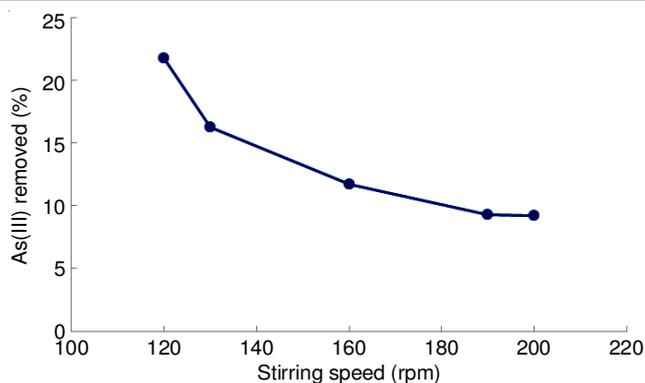

Fig. 8. Effect of stirring speed on As(III) ions adsorption onto fly ash

Effect of solution pH: The effect of pH on As(III) ions adsorption onto fly ash was evaluated at pH from 1.09 to 11. Fig. 9 demonstrates that the percentage of As(III) adsorbed gradually increased as the pH of the solution increased from 1.09 to 10 and was relatively constant afterwards. Approx. 52.5 % of As(III) was adsorbed by fly ash from aqueous solution at a pH of 10, 60 min contact time and a stirring speed of 120 rpm.
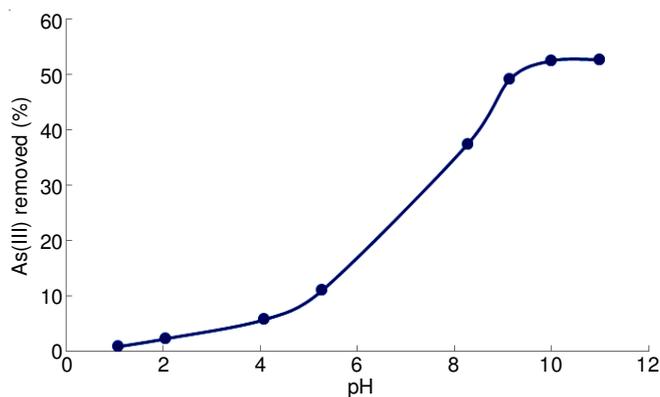

Fig. 9. Effect of pH on As(III) ions adsorption onto fly ash

The increase in the percentage removal of As(III) might be due to the decrease in the concentration of H^+ ions (as the solution becomes less acidic) which initially compete with As(III) ions for the surface of fly ash.

Thermodynamics: The temperatures used in the thermodynamic studies are 293, 326, 333 and 353 K. Fig. 10 showed that the percentage of As(III) ions removed by fly ash increases with temperature from 52.5 % at 293 K to 65.4 % at 353 K.
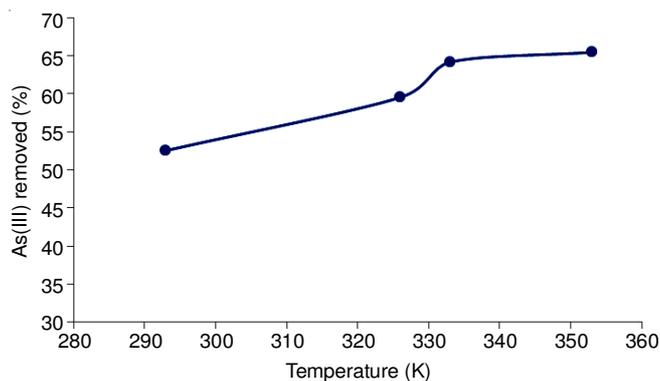

Fig. 10. Effect of temperature on As(III) ions adsorption onto fly ash

The plots of log K_c *versus* 1/T (K^{-1}) for the adsorption of As(III) ions onto fly ash is shown in Fig. 11, thus, the thermodynamic parameters are presented in Table-3. The increase in the rate of adsorption with increasing temperature, as well as, the kinetic plot showed that the adsorption process is endothermic [*i.e.* $\Delta H°$ is positive (+8.04 KJ/mol)]. Additionally, the negative values of $\Delta G°$ indicated that the adsorption process is spontaneous.
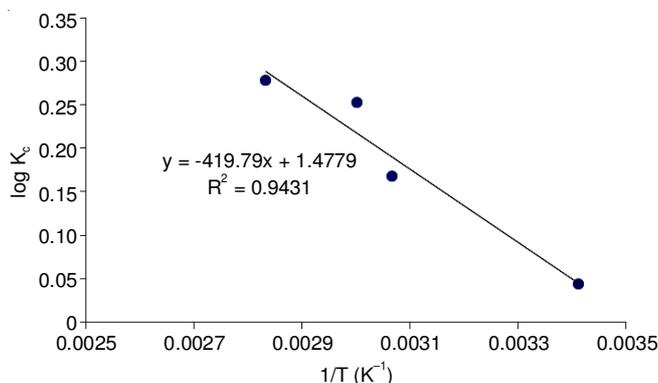

$$y = -419.79x + 1.4779$$
$$R^2 = 0.9431$$

Fig. 11. Plot of log K_c *versus* 1/T(K^{-1}) for the adsorption of As(III) ions onto fly ash

TABLE-3
THERMODYNAMIC PARAMETERS

Temp. (K)	$\Delta G°$ (J/mol)	$\Delta S°$ (J/K/mol)	$\Delta H°$ (KJ/mol)	K_c
293	-246.7			1.11
326	-1044.9	28.30	8.04	1.46
333	-1609.8			1.79
353	-1873.7			1.89

