REMOVAL OF ARSENIC AND LEAD TOXIC METALS BY KYAUK PATAUNG KAOLIN AND CHARACTERIZATION OF ARSENIC AND LEAD LOADED KAOLIN

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Abstract

This research work is focused on the determination of optimum conditions for the removal of arsenic and lead toxic elements in model solutions by using Kyauk Pataung (KPT) kaolin sample. In this research, removal of arsenic and lead ions from the model solutions using KPT kaolin was studied by the effect of contact time (0.5-24 h), effect of dosage (0.5- 3.5 g), effect of pH (4-9), metal concentration (50-800 ppm) at room temperature. The KPT kaolin sample was observed to remove 97.29 % of arsenic (100 ppm of initial concentration) using 2 g of KPT kaolin after 12 h contact time at pH 7, whereas 95.08 % of lead could be removed under the above conditions at pH 5. The amount of arsenic and lead remained in the solutions after treating with KPT kaolin were determined by using AAS technique. The arsenic and lead loaded kaolin sample were characterized by EDXRF, SEM and FT IR analyses.

Keywords: Removal of arsenic and lead, Kyauk Pataung Kaolin

Introduction

The problem of removing pollutants from water is an important process and is becoming more important with the increasing of industrial activities (Yakun *et al*., 2014). Therefore, removal of heavy metals such as cadmium, lead, arsenic, mercury, chromium, iron, zinc and copper from aqueous solution is necessary because of the frequent appearance of these metals in waste streams from many industries (Missana and Garcia, 2007).

The heavy metals in the waste streams can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers (Ulmanu *et al*., 2003). Different techniques for the removal of metal ions from aqueous solutions have been developed as chemical precipitation, filtration, ion-exchange, reverse osmosis, membrane systems and etc. However, all these techniques have their inherent advantages and limitations in application. In the last few years, adsorption has been shown to be an alternative technique for removing dissolved metal ions from liquid wastes (Matta, 2015).

Heavy metals is the generic term for metallic elements having an atomic weight higher than 40.04. Heavy metals enter into the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease control agents applied to plants, air pollution fallout, and a number of others (Morais, 2012). The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human (Matta, 2015). Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration, it is well-known that chronic exposure to heavy metals and metalloids at relatively low levels can cause adverse effects (Castro and Mendez, 2008). While focusing on

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developing countries the conditions is getting more disastrous due to increase in industrial complex minimal follow up of environmental and pollution control guidelines.

The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment (Alloway, 2013). Neurotoxic effects of heavy metals are also well documented, especially for mercury and lead, with numerous reports of neurobehavioral changes after occupational exposure and of developmental effects in children with pre- or early postnatal exposure. However experimental studies suggest that arsenic could also interfere with the nervous system and that all three metals may influence the dopaminergic system in different ways (Pohl, 2003). There is, a need to clear which exposure levels are likely to cause these effects, and to what extent the three metals could interfere in mixed exposures (Alloway, 2013).

In solution, heavy metals can be present either as free-ions or complexes with organic and inorganic ligands (Alleoni *et al.*, 2003). In order to minimize processing costs, several investigations have focused on the use of low cost adsorbents, e.g. agricultural by-products (Samantaroy *et al.*, 1997), biosorbents (Pino *et al.*, 2005), slag and clay materials.

The process of adsorption has become one of the preferred methods for the removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and simple. Adsorption has the additional advantages of applicability at very low concentrations, suitability for being used in batch and continuous processes. Adsorption has acquired global importance for the minimization of water and air contamination. Also, its significant addition to Green Chemistry endeavors (Irshad *et al.*, 2017).

Adsorbents, mainly clay minerals, are readily available, inexpensive materials and offer a cost-effective alternative to conventional treatment. Clay porous structure and high surface area provide benefits in the absorption of liquids and the adsorption of heavy metals.

Kaolin minerals include kaolinite, dickite, nacrite, and halloysite, respectively. Kaolinite ($Al_2Si_2O_5 (OH)_4$) is the most common kaolin mineral with the theoretical chemical composition: 46.54 % SiO_2, 39.50 % Al_2O_3, and 13.96 % H_2O. Kaolinite has 1:1 ratio of tetrahedral and octahedral layers continuous in the z- and x- axes directions, respectively, and stacked above each other in the y-direction. Kaolinite is one of the most important industrial clay minerals useful to man with a wide range of applications as raw material in ceramics, paper filling and coating, (Mefire *et al.* 2004) refractory, fiberglass, cement, rubber and plastics, cosmetics, paint, catalyst, pharmaceutic and agriculture (Ekosse, 2010) because of its relatively low cost and easy availability. Its application is a function of its physical and chemical characteristics in relation to requirements of the end user (Murray, 2007). The physical and chemical properties of kaolinite are strongly influenced by its structural order (Vaculikova *et al.* 2011).

The present study deals with the use of locally available kaolinite clay material as an adsorbent for the removal of arsenic and lead from solutions. The effect of various parameters affecting adsorption behavior as contact time, initial metal ion concentration, amount of adsorbent and pH of solution have been investigated and data on adsorption isotherms have been presented.

