

Adsorption Capacity of Haematite as Adsorbent for Lead and Arsenic from Aqueous Solutions

Dr. P. P. Vishwakarma

Associate Professor Chemistry, Sahu Jain College Najibabad, Distt: Bijnor 246763 (UP), India

Email ID: [drpremprakashvishwakarma06\[at\]gmail.com](mailto:drpremprakashvishwakarma06[at]gmail.com)

Abstract: *The present paper studied the feasibility of the adsorption capacity of Haematite for Pb (II) and As (III) from aqueous solutions. The effect of various operational parameters such as concentration, pH, temperature and contact time on the adsorption of Pb (II) and As (III) was investigated using batch adsorption experiments. It was found that Haematite can be used as a low cost adsorbent for the removal of heavy metals in aqueous solution containing low concentrations of the metals. The maximum ion adsorption capacities followed the trend Pb (II) > As (III) and the percentage adsorption was found to depend on the adsorbent dosage, solution pH, temperature and contact time. Kinetic treatment of the results gave a pseudo-second order type mechanism while the adsorption characteristics of the adsorbent followed the Freundlich adsorption isotherm.*

Keywords: Adsorption, Haematite, Adsorption capacity, Aqueous solutions, Freundlich adsorption isotherm

1. Introduction

Water pollution, contamination of streams, lakes, underground water, bays or oceans by substances harmful to living things as a result of increasing technological development and industrialization has been known to disrupt and destroy the fragile ecology through indiscriminate discharge of industrial and municipal wastes into the sea. The composition of industrial waste cannot be readily characterized by a typical range of values because its makeup depends on the type of manufacturing process involved. Sewage, industrial wastes and agricultural chemicals such as fertilizers and pesticides are the main causes of water pollution. The development of industries such as paint, coating, smelting and electric battery manufacturing, alloy preparation, wood preservation, plating, tanning, corrosion inhibition has resulted in heavy metals finding its way into natural bodies of water. These metals are potentially toxic [1] and [2].

In recent years, management of pollution caused by heavy metals has been a major problem especially in developing countries. The introduction of heavy metals into the body of water and subsequently the consumption of it by human and other living things lead to hazardous effects such as blood and brain disorders (especially in young children), nephropathy, colic-like abdominal pains and miscarriage, as in the case of lead [3]. The maximum permissible limit of Lead and Arsenic were 0.05 ppm and 0.01 mg/l respectively, reported in BIS and ISI standards. Arsenic is poisonous in doses significantly larger than 65 mg (1 gram) and the poisoning can arise from a single larger dose or from repeated small doses, as for example, inhalation of arsenical gases or dust. These metals are known to progressively accumulate in our ecosystem once they are introduced, from very low levels to levels that exceed the threshold in the environment. Most of these metals such as cadmium, lead, arsenic, mercury, copper, chromium, cobalt and nickel are very toxic. They are carcinogenic and at very high concentrations, may lead to brain damage [4]. So their removals from industrial waste waters remain an important challenge.

In spite of the hazards associated with these metals, a number of industries indiscriminately dispose of their waste containing metals directly into the environment, especially in the water bodies (streams, lake, river etc). Also, through the use of domestic antiseptic soaps and pesticides on our farms, these poisonous substances are washed into the water bodies [5]. Consequently, these metals accumulate in aquatic biotas which inhabit these water bodies. Feeding on these aquatic animals such as fishes, and use of the contaminated water for drinking and cooking purposes can lead to poisoning of humans [6-7].