Conclusion

Arsenic is highly toxic even at low concentration. Its toxicity increases with accumulation and bioavailability in water, wastewater and soils, hence, remediation of arsenic contaminated system is a worldwide priority. The process of the adsorption of As(III) ions onto fly ash is a function of contact time, initial As(III) concentration, fly ash dosage, stirring speed and solution pH. The pseudo-second order kinetic precisely described As(III) ion adsorption onto fly ash which suggested that As(III) ions were adsorbed onto the surface of fly ash particles through a chemical interaction. The equilibrium study could best be described by the Langmuir and Freundlich isotherms. The results of this study show that 2.56 g of fly ash was able to remove up to 65.4 % of As(III) from 25 mL of 100 mg/L As(III) solution at a pH of 10, 60min contact time, temperature of 353 K and a stirring speed of 120 rpm. Therefore, fly ash showed good potential for the removal As(III) and could be used for the remediation of water and wastewater contaminated with arsenic.

REFERENCES

1. M. Mosaferi, S. Nemati, A. Khataee, S. Nasseri and A.A. Hashemi, *J. Environ. Health Sci. Eng.*, **12**, 74 (2014); https://doi.org/10.1186/2052-336X-12-74.
2. S. Luther, N. Borgfeld, J. Kim and J.P. Parsons, *Microchem. J.*, **101**, 30 (2012); https://doi.org/10.1016/j.microc.2011.10.001.
3. M.H. Kalavathy, T. Karthikeyan, S. Rajgopal and L.R. Miranda, *J. Colloid Interf. Sci.*, **292**, 354 (2005); https://doi.org/10.1016/j.jcis.2005.05.087.
4. L. Zeng, *Water Qual. Res. J. Canada*, **39**, 267 (2004).
5. K.B. Payne and T.M. Abdel-Fattah, *J. Environ. Sci. Health*, **40**, 723 (2005); https://doi.org/10.1081/ESE-200048254.
6. G. Liu and H. Zhang, The Adsorption of Arsenic on Magnetic Iron-Manganese Oxide in Aqueous Medium, Proceedings of the International Multi-Conference of Engineers and Computer Scientists 2008, vol II, IMECS 2008, Hong Kong (2008).
7. S. Ananta, B. Saumen and V. Vijay, *Int. Res. J. Environ. Sci.*, **4**, 64 (2015).
8. S.C. Chang, Y.H. Yu, C.H. Li, C.C. Wu and H.Y. Lei, *Int. J. Environ. Res. Public Health*, **9**, 3711 (2012); https://doi.org/10.3390/ijerph9103711.
9. K.O. Adebowale, I.E. Unuabonah and B.I. Olu-Owolabi, *Appl. Clay Sci.*, **29**, 145 (2005); https://doi.org/10.1016/j.clay.2004.10.003.
10. Y. Sarita, D.K. Tyagi and O.P. Yadav, *Int. J. Chemtech Res.*, **2**, 59 (2011).
11. Y.S. Ho and G. McKay, *Adsorpt. Sci. Technol.*, **20**, 797 (2002); https://doi.org/10.1260/026361702321104282.
12. S. Laohaprapanon, M. Marques and W. Hogland, *Clean Soil Air Water*, **38**, 1055 (2010); https://doi.org/10.1002/clen.201000105.
13. O.S. Ayanda, O. Adeyi, B. Durojaiye and O. Olafisoye, *Pol. J. Environ. Stud.*, **21**, 1147 (2012).
14. S. Basha and Z.V.P. Murthy, *Process Biochem.*, **42**, 1521 (2007); https://doi.org/10.1016/j.procbio.2007.08.004.
15. S.A. Olushola, S.F. Olalekan, A.A. Folahan, F.P. Leslie and B.J. Ximba, *Water S.A.*, **40**, 659 (2014); https://doi.org/10.4314/wsa.v40i4.11.
16. J. Luo, H. Shen, H. Markström, Z. Wang and Q. Niu, *J. Miner. Mater. Charact. Eng.*, **10**, 561 (2011); https://doi.org/10.4236/jmmce.2011.106043.
17. Z. Eren and F.N. Acar, *J. Hazard. Mater.*, **143**, 226 (2007); https://doi.org/10.1016/j.jhazmat.2006.09.017.
18. O.S. Ayanda, C.O. Akintayo, N.L. Mthembu, F.C.A. Emmanuel and B.J. Ximba, *Res. J. Chem. Environ.*, **20**, 44 (2016).
19. O.S. Ayanda, O.S. Fatoki, F.A. Adekola and B.J. Ximba, *E-J. Chem.*, **9**, 1788 (2012); https://doi.org/10.1155/2012/451801.
20. Y. Jeong, The Adsorption of Arsenic (V) by Iron (Fe_2O_3) and Aluminum (Al_2O_3) Oxides, Retrospective Theses and Dissertations, Iowa State University, Paper 1743, p. 1 (2005).
21. S. Yao, Z. Liu and Z. Shi, *J. Environ. Health Sci. Eng.*, **12**, 58 (2014); https://doi.org/10.1186/2052-336X-12-58.
22. R.C. Vaishya and S.K. Gupta, *J. Chem. Technol. Biotechnol.*, **78**, 73 (2003); https://doi.org/10.1002/jctb.745.
23. K. Shugi, T.S. Singh and K.K. Pant, *Indian J. Environ. Health*, **45**, 151 (2003).
24. S. Yean, L. Cong, A. Kan, V. Colvin and M. Tomson, Sorption/Desorption of Arsenic to Magnetite Nanoparticles, 229th ACS National Meeting, San Diego, CA, United States (2005).