Materials and Methods

Collection and Preparation of Samples

The kaolinite sample was collected from Kyauk Pataung Township, Mandalay Region. After collection, the kaolinite sample was washed with tap water to remove impurities and then air-dried under shade to prevent some reaction of sunlight. Then the kaolinite was ground to fine particles and sieved into 90 μm aperture size and stored in air tight plastic bag so that the sample was free from getting molds to prevent moisture, as well as other contaminations and was ready to be used for the experimental works.

Preparation of the Adsorptive Compounds

Deionized water was used through the experiment. Stock solutions (1000 mg/L) of lead(II) nitrate solution and arsenic(III) oxide (As_2O_3) solution were prepared in deionized water. The stock solutions were diluted as required to obtain standard solutions.

Adsorption Method

Adsorption measurements were made by a batch technique at room temperature. The batch mode was selected because of its simplicity and reliability. In all experiments, the required volume (50 mL) of the adsorptive compound solution was added to kaolin absorbent at room temperature. The solutions were then shaken vigorously for a given time period to reach equilibrium. After completion of a selected shaking time, the suspensions were then filtered. The amount adsorbed was determined by analyzing the metal content before and after each experiment using Atomic Absorption Spectrometer (AAS).

Determination of Arsenic(III) Ions Sorption Capacity onto the Kyauk Pataung Kaolin

The arsenic sorption capacities of Kyauk Pataung Kaolin (KPT kaolin) sample were studied at various contact times (0.5, 1, 2, 3, 5, 7, 9, 12, 15, 18, 20, 22 and 24 h). The effect of dosage of KPT Kaolin samples (0.5 g -3.5 g) on sorption of arsenic ion was studied at initial pH. The arsenic sorption efficiencies of KPT Kaolin sample was studied at various pH (4-8). The arsenic sorption capacity of KPT Kaolin sample was studied at various concentrations of model solutions   (50-500 ppm).

Determination of Lead(II) Ions Sorption Capacity onto the Kyauk Pataung Kaolin

The Pb(II) sorption capacity of KPT Kaolin sample was studied at various contact times (0.5, 1, 2, 3, 5, 7, 9, 12, 15, 18, 20, 22 and 24 h). The effect of dosage of KPT Kaolin samples (0.5 g -3.5 g) on sorption of Pb(II) ion was studied at initial pH. The Pb(II) sorption efficiencies of Kyauk Pataung Kaolin sample was studied at various pH (4-9). The Pb(II) sorption capacity of KPT Kaolin sample was studied at various concentrations of model solutions (50-900 ppm).

Elemental Analysis of the Samples by EDXRF Method

Elemental compositions in Kyauk Pataung Kaolin sample and metal loaded KPT kaolin sample were determined by EDXRF using EDX-720 spectrometer (Shimadzu Co. Ltd., Japan) at West Yangon University, Yangon.

Scanning Electron Microscopy (SEM) Analysis of the Samples

The surface morphology of the KPT Kaolin and metal loaded KPT kaolin samples were observed by using SEM technique on JSM 5610 LV scanning electron microscope, JEOL-Ltd., Japan.

FT IR Analysis of the Samples

Fourier Transform Infrared (FT IR) spectra of KPT Kaolin sample and the metal loaded KPT Kaolin sample were recorded in a range of wave number from 4300 to 400 cm^{-1} on a FT IR spectrometer (FT IR-8400 SHIMADZU, Japan) at Department of Chemistry, Yangon University.

Results and Discussion

The arsenic and lead from the respective model solution: lead(II) nitrate model solution and arsenic(III) solution were removed by using KPT kaolin sample, collected from the Kyauk Pataung Township, Mandalay Region. The removal percent of the metals (metal sorption capacities) were studied at different contact times, at different dosages of the adsorbent, at different pH of the solution and at different concentrations of the adsorptive compounds.
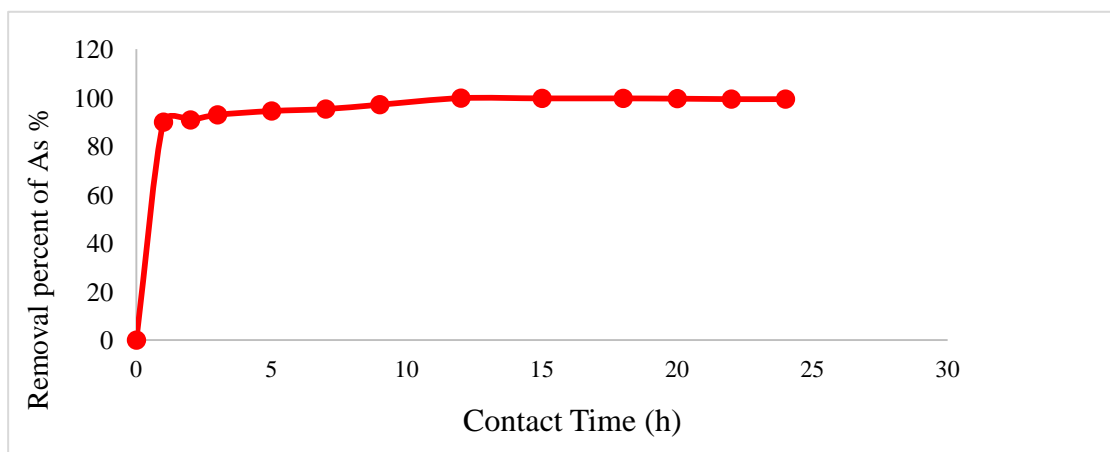
Effect of Contact Time on the Removal Percent of Arsenic by Kyauk Pataung Kaolin