Unlike organic pollutants, heavy metals do not biodegrade and thus, pose a different kind of challenge for remediation. To alleviate the problem of water pollution by heavy metals, various methods have been used to remove them from waste water as chemical precipitation, coagulation, floatation, adsorption, ion exchange, reverse osmosis and electro dialysis [8-10]. The production of the sludge in the precipitation methods poses challenges in handling treatment and hand filling of the solid sludge. Ion exchange usually requires a high capital investment for the equipment as well as high operational cost. Electrolysis allows the removal of metal ions with the advantage that there is no need for additional chemicals and also there is no sludge generation. However, it is inefficient at a low metal concentration. Membrane processes such as reverse osmosis and electro dialysis tend to suffer from the in-stability of the membranes in salty or acidic conditions and fouling by inorganic and organic substances present in waste water [11]. Most of these techniques have some pretreatments and additional treatments. In addition, some of them are less effective and require high cost [12].

This study was carried out using Haematite as the adsorbent for the removal of lead and arsenic from aqueous solutions.

2. Materials and Method

2.1 Haematite

Haematite was obtained from Noamundi Mine, Bihar

(India). It is an important mineral of iron metal. It has been respectively, used as unconventional adsorbent in water and wastewater treatment [13-14]. It was crushed and sieved to have particles of size 53 μm and used as such without any pretreatment. The chemical analysis and characterization of adsorbent was given below:

Table: Chemical analysis of Red mud Adsorbent

Constituents	Percentage by weight
Fe ₂ O ₃	80.80
CaO	4.80
SiO ₂	4.00
Al ₂ O ₃	2.10
FeO	1.49
MnO	0.08
P	0.05
TiO ₂ , MgO, P ₂ O ₃ etc.	6.78

Physical properties like mean particle size diameter (4.8×10^3 cm), surface area ($14.40 \text{ m}^2\text{g}^{-1}$), Porosity (0.410) and Density (5.1 g cm^{-3}) of the adsorbent were also noted.

2.2 Aqueous solution of heavy metals

All reagents used for this study were analytical reagent grade. 1000 mg/l aqueous solutions of the metals ions were prepared as stock solution from their salts (Pb (NO₃)₂ and As₂O₃). From the stock solution, working solutions of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l were prepared from appropriate aliquots diluted to the appropriate concentration. The total concentration of each metal ion in the aqueous solution was confirmed by analysis using Unicam thermo/solar system 2009 model and Spectronic-20 Spectrophotometer.

2.3 Experimental procedure

Batch adsorption experiments were carried out to study the effect of initial metals ion concentration, contact time and temperature on the adsorption of Pb (II) and As (III) on Haematite. Adsorption studies were carried out using 25 ml of each metal ion solution and 0.5 g of the adsorbent. Batch adsorption experiments were carried out in a shaking incubator at a constant speed 125 rpm by agitating different glass bottles containing 0.5 gm adsorbent with 50 ml aqueous solutions at desire temperature and pH. The pH of the adsorbate solution was adjusted by HCl or, NaOH. The progress of adsorption was noted at different time intervals till saturation. The suspension was centrifuged and supernatant adsorbate solution was analysed by Spectronic-20 Spectrophotometer at a definite λ_{max} to determine residual adsorbate concentration.

2.4 Variation of initial metal ion concentration

Batch adsorption was carried out using initial metal ion concentrations of 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/l each for aqueous solution of Pb (II) and As (III) ions. 0.5 gm adsorbent was added into each system and 25 ml of 0.5 mg/l solution of each metal was measured into beakers. The adsorption mixtures were uniformly and continuously agitated at a fixed temperature of 30°C for 30 minutes.

2.5 Variation of contact time

The adsorption of the metal ions on Haematite was studied at various time intervals (0-180 min). Kinetic sorption studies were carried out using 25 ml of each metal ion solution with initial metal ion concentration of 0.5 mg/l. The metal ions solutions were measured into labeled beakers each containing 0.5 g of the adsorbent. The mixtures were uniformly agitated at 30°C for 30 minutes. The experimental setup was thereafter repeated for various time intervals of 60, 90, 120, 150 and 180 minutes. At the end of each contact time, the content of each tube was centrifuged and determined. The concentration of metal ions in the filtrates was determined and the amount of metal ions adsorbed was calculated.

