Lead sorption from aqueous solutions by kaolinite: laboratory experiments

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Abstract

The lead has adverse effects in contamination the aquatic environment, for this reason, a laboratory experiment was conducted using kaolinite collected from the Ga'ara Formation in western Iraq to be considered as a natural sorbent material that can be addressed lead (Pb^{2+}) from the aqueous environments. The Energy-Dispersive X-ray Spectroscopy and atomic absorption spectroscopy clarifying very fine grains and pure phase with a very little quantity of quartz and have a number of active sites for adsorption. The sorption of kaolinite for the Pb^{2+} has been carefully tested by several designed laboratory experiments. Five lead solutions of different concentrations (25, 50, 75, 100 and 125 ppm) were tested under different values of pH (1.3-9). The best sorption (94%) has been recorded at pH 9, with an equilibrium reaction time of 40 min of a solution with has initial concentration of 25 ppm Pb^{2+} and the solid-liquid ration of 1.25 gm:50 ml. The sorption reaction is endothermic with two main mechanisms were identified, the rapid ion exchange which gets at the beginning of the reaction during the first 10 m, and ion exchange, which gets slow later due to form ionic complexes

1. Introduction

The toxic heavy metals are pollutants of water, with a major concern for human health along with the environmental quality. They are commonly found dissolved in a different aqueous solution including drinking water causing dangerous for the environment [1]. Their concentrations in aquatic ecosystems, especially lead, cadmium, chromium, cobalt, nickel, vanadium, zinc, copper, iron and manganese have increased considerably as a result of inputs from human production and consumption activities. Consequently, it is necessary to find a method able to treat the environment. Lead (Pb) is one of the heavy metals that is known to be highly toxic even at low concentrations in water [2]. Different methods (ion exchange, chemical precipitation, filtration and reverse osmosis) for reducing heavy metal from the aqueous solution are well known [3]. Most of these methods are costly and sometimes complex and not efficient. The sorption (adsorption and absorption) method is a promising technique for the removal of heavy metals from aqueous solutions [4]. This method depends on cation exchange capacity (CEC) and adsorption can be used for the elimination of such pollutants. Clay minerals have a wide range of environmental applications due to the high CEC and high surface area [5]. Bentonite is a very good adsorbent material for lead ions from the aqueous solutions [6]. Kaolinite ($Al_2Si_2O_5(OH)_4$) is the most abundant mineral of the kaolinite group used as an important industrial raw material used extensively as additive and filler in the paper, plastics, rubber, pharmaceutical and polymer industry [7]. In this research, the sorption efficiency of kaolinite in the removal of potentially harmful lead ions from aqueous solutions was detail studied. The kaolinite used in this research is natural kaolinite collected from the Ga'ara Formation that was tested for absorbent efficiency with several aqueous solutions containing different concentrations of lead. The process of sorption (adsorption and absorption) is considered to be one of the best water treatment technologies around the world. Lead due to its toxic and hazardous nature is possibly the most widespread, so it is targeted in this research due to its abundance in natural systems following anthropogenic and natural inputs. This research has been built on a set of laboratory experiments aiming to discuss the sorption efficiency of kaolinite as a natural scavenger that can be used to reduce the lead content from the aqueous solutions in a further contribution for the environmental protection.

2. **Materials and Methods**

Sampling was carried out on kaolinite zone in the Ga'ara Formation, western Iraq, (Longitude 42° 28′ E Latitude 33° 31′ N), in which many kaolinite exposures have existed. A fresh kaolinite exposure was selected (Fig. 1). Enough quantity of kaolinite was collected for the laboratory experiments. Samples were prepared by drying, grinding, and weighing in the Laboratory of Geochemisrty, Department of Geology, College of Science, University of Baghdad. Kaolinite was dried in an electric oven at 60°C for 2h. Mineralogy of kaolinite was conducted at Geological Faulty, Warsaw University using the Energy-Dispersive X-Ray Spectroscopy (EDS). The laboratory experiments were designed and conducted using a batch procedure to investigate the sorption efficiency of kaolinite. Solutions with five concentrations (25, 50, 75, 100, and 125 ppm) of Pb^{2+} were prepared using a colorless standard solution of $Pb(NO_3)_2$. Distilled water was used for diluting solutions. The measurements of pH, TDS and EC have been done using a Hanna pH-meter with calibration solutions according to Perrin and Dempsey [8]. Filtration was used at the end of each experiment to separate kaolinite from the solution. The lead content (%) adsorbed by on kaolinite was determined from the difference between initial concentration (*Ci*) and final concentration (*Cf)* of lead in the aqueous solutions by using the following equation:

