Investigation of Adsorption of Lead(II) onto a Montmorillonite Clay modified by Humic Acid

[1]Iffat Aziz, [2]Muhammad Sirajuddin*, [3]Muhammad Haleem Khan, [1]Shafqat Nadeem,
[1]Syed Ahmad Tirmizi**, [4]Rafaqat Ali Khan[b]
[1]Department of Chemistry, Quaid-i-Azam University 45320, Islamabad, Pakistan.
[2]Department of Chemistry, University of Science and Technology, Bannu, Pakistan.
[3]Department of Chemistry, University of Azad Jammu and Kashmir, Muzaffarabad.
[4]Department of Chemistry, University of Science and Technology, Abbottabad, 22060, Pakistan.
m.siraj09@yahoo.com*, satirmizi_qau@yahooo.com**

(Received on 23rd January 2015, accepted in revised form 6th June 2015)

Summary: This study investigated the adsorption of Pb(II) in aqueous solution onto humic acid (HA) surface. The adsorption of lead(II) ions was studied using montmorillonite clay as adsorbent in the presence of humic acid under fix pH condition. The effect of HA on the adsorption of Pb(II) onto montmorillonite depends on its concentration in the solution, i.e., metal adsorption decreases with increasing concentration of HA in the solution. The HA was found to enhance the metal adsorption capacity of mineral surfaces in ternary system. The adsorption for Pb(II) on HA was high and this may due to its strong affinity for carboxylic and phenolic groups of humic substances. Since Pb(II) is divalent cation so its adsorption may have consumed two carboxylic/phenolic groups of HA. The decrease in adsorption of Pb(II) in the presence of HA in a ternary system is may be due to the blocking of adsorptive surfaces and reduction of cation exchange capacity by the clay in the presence of HA through its polar adsorption on mineral surface.

Keywords: Montmorillonite clay; Adsorption of Pb(II); Humic acid; Fixed pH; Spectrophotometric method.

Introduction

Humic substances are structurally large complex of macromolecules which have yellow to black appearance, are acidic and generally heterogeneous. They consist of carbon, oxygen, hydrogen and sometimes small amounts of nitrogen and occasionally phosphorous and sulpher. The major functional groups in humic acid are carboxyl, phenolic, carbonyl and hydroxyl groups connected with the aliphatic or aromatic carbons in the macromolecules [1]. The existence of carboxyl and phenolic groups causes humic acid (HA) to have negative charges in aqueous solutions [2]. The solubility of humic acid in aqueous media also depends on the number of COOH and OH groups [3, 4].

Humic substances can significantly alter the characteristics of mineral surfaces [5, 6], particularly trace metal adsorption [7]. Organic coatings by humic acids significantly affect the surface electrostatic properties of clays and, hence, influence clay adsorption characteristics and flocculation behavior [8]. Furthermore, there is evidence that organic acids may play a decisive role in catalyzing the dissolution of minerals since metal-organic complex formation might increase the solubility of metals [9-11].

Heavy metal discharge into the environment causes serious soil and water pollution, endangering the quality of water and natural resources used for human consumption. Cd(II), Pb(II), Cu(II), Fe(II) and Cr(III) are among the most hazardous as they tend to accumulate in organisms causing numerous diseases and disorders [12]. As a result of increased awareness of the ecological effects of toxic metals, their removal from solution has received detailed attention in recent years. Conventional methods for achieving this include chemical precipitation [13], ion exchange [14] and electrochemical techniques [15]. These processes may be ineffective or extremely expensive, especially when the metals are present in solutions of low concentration. Adsorption as an alternative technique for heavy metal removal has proven to be competitive and effective [16]. Activated carbon has been found to be a good adsorbent and is the most commonly used in wastewater treatment [17]. However, because of its high cost of production and regeneration [18, 19], the development of more economical and effective adsorbents has been the target of recent research.

Clays attract attention due to the heterogeneity of their surfaces and some have been found to possess the ability to sorb ions from solutions and release them later, when the conditions change [20]. There are about thirty different types of "pure" clays but most natural clays are mixtures of these different types, along with other weathered

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[*]To whom all correspondence should be addressed.

minerals [21]. Studies have shown that natural clay is an appropriate adsorbent for heavy metal removal due to its efficiency, low cost and availability [22]. The adsorption capabilities of natural clay are attributable to their high surface area and exchange capacities [23], including the presence of negative charges on the clay mineral structure which can attract positively charged metal ions [24].