2.6 Variation of temperature

The adsorption of the metal ions on adsorbent was studied at various temperatures (30-60°C) with the use of a thermostat water bath. Kinetic sorption studies were carried out using 25 ml of each metals ion solution of initial concentration 0.5 mg/l and containing 0.5 gm of the adsorbent. The mixtures were uniformly agitated at 30°C for 30 minutes. The experimental setup was repeated for 40-60°C. At the end of each contact time, the content of residual concentration of metal ions was determined and the amount of metal ions adsorbed was calculated.

2.7 Variation of pH value

The adsorption of the metal ions was studied at various pH (2, 6, 8, 10). Kinetic sorption studies were carried out using 25 ml of each metal ion solution with initial metal concentration of 0.5 mg/l, containing 0.5 g of the adsorbent. The mixtures were uniformly agitated at 30°C for 30 minutes. At the end of analysis, the content of each tube was centrifuged and filtered. The concentration of metal ions in the filtrates was determined and the amount of metal ions adsorbed was calculated.

3. Results and Discussion

Effect of concentration on the removal of Pb (II) and As (III) solutions The effect of initial concentration of metal ions on metal ion adsorbed by Haematite was studied at 30°C. It was found that the concentration of metals ions adsorbed increased with increase in initial metal ion concentration (Table: 1). This is due to the fact that as the concentration is increased, more metal ions are available in the solution for the adsorption process [15]. Figure: 1 shows the variation of quantity of metal ions adsorbed by Haematite with concentration. It was observed that it increased with increase in metal ion concentration, and that the rate of adsorption with respect to concentration was uniform and progressive for both the ions.

Table 1: Concentration of the metal ions adsorbed at various concentration at 30°C and ambient pH on Haematite.

Concentration (mg/l)	Concentration of the metal ions adsorbed (mg/l)	
	Pb (II)	As (III)
0.5	0.31	0.09
1.0	0.82	0.25
2.0	1.79	0.72
3.0	2.73	1.32
4.0	3.78	1.82
5.0	4.72	2.02

Effect of contact time on the removal of Pb (II) and As (III) solutions The adsorption of Pb (II) and As (III) on Haematite was studied as a function of time in order to find out the equilibrium time required for maximum adsorption of metallic ions (Table: 2 and Figure: 2). It was observed that

the concentration of metal ions adsorbed on adsorbent increased with increase in time. This is also due to the migration of higher fraction of the metal ions from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent as time progresses [6]. This enhanced adsorption of the metal ion with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in kinetic energy of the hydrated metal ions [6]. The removal of metal ions on Haematite could also be due to difference in sorption processes: ion-exchange, adsorption (physic-sorption/chemisorption) co-ordination, complexation as a result of the various types of ion binding groups.

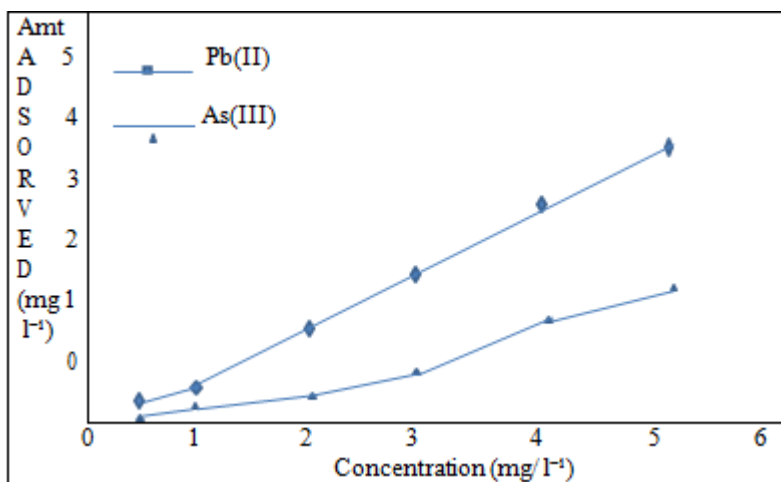


Figure 1: Variation of quantity of ion adsorbed by Haematite with concentration of metal ions at 30°C temperature

The initial faster rate may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents. The Pb (II) adsorption take place at the more reactive sites. As these sites were progressively filled, the more difficult the sorption becomes, as the sorption process tend to be more unfavorable. This is the general characteristics of adsorption of metal ions [16-20]. The quantity of metal ions adsorbed follow the trend Pb (II) >As (III) for Haematite.