$$C \ (\%) \ of \ heavy \ metal = [(Ci - Cf)/ \ Ci]100 \qquad (1)$$

The effects of pH, initial concentration, ionic strength, time and solid-liquid ratio were studied to evaluate the kaolinite sorption capacity and lead ion behavior. Accuracy and precision were done and show that all chemical results are accepted according to [9], [10].

Figure 1. kaolinite deposits in the Ga'ara Formation used in this research.

3. **Kaolinite mineralogy and charge distribution**

The structure of kaolinite and mineralogy are presenting in Figs 2 and 3 respectively. Kaolinite has consisted of tetrahedral and octahedral layers. The tetrahedral layer contains a siloxane surface in which the main substitution is Al^{3+} for Si^{4+}; resulted in a negative charge [11]. The substitution of Mg^{2+} for Al^{3+} is common in the octahedral layer resulted in a negative charge [12]. The knowledge of the charge distribution on the kaolinite surface would be helpful in the adsorption process**.** The formula of kaolinite is $(Si_4) \ (Al_4) \ O_{10} \ (OH)_8$ indicates no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer, and no substitution of Al^{3+} with Mg^{2+}, Fe^{2+} in the octahedral layer, and Ca^{2+}, Na^+ and K^+ in the interlayer. The net charge of kaolinite is calculated based on Si^{4+}, Al^{3+}, O^{2-} and the OH^{-1} as shown below:

$= [4(+4)] + [4(+3)] + [10(-2)] + [8(-1)]$
$= 28 - 28$
$= 0$

Kaolinite has a heterogeneous surface charge able to adsorb and absorb certain ions from aqueous solutions and maybe retaining them in an exchangeable state [13]. The exchangeable cations occur mostly on the edges and on the basal (OH^-) surfaces of the kaolinite [14]. The permanent negative charge resulted from the replacement of Al^{3+} for Si^{4+} is insignificant. The Al^{3+} can substitute Si^{4+} in the tetrahedral layer resulting negative charge. Such this charge may participate to attract heavy metal ions like Pb^{2+} from contacted aqueous

solution. The charge distribution in each layer of kaolinite was calculated and presented in Table 1. The layers of tetrahedral and octahedral sheets charged will be balanced by interlayer cations such as Na^+, K^+ or may be Ca^{2+}. In each case, the interlayer can also contain water. A huge of tetrahedral and octahedral sheets connected together in kaolinite giving two types of planes Si, Al, Mg and O and OH group planes.
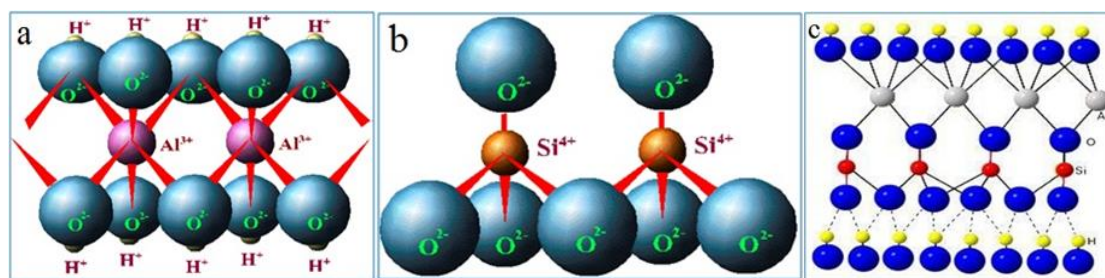