The effect of contact time on removal percent of arsenic by Kyauk Pataung Kaolin is shown in Table 1 and Figure 1. The arsenic sorption capacity of Kyauk Pataung Kaolin sample was studied at various contact times (0.5- 24 h). Adsorption of arsenic by KPT Kaolin was very fast at the initial state and adsorbed arsenic ion is slowly released into the solution. After 24 h, the adsorption process reached equilibrium and optimum contact time was selected at 12 h with the maximum removal percent of arsenic (99.8 %).

Table 1 Effect of Contact Time on the Removal Percent of Arsenic by Kyauk Pataung Kaolin

No.	Contact time (h)	Equilibrium concentration of arsenic (ppm)	Removal % of As
1	1.0	10.1	89.9
2	2.0	9.2	90.8
3	3.0	7.1	92.9
4	5.0	5.5	94.5
5	7.0	4.7	95.3
6	9.0	2.9	97.1
7	12.0	0.2	99.8
8	15.0	0.3	99.7
9	18.0	0.3	99.7
10	20.0	0.4	99.6
11	22.0	0.6	99.4
12	24.0	0.6	99.4

Initial pH = 6.8, Dosage = 2 g, Initial concentration of Arsenic = 100 ppm

*Initial pH = 6.8, Dosage = 2 g, Initial concentration of Arsenic = 100 ppm

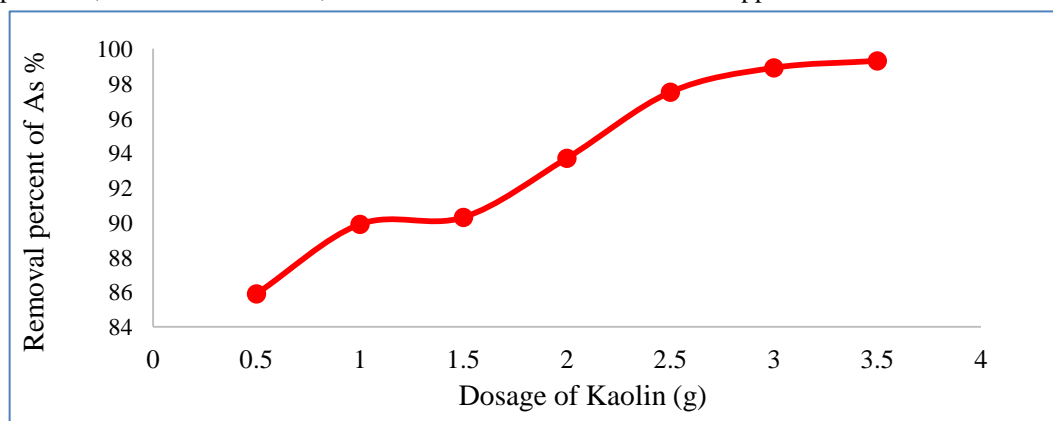**Figure 1**   Removal percent of arsenic as a function of contact time

Effect of Dosage on the Removal Percent of Arsenic by Kyauk Pataung Kaolin

The effect of dosage on removal percent of arsenic by Kyauk Pataung kaolin was shown in Table 2 and Figure 2. The effect of dosage of KPT Kaolin samples (0.5 g -3.5 g) on sorption of arsenic ion was studied at initial pH. It was found that the percent arsenic ion adsorption efficiency increased with increasing dosage of Kaolin samples and optimum dosage of kaolin sample was 2 g with the maximum removal percent of arsenic (93.7 %).

Table 2   Effect of Dosage on the Removal Percent of Arsenic by Kyauk Pataung kaolin

No.	Dosage (g)	Equilibrium concentration of As (ppm)	Removal (%) of As
1	0.5	14.1	85.9
2	1.0	10.1	89.9
3	1.5	9.7	90.3
4	2.0	6.3	93.7
5	2.5	2.5	97.5
6	3.0	2.1	98.9
7	3.5	0.7	99.3

Initial pH = 6.8, Contact time = 12 h, Initial concentration of Arsenic = 100 ppm

*Initial pH = 6.8, Contact time = 12 h, Initial concentration of Arsenic = 100 ppm