Table 2: Concentration of the metal ions adsorbed at various time interval at 30°C and ambient pH by Adsorbent

Time (minutes)	Concentration of the metal ions adsorbed (mg/l)	
	Pb (II)	As (III)
30	0.11	0.04
50	0.23	0.05
90	0.24	0.06
120	0.27	0.07
150	0.34	0.08
180	0.35	0.09

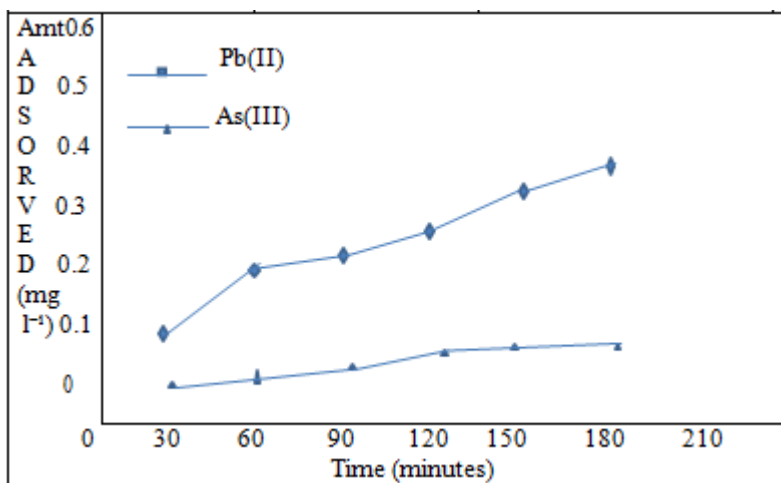


Figure 2: Variation of quantity of ion adsorbed by Haematite with concentration of metal ions at 30°C temperature.

Effect of temperature on the removal of Pb (II) and As (III) from solutions:

Temperature can affect the adsorption behavior of metallic ions in solutions. The effect of temperature on the adsorption of Pb (II) and As (III) from solutions containing adsorbent was studied at a concentration of 0.5 mg/l for 30 minutes. Table: 3 and Figure: 3 show that the removal of Pb (II) and As (III) from aqueous solution by adsorbent is temperature dependent. Increase in temperature from 30°C to 60°C was found to result in a continuous increase in the removal efficiency of the adsorbent for the metal ions. This is probably due to the effect of temperature; there was interaction between adsorbent surface sites and metal ions in solution.

Increase in temperature probably weakens the bond formed between the metal ions and the adsorption sites on the

adsorbent thereby resulting in an increase in the amount of metal ions adsorbed on the adsorbent. This indicates that increase in temperature creates a wider surface area for adsorption at the adsorbent. Some researchers have suggested that sorption from aqueous solution is by a different adsorption mechanism, which may be described as either physical adsorption or chemisorption.