Figure 2. Kaolinite sheets and final structure. a: Tetrahedral sheet of kaolinite bound by shared oxygens; b: Octahedral

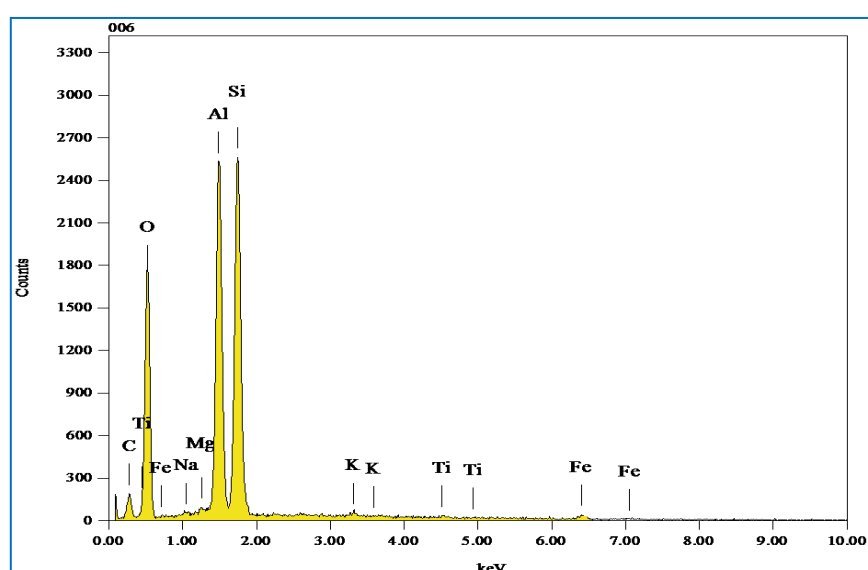sheet bound by shared oxygen atoms; c: Kaolinite structure.

Figure 3. EDS spectra show the spectra of kaolinite.

Table 1. Calculation the charge distribution in the kaolinite structure.

Oxides	%	M.W	Mol Equi	Cation Equi	Charge Equi	Valency Per 28 charge	Cation Per unit cell	Distribution in the lattice layer		Charge	
SiO$_2$	47.81	60	0.79	0.79	3.16	16.21	4.05	Tetrahedral	Si^{4+} 4.05		
Al$_2$O$_3$	35.11	102	0.34	0.68	2.04	10.46	3.48		Al^{3+} 3.95	8	Al^{3+} 3.95
Fe$_2$O$_3$	2.50	160	0.015	0.03	0.09	0.46	0.15	Octahedral	Al^{3+} 0.0		
MgO	0.02	40	0.0005	0.0005	0.001	0.005	0.003		Fe^{3+} 0.15		
CaO	2.21	56	0.039	0.039	0.078	0.4	0.3		Mg^{2+} 0.003	0.223	3.49
K$_2$O	0.31	71	0.004	0.008	0.008	0.04	0.04		Ti^{4+} 0.07		
Na$_2$O	0.75	62	0.012	0.024	0.024	0.12	0.12	Interlayer	Ca^{2+} 0.3		
TiO$_2$	1.13	79.7	0.014	0.014	0.056	0.29	0.07		K$^+$ 0.04		
LOI	10.3	---	---	---	---	---	---		Na$^+$ 0.12	0.46	
Total	100.14				5.457	28					

The releasing of H^+ and the adsorption of the Pb^{2+} could create an internal stress in the molecule. In addition to that replacing of H^+ instead of Pb^{2+} may be change the van der Waals forces in the kaolinite structure [15].

4. Results and discussion

4.1 pH value

The CEC of kaolinite is mainly depended on the pH value [14]. A higher pH value gives rise to more negative charges leading to a higher CEC value. The charge on the edges of kaolinite depends on the pH value of the solution due to the protonation/deprotonation of exposed hydroxyl groups, whereas the basal siloxane surfaces have a constant structural charge due to the isomorphous substitution of Si^{4+} by Al^{3+} [13].