Figure 2 Removal percent of arsenic as a function of dosage of KPT kaolin
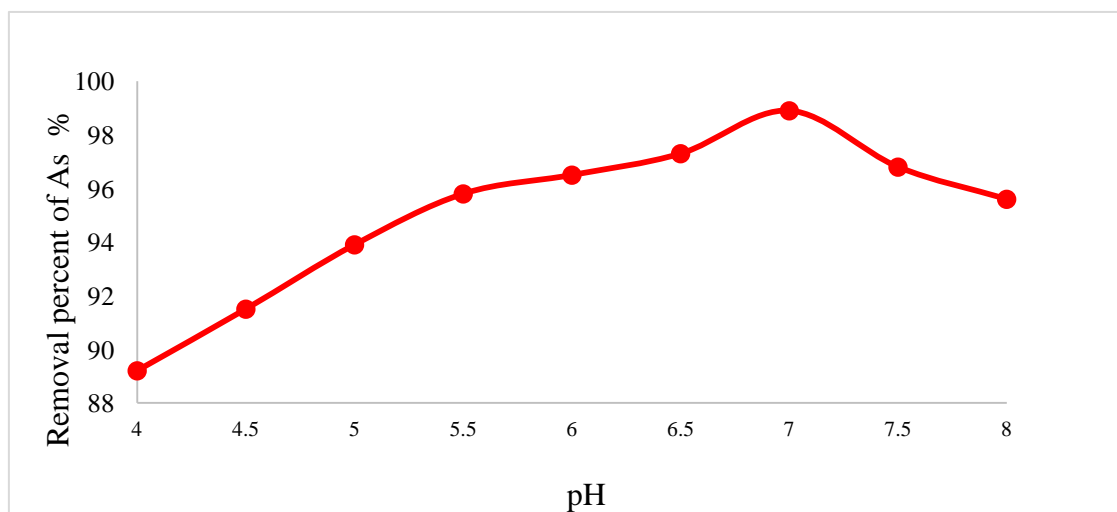
Effect of pH on the Removal Percent of Arsenic by Kyauk Pataung Kaolin

       The effect of pH on Removal Percent of Arsenic by Kyauk Pataung Kaolin was shown in Table 3 and Figure 3. The arsenic sorption efficiencies of Kyauk Pataung Kaolin sample was studied at various pH (4-8). The pH of the solutions were adjusted by using HNO_3 solution. At pH values of greater than 7, the sorption capacity was slowly decreased and the removal percent of arsenic ion was selected at optimum pH 7 with the maximum removal percent of arsenic (98.9 %).

Table 3 Effect of pH on the Removal Percent of Arsenic by Kyauk Pataung Kaolin

No.	pH	Equilibrium Concentration of Arsenic (ppm)	Removal % of As
1	4.0	10.8	89.2
2	4.5	8.5	91.5
3	5.0	6.1	93.9
4	5.5	4.2	95.8
5	6.0	3.5	96.5
6	6.5	2.7	97.3
7	7.0	1.1	98.9
8	7.5	3.2	96.8
9	8.0	4.4	95.6

Dosage = 2 g, Contact time = 12 h, Initial concentration of Arsenic = 100 ppm

*Dosage = 2 g, Contact time = 12 h, Initial concentration of Arsenic = 100 ppm

Figure 3   Removal percent of arsenic as a function of pH

Effect of Concentration on the Removal Percent of Arsenic by Kyauk Pataung Kaolin
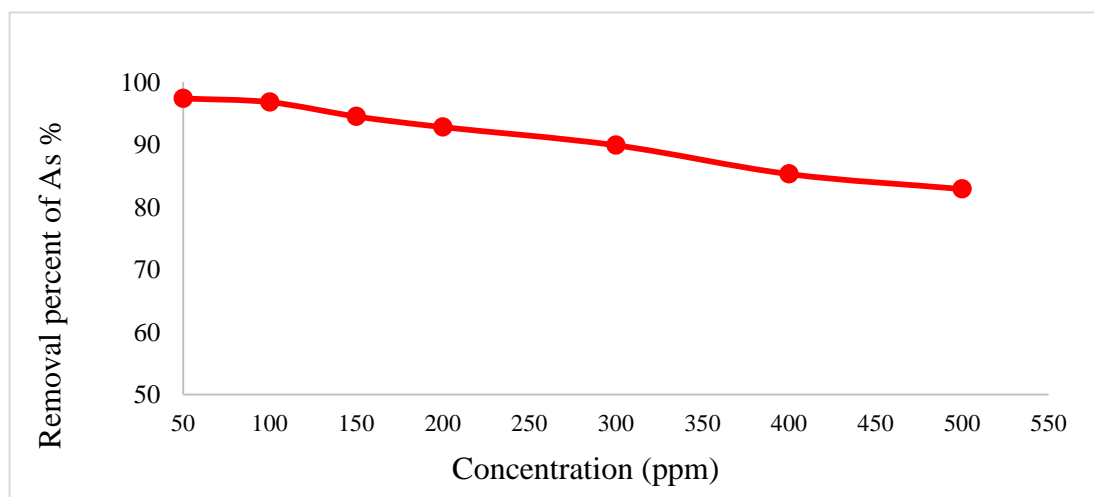
       The effect of concentration on removal percent of arsenic by Kyauk Pataung Kaolin was shown in Table 4 and Figure 4. The arsenic ion sorption capacities of Kyauk Pataung Kaolin sample was studied at various concentrations of model solutions (50-500 ppm). The sorption efficiency become decrease as the concentration of metal ions increase and the sorption site

decrease and the optimum metal concentration was selected at 100 ppm the maximum removal percent of arsenic (96.79 %).