Table 3. Concentration of the metal ions adsorbed at various temperature and ambient pH on Haematite

Temperature (°C)	Concentration of the metal ions adsorbed (mg/l)	
	Pb (II)	As (III)
30	0.31	0.07
40	0.32	0.10
50	0.37	0.31
60	0.40	0.45

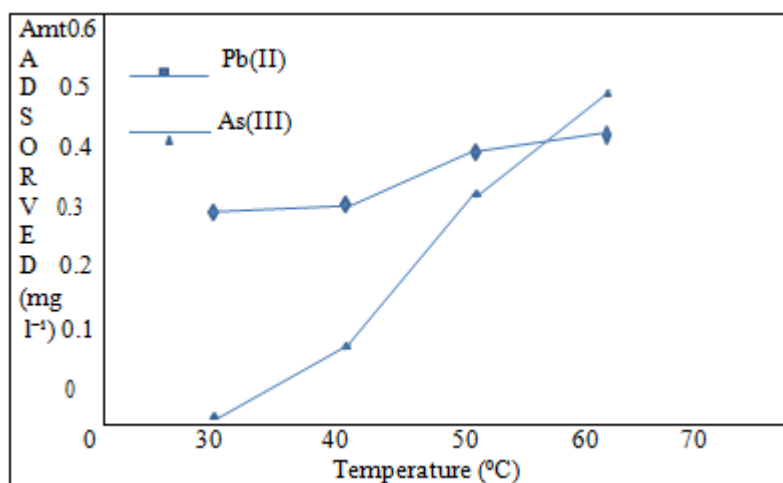


Figure 3: Variation of quantity of ion adsorbed with temperature on Haematite

3.4 Effect of pH on the removal of Pb (II) and As (III) from solution

pH is an important controlling parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on adsorbent and the degree of ionization of the adsorbate during reaction [21-22]. The heavy metal cations are completely released in extreme acidic condition [23]. At lower pH values, the H⁺ ions compete with the metal cation for the adsorption sites in the system [24-25]. The effect of pH on the adsorption of Pb (II) and As (III) from solutions containing Haematite was studied at a concentration of 0.5 mg/l for 30 minutes and at 30°C. Table.4 shows that the concentration of the metal ions increased as the pH moves from the acidic pH 2 to alkaline pH 10. This result of the effect of pH on the adsorption of metal ions on adsorbent is represented in Figure 4. It shows that alkaline medium tend to support adsorption more than acidic medium. At low pH values the surface of the adsorbent would be closely associated with hydronium ions (H₃O⁺), by repulsive forces, to the surface functional groups, consequently decreasing the percentage adsorption of metal [27]. As the solution pH increases, the onset of metal hydrolysis and precipitation begins and onset of adsorption therefore occurs before the beginning of hydrolysis [21].

When the pH of the adsorbing medium was increased from pH 2 to 10, there was a corresponding increase in the deprotonation of the adsorbent surface, leading to a decrease in H⁺ ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favors adsorption of positively charge species and the positive sites on the adsorbent surface [19, 29-30].

The hydrolysis of cations occurs by the replacement of metal ligands in the inner coordination sphere with the hydroxyl groups [22]. This replacement occurs after the removal of the outer hydration sphere of metal cations. The results obtained agreed with the findings of some researchers [17, 31]. The solubility of metals is known to be lowered at higher pH (at pH > 8) values [32].

Table 4: Concentration of the metal ions adsorbed at various pH at 30°C on adsorbent

pH of solution	Concentration of the metal ions adsorbed (mg/l)	
	Pb (II)	As (III)
2	0.17	0.14
6	0.31	0.18
8	0.34	0.22
10	0.35	0.37

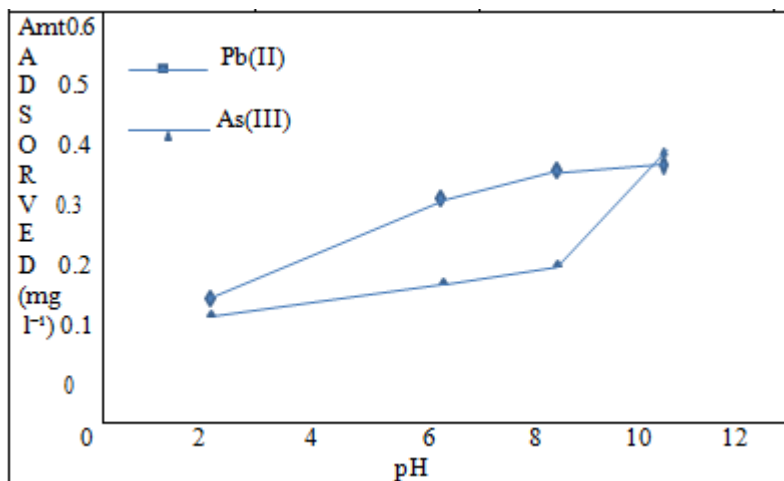


Figure: 4 Variation of quantity of ion adsorbed vs pH.