This research shows that the hydroxyls on the exposed basal surfaces may be ionizable in aqueous solutions. Accordingly, the sorption efficiency of kaolinite was higher at high pH (alkali aqueous solutions). The pH value of the solution is one of the factors that clearly controls the adsorption property of the solution [16]. In the present study, pH was investigated through 4 experiments presented in Table 2. The pH value has been observed by varying the pH of the kaolinite slurry in a wide range (1.3 - 9). The response of kaolinite sorption is illustrated in Fig. 4, which clearly reveals that good kaolinite sorption was at pH 5, but the optimal sorption was at pH 9.

Table 2. Results of sorption efficiency of kaolinite for Pb at different pH.

No.	Before experiment							
	Time (min)	Weight mass (gm)	C_i (ppm)	Total vol. (ml)	pH	TDS (mg/l)	EC (µs/cm)	T (Cº)
Pb1	10	2.0	100	50	1.3	9500	16150	24
Pb2	10	2.0	100	50	5	9500	16150	24.1
Pb3	10	2.0	100	50	7	9500	16150	24.2
Pb4	10	2.0	100	50	9	9500	16150	24

No.	After experiment						
	pH	TDS (mg/l)	EC (µs/cm)	T (Cº)	C_f (ppm)	Sorption (ppm)	Sorption (%)
Pb1	1.19	5400	8750	23.9	82.75	17.25	17.25
Pb2	6.88	4800	7730	23.8	25.72	74.28	74.28
Pb3	6.86	5100	8240	23.8	29.3	70.7	70.7
Pb4	7.11	3930	6360	23.7	6.66	93.34	93.34

C_i: Initial Concentration. C_f: Final Concentration.

Many researchers, for example [17]–[19], have stated the maximum adsorption efficiency happens in the range pH 6-8; the decreasing negative charge density for lower adsorption efficiency above this pH [20], [21]. Before starting experiments, the TDS (9500 ppm) and EC (16150 µs/cm) for the initial solutions are constant, because all solutions have the same Pb concentrations (100 ppm) (Table 2); but after the experiment ended, TDS and EC were proportionally changed indicating good sorption has happened in pH 5, whilst pH 9 was most favorite and the best for removing heavy metal ions from aqueous solutions (Table 2).
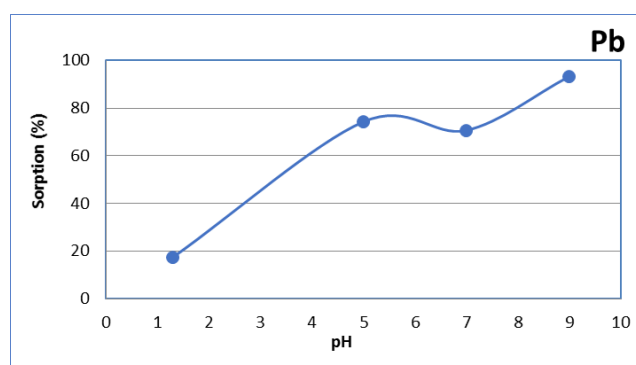

Figure 4. Response curve illustrating the pH affects the sorption of lead ions on kaolinite surfaces from a solution with a concentration of 100 ppm Pb^{2+}.

4.2 Initial ion concentration

Lead (Pb^{2+}) is controlled less by the cation exchange mechanism than most other heavy metals, meaning that adsorption of Pb^{2+} is highly influenced by pH [22]. The amount of adsorbed of Pb increases with pH ranges from 1 to 6 [23]. At high pH, The Pb has high sorption on the vacant site on kaolinite. The substitution of Pb^{2+} (atomic radii (a.r.) = 1.81A°), for H^{+} (a.r. = 0.79 A°) could produce stress in the kaolinite structure [15]. Laboratory experiments were conducted to investigate the influence of lead concentration on kaolinite sorption. For this reason, five initial solutions of Pb were prepared with concentrations of 25, 50, 75, 100 and 125 ppm. Then 50 ml of these solutions were separately treated with 1.25gm kaolinite for 40 min at the condition of pH 9. The temperature along with the necessary dataset of these experiments are listed in Table 3. Upon the experiment ended, the Pb^{2+}concentrations in the final solutions become 1.5, 4.4, 7.3, 44.6, 70.3 ppm respectively, with kaolinite sorption as 23.5, 45.6, 67.7, 55.4 and 54.7 ppm meaning 94, 91.2, 90.3, 55.4 and 43.8 % (Table 3).