Table 4 Effect of Concentration on the Removal Percent of Arsenic by Kyauk Pataung K

No.	Initial Concentration of As (ppm)	Equilibrium Concentration of As (ppm)	Removal % of As
1	50	1.31	97.38
2	100	3.21	96.79
3	150	8.25	94.50
4	200	14.4	92.80
5	300	30.3	89.90
6	400	58.8	85.30
7	500	85.5	82.90

Dosage = 2 g, Contact time = 12 h, Initial pH = 6.8

*Dosage = 2 g, Contact time = 12 h, Initial pH = 6.8

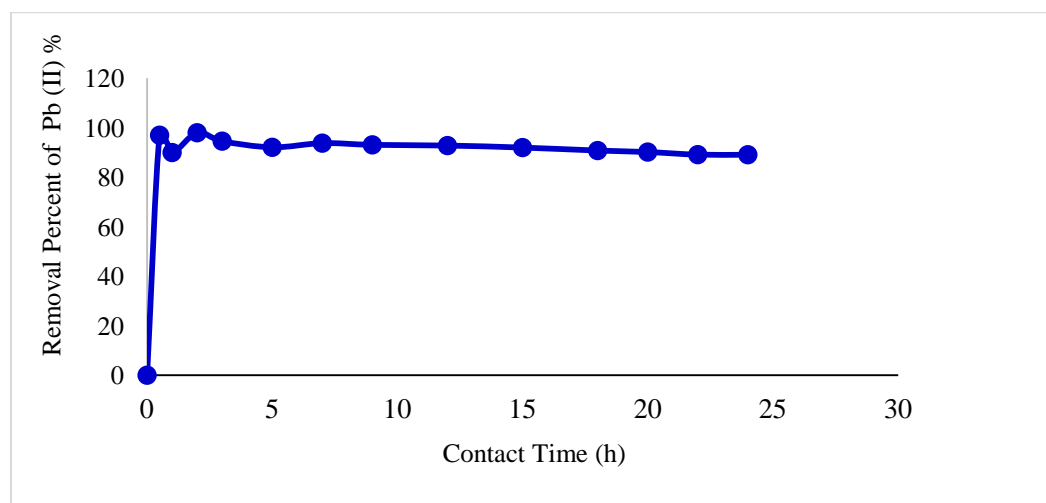**Figure 4**   Removal percent of arsenic as a function of concentration

Effect of Contact Time on the Removal Percent of Lead by Kyauk Pataung Kaolin

The effect of contact time on removal percent of lead by Kyauk Pataung Kaolin was shown in Table 5 and Figure 5. The Pb(II) sorption capacities of Kyauk Pataung Kaolin sample was studied at various contact times (0.5- 24h). Adsorption of Pb(II) by KPT Kaolin was very fast at the initial state and adsorbed Pb(II) ion is slowly released into the solution. After 24 h, the adsorption process reached equilibrium and optimum contact time was selected at 12 h with the maximum removal percent of lead (92.72 %).

Table 5 Effect of Contact Time on the Removal Percent of Lead by Kyauk Pataung Kaolin

No.	Contact time (h)	Equilibrium Concentration of Pb (ppm)	Removal % of Pb
1	0.5	3.80	96.90
2	1.0	10.10	89.90
3	2.0	2.10	97.90
4	3.0	5.50	94.50
5	5.0	7.99	92.01
6	7.0	6.30	93.70
7	9.0	6.99	93.01
8	12.0	7.28	92.72
9	15.0	8.09	91.91
10	18.0	9.30	90.70
11	20.0	9.90	90.10
12	22.0	10.95	89.05
13	24.0	10.98	89.02

Initial pH = 5.9, Dosage = 2 g, Initial concentration of Pb = 100 ppm

*Initial pH = 5.9, Dosage = 2 g, Initial concentration of Pb = 100 ppm

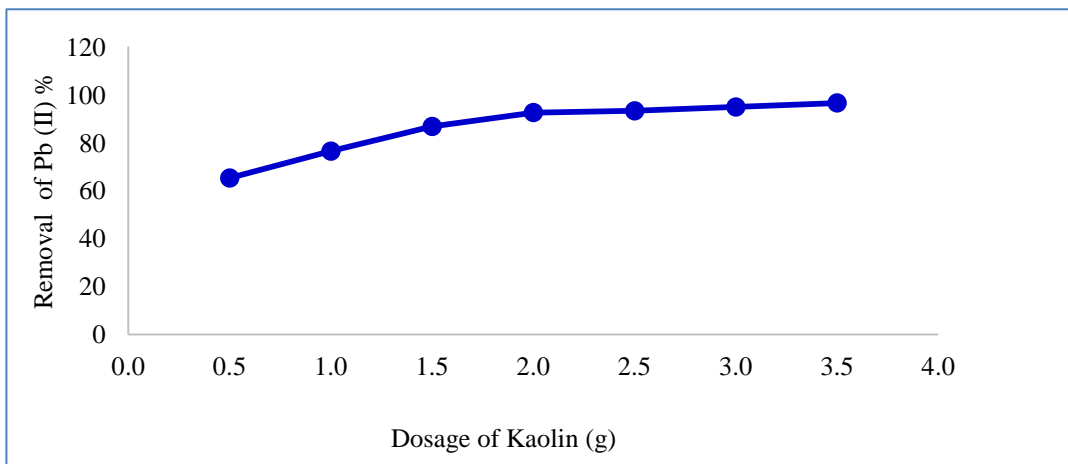**Figure 5**   Removal percent of lead as a function of contact time