3.5 Adsorption model isotherm

The result of the analysis was used to obtain metal adsorption isotherms. The adsorption isotherm was used to characterize the equilibrium between the amount of adsorbate that accumulated on the adsorbent and the concentration of the dissolved adsorbate. In this study, the experimental data obtained was fitted using Freundlich adsorption isotherm model which may be formulated as [15]:

$\log x/m = \log k + n \log c \dots (1)$ where x/m is the concentration of metal ion adsorbed per unit mass of adsorbent (x is the amount of metal ion adsorbed, m is the mass of adsorbent), c is concentration of metal ion in solution, k and n are empirical constants. Experimental data fitted on Freundlich isotherm equation (Figure: 6) and value of reliability data (R^2) was over 92% in both cases.

Value of k and n were calculated from the intercept and

slope of the plot (Figure: 5 and Table: 5). The Freundlich exponent (n) indicates the favorability of adsorption. The value of $n > 1$ represents a favorable adsorption condition [33]. The values of n obtained in this study for the adsorption of Pb (II) and As (III) on Haematite is greater than unity, indicating the favorable adsorption of the metal ions. Freundlich isotherm model is indicative of surface heterogeneity of the adsorbent, i.e. the adsorbate sites (surface of adsorbent) are made of small heterogeneous adsorption patches that were homogenous in themselves. The activation of adsorption site takes place, leading to increased adsorption capacity through the surface exchange mechanism.

Table 5: Freundlich adsorption isotherm empirical constants

Metal Ions	Empirical constant (n)	Empirical constant (k)	Reliability data (R^2)
Pb (II)	1.17	1.51	0.997
As (III)	1.41	0.50	0.993

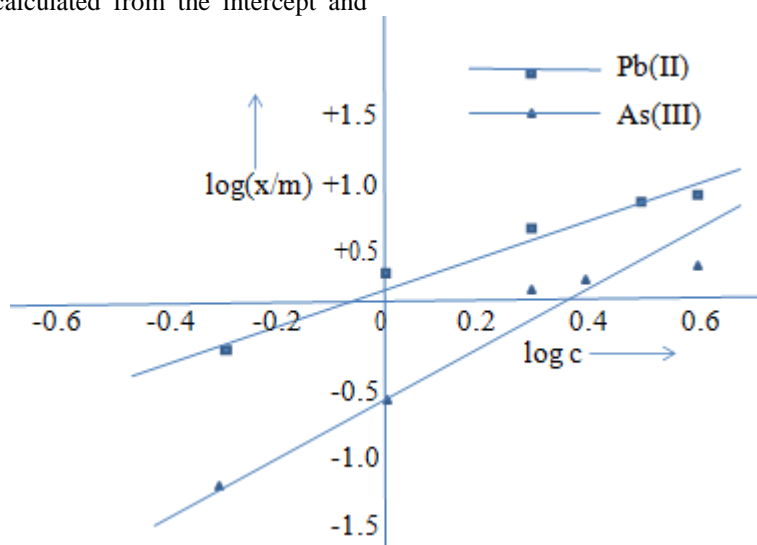


Figure 5: Freundlich adsorption isotherm for the adsorption of metal ions from solution on Haematite