Table 3. Results of kaolinite sorption efficiency in removal Pb ions from the aqueous solution with different initial concentration.

No.	Before experiment						After experiment				
	Time (min)	Weight mass (gm)	C_i (ppm)	Total vol. (ml)	pH	T (C°)	pH	T (C°)	C_f (ppm)	Sorption (ppm)	Sorption (%)
Pb-1	40	1.25	25	50	9	15.2	8.5	15.1	1.5	23.5	94
Pb-2	40	1.25	50	50	9	15.2	8.7	15.1	4.4	45.6	91.2
Pb-3	40	1.25	75	50	9	15.2	8.3	15.1	7.3	67.7	90.3
Pb-4	40	1.25	100	50	9	15.3	8.8	15.1	44.6	55.4	55.4
Pb-5	40	1.25	125	50	9	15.2	9.0	15.0	70.3	54.7	43.8

C_i: Initial Concentration. C_f: Final Concentration.

The maximal sorption was on the initial solution of 75 ppm. The rate of kaolinite sorption for each concentration is illustrated in Fig.5. The initial concentration and the percent of sorption were described by the relationship shown in Fig.6 which confirms that the best kaolinite sorption is with an initial solution of 75 ppm Pb^{2+}.
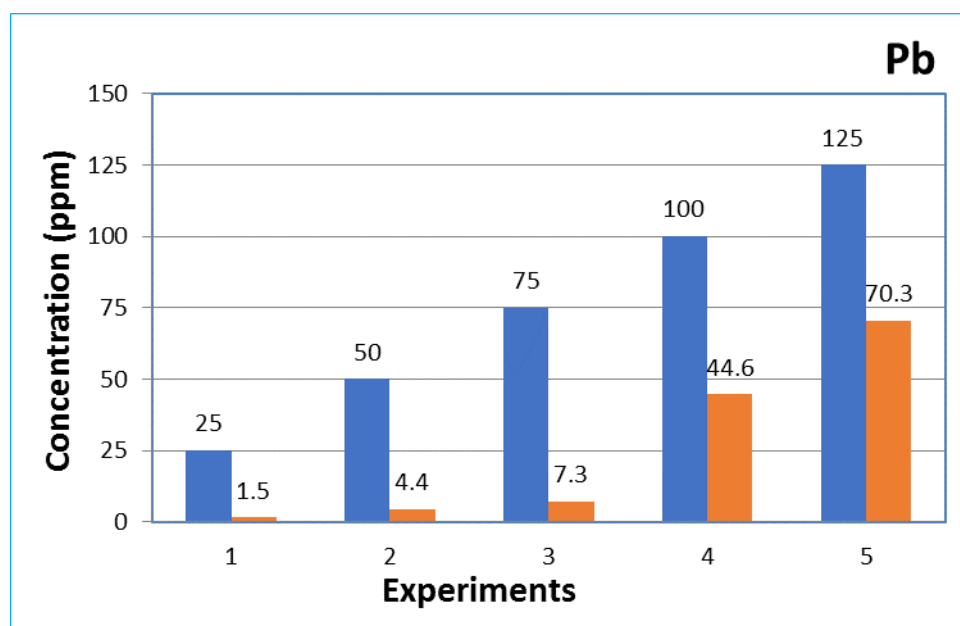