Effect of Dosage on the Removal Percent of Lead by Kyauk Pataung Kaolin

The effect of dosage on removal percent of lead by Kyauk Pataung Kaolin was shown in Table 6 and Figure 6.The effect of dosage of KPT Kaolin samples (0.5 g -3.5 g) on sorption of Pb(II) ion was studied at initial pH. It was found that the percent Pb(II) ion adsorption efficiency increased with increasing dosage of Kaolin samples and optimum dosage of KPT kaolin was selected was 2 g with the maximum removal percent of lead (92.5 %).

Table 6   Effect of Dosage on the Removal Percent of Lead by Kyauk Pataung Kaolin

No.	Dosage (g)	Equilibrium concentration of Pb (ppm)	Removal (%) of Pb
1	0.5	34.8	65.2
2	1.0	23.6	76.4
3	1.5	13.3	86.7
4	2.0	8.5	92.5
5	2.5	7.3	93.2
6	3.0	5.2	94.8
7	3.5	4.5	96.5

Initial pH = 5.9, Contact time = 12 h, Initial concentration of Pb = 100 ppm

*Initial pH = 5.9, Contact time = 12 h, Initial concentration of Pb = 100 ppm

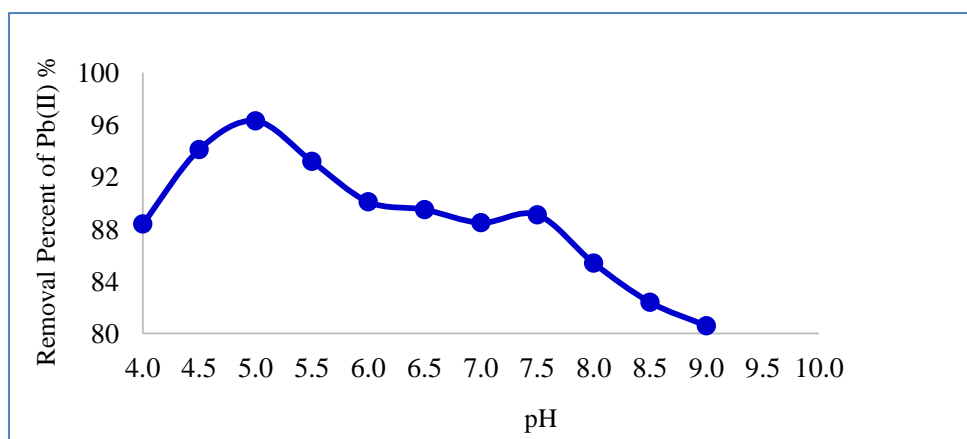**Figure 6**   Removal percent of lead as a function of dosage of KPT kaolin

Effect of pH on the Removal Percent of Lead by Kyauk Pataung Kaolin

The effect of pH on removal percent of lead by Kyauk Pataung Kaolin was shown in Table 7 and Figure 7. The Pb(II) sorption efficiencies of Kyauk Pataung Kaolin sample was studied at various pH (4-9). The pH of the solutions were adjusted by addition of HNO_3 solution At pH values of greater than 5, the sorption capacity was slowly decreased and the removal the removal percent of Pb(II) was at optimum pH 5 with the maximum removal percent of lead (96.3 %).

Table 7 Effect of pH on the Removal Percent of Lead by Kyauk Pataung Kaolin

No.	pH	Equilibrium Concentration of Pb (ppm)	Removal % of Pb
1	4.0	11.6	88.4
2	4.5	5.9	94.1
3	5.0	3.7	96.3
4	5.5	6.8	93.2
5	6.0	9.9	90.1
6	6.5	10.5	89.5
7	7.0	11.5	88.5
8	7.5	10.9	89.1
9	8.0	14.6	85.4
10	8.5	17.6	82.4
11	9.0	19.4	80.6

Dosage= 2 g, Contact time = 12 h, Initial concentration of Pb = 100 ppm

*Dosage= 2 g, Contact time = 12 h, Initial concentration of Pb = 100 ppm

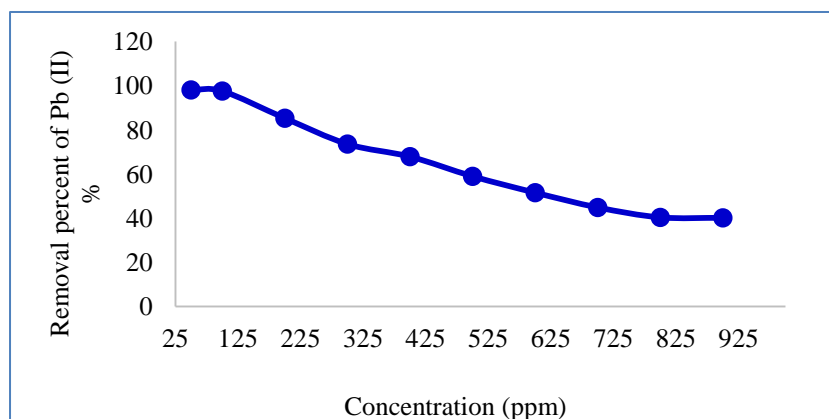**Figure 7**   Removal percent of lead as a function of pH