The structure of the particle network in soils, and the mobility and transport of colloidal particles are inherently influenced by the natural organic matter bound to the mineral matrix. The presence of cementing cations like calcium is essential for the formation of bridges between mineral particles and between organic matter and mineral phase. Particle aggregation depends on the type of soil. The polycation bridges between clay and organic matter are characteristic of Vertisols, where clay size fractions and polycations are the main aggregating factors [25]. Therefore, not only the type of soil, the mineral constituents and the organic matter content, but also the composition of the soil solution, are responsible for the structure formed in soils, which controls transport through the porous system [26]. The chemical and mineralogical controls on humic acid adsorption to clay mineral surfaces have been studied recently [27] using kaolinite and montmorillonite as common clay particles in soil under different conditions of pH, ionic strength and solution cations (Na^+ and Ca^{2+}). In this work, montmorillonite was chosen as it is the most studied 2:1 type layer silicate. The layered clay are built from silica tetrahedral and alumina octahedral layers, and have permanent negative charge sites on the faces [28, 29].

As a contribution to the current interest on the potential application of clays, the present study investigates the adsorption of Pb(II) onto the montmorrilonite clay. The current work is about adsorption characteristics of lead on montmorrilonite clay at fixed pH in the presence of humic acid by spectrophotometric method. Since humic acids present a good solubility in water and this characteristic decreases the adsorption procedures. In order to overcome this disadvantage, humic acid can be attached onto montmorillonite surface to obtain a new material with complexation characteristics of the humic acids and with insolubility characteristics. Clay-humic complexes play very important roles in regulating the transport and adsorption of cations.

Experimental

Materials

Humic acid (HA) (Aldrich, UK) was used in the form of technical grade Na-Salt. Montmorillonite clay (Aldrich, UK) was used in the form of montmorillonite K 10. 2-(N-morpholino) ethane sulfonic acid (MES) buffer was obtained from fisher scientific Ltd, UK. Cadmium nitrate salt from fisher scientific Ltd UK was used. Whatman cellulose nitrate membrane filters (0.1 µm) of fisher scientific UK were used in experimental work. Single use filter unit of Minisart Germany and plastic syringes (5 mL) from BD plastic pack, Spain were used. Deionized water was used throughout these studies.

Preparation of Solutions

Solutions of different concentrations of humic acid, MES and metal ions were prepared for subsequent use in experimental work as:

Purification of Humic Acid

Aldrich Na-humate salt (1.0 g) was dissolved in 1 dm^3 of deionized water with approximately 4 cm^3 of 0.1 M NaOH solution in a 2 dm^3 conical flask. Volume was made by batch wise addition of deionized water and then solution was sonicated for an extended period (≈ 24 h) to ensure that Na-humate had completely dissolved. The pH of the solution was then lowered ($pH < 2$) using approximately 10 cm^3 of concentrated HCl. The solution was left overnight to allow the humate to precipitate completely. A large portion of the yellow solution (fulvic acid fractions) was carefully removed by decanting. The solid was finally isolated by filtration under vacuum, using a magnetic filter funnel and a filter pump. A 0.45 µM cellulose nitrate membrane was used for this purpose. The solid was than dried in a desiccator. The process of humic acid purification was repeated twice by taking purified Aldrich Na-humate. The solid was than dried in a desiccator as purified Na-humate. Dried humate salt was added into a magnetic filter funnel containing a 0.45 µM cellulose nitrate membrane. Finally the solid was washed with ≈ 1 dm^3 deionized water and dried in a dryer at 80°C.

Preparations of humic acid solutions

A 1000 mg/dm^3 HA stock solution was prepared by adding 1.0 g purified Aldrich Na-humate into a 1dm^3 measuring flask to approximately 200 cm^3 of 0.1 mol/dm^3 MES (buffer solution of pH 6) and sonicated to dissolve completely. To ensure the dissolution of HA, concentrated NaOH (≈ 2.5 cm^3) was added drop wise. The humic acid solution was adjusted to pH 6.0 using a minimum volume of either NaOH or HCl. The stock solution was then made up to the volume with MES solution.

Humic Acid Sub-Stock Solution

A series of humic acid solutions (8 solutions) in MES (0.1 mol/dm^3) ranging from 5 mg/dm^3 to 50 mg/dm^3 were prepared in a 500 cm^3 measuring flask by taking measured volume of humic acid stock solution. The pH of the solution was checked and adjusted to 6.0 where necessary by using minimum volume of NaOH or HCl. Humic acid concentration were 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/dm^3 in 0.1 mol/dm^3 MES adjusted to pH 6.0.