Figure 5. Lead ion concentrations before (blue column) and after experiment (red column) at pH 9, reaction time 40 min, solid-liquid ratio is 1.25 gm:50 ml.
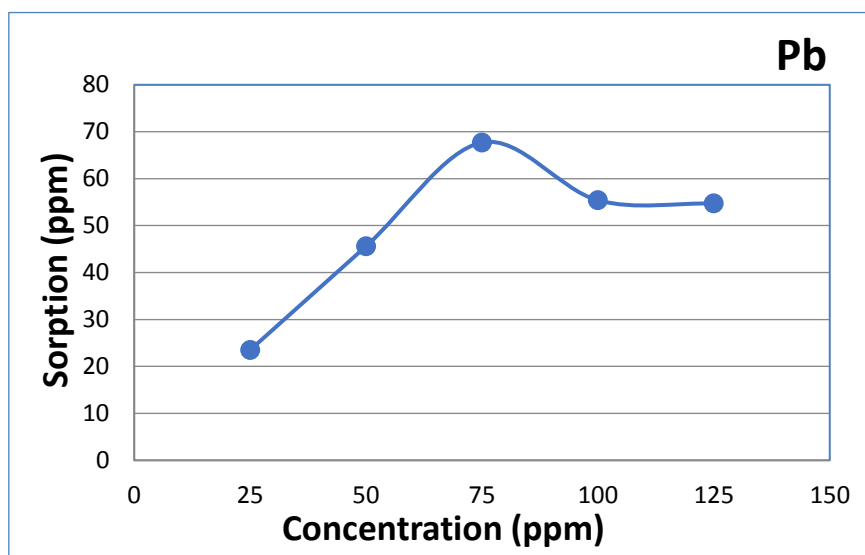
Figure 6. The response of kaolinte sorption (%) to the different Pb^{2+} concentrations.

All laboratory experiments indicate that the lead sorption on kaolinite was an endothermic reaction as temperature decreases after the experiment ended (Tables 3). Higher pH leads to a higher CEC value [24]. The removal efficiency of heavy metals by clay minerals decreases at lower pH values (pH< 4) and increases at pH values up to 4 [21], [25]. The experiments in this research have been accordingly designated on pH 9. The solid: liquid ratio was suggested by Yong et al [26].

as 1:10, but this research suggested a new ratio 1.25:50 due to the using of different lead concentration. The negative charge increases at the kaolinite surface due to the release of hydrogen ions from it after absorption of the lead ions. Adsorption onto kaolinite depends on the concentration of heavy metal ions in an aqueous solution [17]. The initial heavy metal concentration has been seen to have a considerable influence on the effect of increased contact time. When a higher initial metal concentration used a greater length of contact time is required to achieve complete sorption.

5. Conclusions and recommendations

The sorption characteristics of lead ions onto the kaolinite surface have been studied based on its adsorption ability as a function pH, solid-liquid ratio, and ion concentration and equilibrium reaction time. Several findings from this research can by drown here:

i.   Mineralogy has been shown that the kaolinite sheet structure provides a number of active sites for adsorption and therefore it has a good ability to remove heavy metals.

ii. It was found that the adsorption of lead ions onto kaolinite was strongly dependent on initial lead ion concentration in addition to pH values, where the sorption efficiency of led ions increases with pH till pH 9.

iii. The sorption efficiency of kaolinite in the removal of Pb ions was found to be influenced by pH,

initial concentration of heavy metal ions, contact time and solid-liquid ratio.

iv. Two major mechanisms control the kaolinite sorption, the initially rapid ion exchange phase happens for 10 minutes, and the slower inner-complex forming phase happens for 40 minutes.

v.   The H^+ ions are released from the kaolinite structure, yielding an increase of negative charge on the surface. This mechanism was detected to be happening, particularly at initial solutions of high concentrations.

vi. Peak sorption of Pb^{2+} was happened firstly at the beginning of the experiment due to strong attraction occurred by substitution, and later adsorption needs more time to complete due to repulse and may be complex molecules formation.

Depending on the results of the current research, we recommend using kaolinite in the purification the contaminated aquatic environments, especially water and industrial effluents.

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