Effect of Concentration on the Removal Percent of Lead by Kyauk Pataung Kaolin

The effect of concentration on removal percent of lead by Kyauk Pataung Kaolin was shown in Table 8 and Figure 8. The Pb(II) sorption capacities of Kyauk Pataung Kaolin sample was studied at various concentrations of model solutions (50-900 ppm). The sorption efficiency become decrease as the concentration of metal ions increase and the sorption site decrease and the optimum metal concentration was selected at 100 ppm with the maximum removal percent of lead (98.0 %).

Table 8 Effect of Concentration on the Removal Percent of Lead by Kyauk Pataung Kaolin

No.	Concentration of Pb (ppm)	Equilibrium Concentration of Pb (ppm)	Removal % of Pb
1	50	2.0	98.0
2	100	2.5	97.5
3	200	29.6	85.2
4	300	78.6	73.8
5	400	128.8	67.8
6	500	205.5	58.9
7	600	291.0	51.5
8	700	386.4	44.8
9	800	477.6	40.3
10	900	539.1	40.1

Dosage= 2 g, Contact time = 12 h, Initial pH = 5.9

*Dosage= 2 g, Contact time = 12 h, Initial pH = 5.9

Figure 8   Removal percent of lead as a function of concentration

Adsorption of model solution of arsenic and lead by KPT Kaolin was very fast at the initial state and then adsorbed Arsenic and lead ions are slowly released into the solution. After 12 h the removal percent of arsenic and lead were nearly the same and reached the equilibrium. The contact time was selected at 12 h. The effect of dosage of KPT Kaolin samples (0.5 g -3.5 g) on sorption of arsenic and lead ions were studied at initial pH. It was found that the percent arsenic and lead adsorption efficiency increased with increasing dosage of Kaolin samples. The sorption efficiencies of arsenic was studied at various pH (4-8) and the sorption efficiencies of lead was studied at various pH (4-9). It was found that, the removal percent of arsenic at optimum pH 7 and the removal percent of lead was at optimum pH 5. The arsenic sorption capacity of Kyauk Pataung Kaolin sample was studied at various concentrations of model solutions (50-500 ppm) and the lead sorption capacity of Kyauk Pataung Kaolin sample was studied at various concentrations of model solutions (50-900 ppm). The sorption efficiency become decrease as the concentration of metal ions increase and the sorption site decrease.

EDXRF Analysis of the Kyauk Pataung Kaolin and Metal Loaded Kaolin Samples

Relative abundance of elements in kaolin samples were determined by EDXRF analysis. Figure 9 is the EDXRF spectra of KPT kaolin, lead loaded kaolin and arsenic loaded kaolin. Table 9 shows the relative abundance of elements present in kaolin samples. From EDXRF analysis,   Si was observed to be present in the highest amount (32-72 %) in kaolin samples followed by Fe (17-37 %) and Ti (7-8 %). The EDXRF spectra showed the presence of As (2.33 %) in arsenic loaded KPT kaolin and Pb (7.50 %) in lead loaded KPT kaolin.
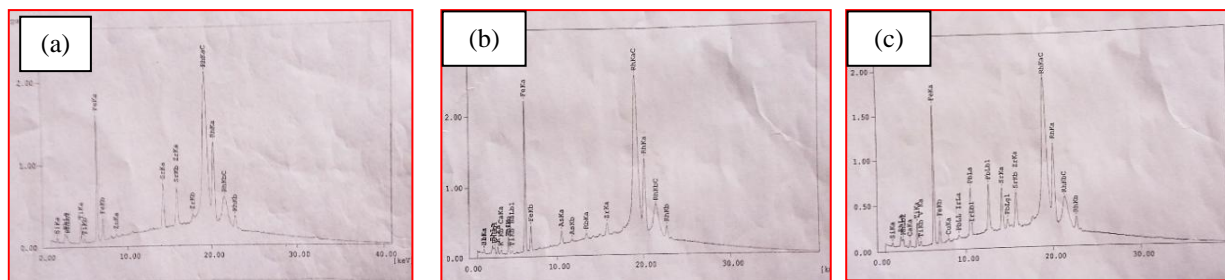
Figure 9   EDXRF spectra of (a) KPT kaolin (b) arsenic loaded kaolin (c) lead loaded kaolin

Table 9   Relative Abundance of Elements Present in KPT Kaolin, Arsenic Loaded Kaolin and Lead Loaded Kaolin

Element	Relative Abundance (%) of Elements		
	KPT Kaolin	Arsenic Loaded Kaolin	Lead Loaded Kaolin
Si	72.04	32.43	53.18
Fe	17.08	37.51	20.08
Ti	7.28	7.81	8.47
Pb	-	-	7.50
As	-	2.33	-
Sr	1.99	-	2.71
Zr	1.28	1.21	1.21