3.6 Adsorption kinetics

The adsorption kinetics of adsorbent depends on the properties of the adsorbate, the experimental conditions, temperature, concentrations and pH values. Each

combination of adsorbent and adsorbate has a unique metal ion-adsorbent interaction. To explain the kinetics of the adsorption of Pb (II) and As (III) ions by Haematite at 30°C, it is necessary to determine empirically which adsorption kinetic model fits best to the adsorption equilibrium data in

order to determine the kinetic parameters pertaining to adsorption. From the results, it was found that the experimental data fitted the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is expressed as:

$$t/q_t = 1/kq^2e + t/q_e \quad \dots \dots (2)$$

Where, q_e and q_t are the amounts of adsorbate adsorbed (mg/l) at equilibrium and at contact time t (min), respectively and k is the pseudo-second-order rate constant (min^{-1}) [23, 25]. The plots of t/q against t (min) for the

adsorption of Pb (II) and As (III) on Haematite (Figure: 6) which indicates that the experiment data for the adsorption of Pb (II) and As (III) ion on adsorbent fits the pseudo-second-order adsorption kinetic model. The k and q values determined from the slopes and intercept of the plots (Table: 6) and also determined corresponding values of the correlation coefficients. From the results, it can be seen that the values of correlation efficient (R^2) indicates that the adsorption of Pb (II) and As (III) could be best described by the pseudo-second-order model [23, 33].

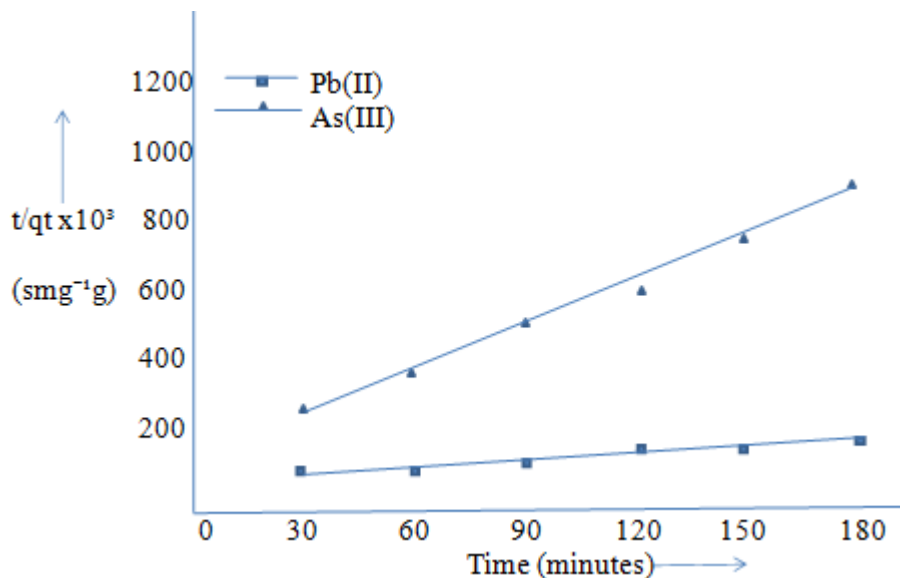


Figure 6: Pseudo-second order diffusion model for the adsorption of metal ions from solution on Haematite

The intraparticle diffusion can be estimated by using the Weber-Morris intraparticle diffusion model.

$$q_t = k_{id} t^{1/2} + C \quad (3)$$

where q_t is the amount of metal adsorbed at any time t , k_{id} is the intraparticle diffusion rate coefficient and C gives an idea about the thickness of the bounding layer i.e. the larger the intercept, the greater the contribution of surface sorption in the rate determining step [25]. The values of k_{id} and C were determined from the slopes and intercepts of the plots of q_t vs $t^{1/2}$ (Figure: 7) were presented in Table: 6.