SEM Analysis of Kyauk Pataung Kaolin and Metal Loaded Kaolin Samples

Figure 10 is the SEM micrographs of Kyauk Pataung kaolin, lead loaded kaolin and arsenic loaded kaolin.The SEM micrographs of Kyauk Pataung Kaolin is formed by sheets and every sheet clinged closely to each other. Consequently, Kyauk Pataung kaolin has a large surface area and leads to adsorption of metal ions. After removal of arsenic and lead metal ions with Kayauk Pataung kaolin, arsenic and lead metal ions were adsorbed and filled onto the pores and surface of Kyauk Pataung kaolin and the surface of Kyauk Pataung kaolin was found as platelet shaped by adsorbed metal ions.
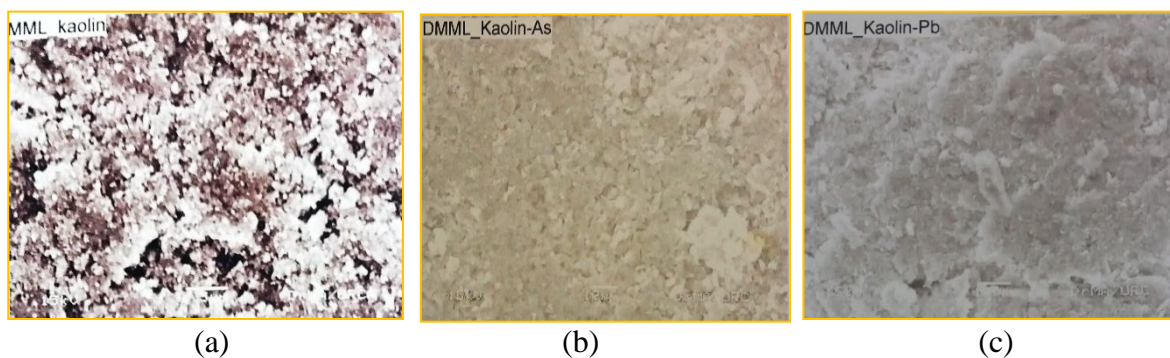

Figure 10 Scanning electron micrographs of (a) KPT kaolin (b) arsenic loaded kaolin (c) lead loaded kaolin

FT IR Analysis of Kyauk Pataung Kaolin and Metal Loaded Kaolin Samples

FT IR spectra of Kyauk Pataung kaolin, lead loaded kaolin and arsenic loaded kaolin are shown in Figure 11. In IR-spectra of all samples OH-stretching modes lie in the spectral region of 3619-3700 cm^{-1}. Si-O stretching modes are found in the 1004- 1028 cm^{-1} range. O-H deformation of inner hydroxyl modes occur in the 908-912 cm^{-1} region. OH deformation linked to metal modes are found in the 684-789 cm^{-1} range (Paul and Daniel, 2013).

(a)   (b)   (c)
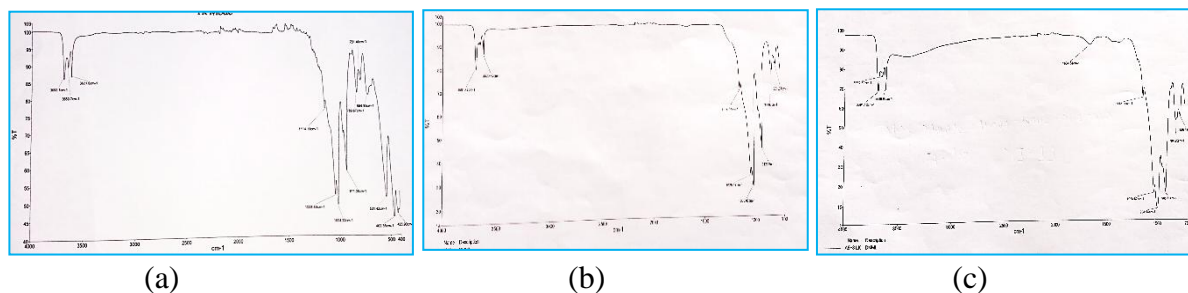
Figure 11 FTIR spectra of (a) KPT kaolin (b) arsenic loaded kaolin (c) lead loaded kaolin

Conclusion

KPT Kaolin sample was found to remove 97.29 % of arsenic and 95.08 % of lead under the optimum conditions of dosage 2 g, pH 5-7, contact time 12 h and initial concentration of 100 ppm. The KPT kaolin, arsenic loaded kaolin and lead loaded kaolin were characterized by modern techniques such as EDXRF, SEM and FT IR analyses. The EDXRF spectra showed the presence of As in arsenic loaded KPT kaolin and Pb in lead loaded KPT kaolin. It confirmed that KPT kaolin could remove the arsenic and lead. The SEM micrographs of Kyauk Pataung Kaolin after removal of arsenic and lead showed that arsenic and lead were adsorbed onto the pores of Kaolin and the surface of KPT kaolin was found as platelet shaped. From the FT IR spectra of KPT kaolin, arsenic loaded KPT kaolin and lead loaded KPT kaolin were observed the corresponding functional groups. Therefore, Kyauk Pataung Kaolin can be used as effective adsorbent for the removal of heavy metals (arsenic and lead) from groundwater.

Acknowledgements

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