Table 6: Kinetic parameters for the adsorption of metal ions from solution on Haematite

Models	Parameters	Pb (II)	As (III)
Pseudo Second Order Models	q_e (mg g ⁻¹)	0.029	0.004
	K_1 (gmg ⁻¹ min ⁻¹)	16.56	604.24
	R^2	0.925	0.996
Intraparticle Diffusion Models	$K_{id} \times 10^{-3}$ (gmg ⁻¹ min ⁻¹)	11.30	1.20
	C (mg g ⁻¹)	0.002	0.001
	R^2	0.941	0.942

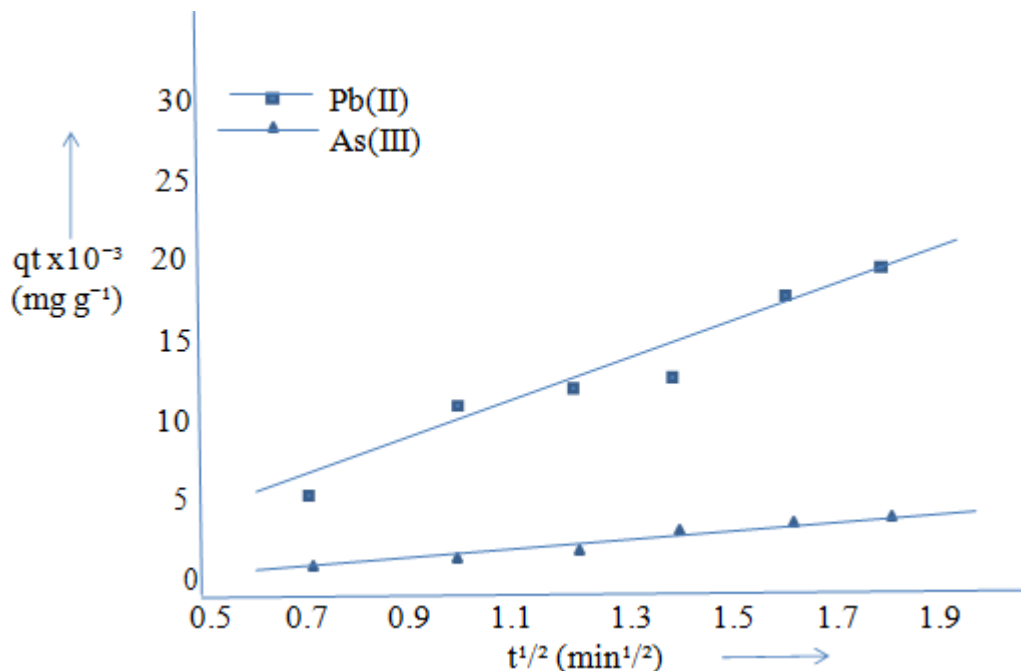


Figure 7: Intraparticle diffusion model for the adsorption of metal ions from solution on Haematite

From the result it was clear that the plots are linear but do not pass through the origin, suggesting that the adsorption of Pb (II) and As (III) involved intraparticle diffusion. It also shows that the pore diffusion is not the sole rate-controlling step [34, 35-36].

4. Conclusions

Haematite adsorbed Pb (II) and As (III) ions from aqueous solutions and the concentration of the metal ions adsorbed increased with increase in concentrations, increase in contact time, increase in temperature and increases in pH for each metal. The rate of adsorption of the metal ions by Haematite was rapid initially but decreases gradually due to the gradual blocking of the initial available uncovered surface area of the adsorbent. The rate of adsorption of metal ion in aqueous solution on the active sites on the surface of the Haematite is higher for Pb (II) and lower for As (III). This may be due to its larger ion size. Adsorption for the metal ions increases with increase in metal ion concentration because at low concentrations, the active site on the surface of the adsorbent are not completely covered. Analysis of the data showed that Freundlich isotherm described the data more appropriately than any other isotherm.

Kinetic studies showed that the adsorption of the metal ions can describe by both pseudo-second-order and intra-particle diffusion models. It is therefore, concluded that Haematite was a cheap, readily available effective adsorbent for the removal of Pb (II) and As (III) from wastewater as a way of treatment before discharge into the environment.

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