Sodium Hydroxide Solutions

Two solutions (1 M and 10 M) of NaOH were prepared by dissolving 4.0 g and 40.0 g of reagent grade NaOH in 100 cm^3 deionized water in measuring flasks, respectively.

MES-Buffer Solution

MES, [2-(morpholino) ethanesulfonic acid], has a buffer range between pH 4.5-7.0 the adsorption studies were carried out at pH 6.0 as this is comparable to natural aquifer system. A stock solution of MES (0.1 mol/dm^3) was prepared by dissolving 42.63 g of MES in approximately 1.9 dm^3 deionized water in a 2 dm^3 measuring flask (≈ 3.4 pH). pH of the solution was adjusted 6.0 using required volume of NaOH and HCl .

Lead Nitrate Solution

Lead(II) stock solution (1 mol/dm^3) was prepared by dissolving 30.85 g of lead nitrate salt into 90 cm^3 of 0.1 mol/dm^3 MES of pH 6.0 in a 100 cm^3 measuring flask and made up the volume with MES solution.

Lead(II) Sub-Stock Solution

A series of different concentration solutions (12 solutions) of Pb(II) were prepared by appropriate dilution of stock solution with 0.1 mol/dm^3 MES buffer. Pb(II) solutions of different concentration (50, 100, 150, 200, 250, 300, 350 and 400 ppm) were prepared.

Adsorption Processes

Binary and Ternary Experimental Sets of Samples

Lead(II) -Montmorillonite

Batch adsorption experiments were carried out by weighing 0.1 g quantities of montmorillonite clay suspended in 10 cm^3 (duplicate) containing metal ion solution of known concentration (50, 100, 150, 200, 250, 300, 350 and 400 ppm) in plastic scintillation vials in duplicate in MES solution. Control or reference set was also prepared in the same way (without solid). These sets were alternatively shook and equilibrated in water bath at 25°C for 7 days. Absorption was measured at 301 nm after measuring the pH of the solution.

Humic Acid-lead(II)

To determine the individual interactive adsorption of metal ion and humic acid, a set of experiment was designed. In this set 10 cm^3 of humic acid of different concentration ranging from 50 ppm to 400 ppm (8 concentrations) was contacted with 0.1 g montmorillonite clay individually. The solutions were shook and left for equilibration for 7 days for subsequent measurements of absorbance in the UV range.

Lead(II)-Humic Acid-Montmorillonite

Three experiments set was prepared in duplicate by weighing 0.1g quantities of montmorillonite clay suspended in 10 cm^3 humic acid solutions of known concentrations (50, 100, 150, 200, 250, 300, 350 and 400 ppm) in 0.1 M MES buffer solution adjusted at pH 6.0 in plastic scintillation vials. These sets were alternatively shook and equilibrated in water bath at 25° C for 7 days.

Instrumentation

Optical density of HA was measured using UV/Vis spectrophotometer of Model UV/Vis 1601 Shimadzu (Japan) coupled with personal monitor and 1 cm^3 quartz cuvette. A Decon FS Frequency Sweep Ultrasonic Bath Ltd., England was employed for sample sonication. A pH meter, 720A, of Romania was used with a pH electrode. Vacuum pump (ILMVAC GmbH, Type 4000481-14) was used during the experiment. Deionized water was used throughout the experimental work. Experiments were conducted in pre-washed and dried polyethylene Scintillation vials (20 cm^3).

Results and Discussion

Investigation of Adsorption of Humic Acid onto Clay

This study is focused on the experimental observations to determine the metal adsorption process within a binary as well as a ternary system. A calibration curve was constructed from HA control samples of different concentrations as reference for all lead adsorption experiments. To evaluate the maximum absorbance of HA, each concentration solution (5-60 mg/dm^3) was scanned in the wavelength range of 200-360 nm. However, maximum absorbance was noted at 301 nm and is therefore, selected as standard reference graph (Fig. 1). The data show a gradual increase in absorbance with increasing HA concentration in the range studied. It was also noted that HA absorbance is affected by change in pH and ionic strength. Humic acid when interacts with buffer, it appears to increase in the pH of the solution due to buffering nature of humic acid. Keeping in view, all experiments were carried out at a fixed pH 6.0 as it is close to the pH of many natural waters. MES buffer solution was used as blank reference or baseline for the absorbance measurements. Absorbance values for HA solution of different concentrations at 301 nm are given in Table-1.

Table-1: Humic acid standard absorbance.

HA (Conc. in ppm)	Absorbance (at 301 nm)
5	0.190
10	0.316
15	0.468
20	0.620
25	0.800
30	0.940
35	1.12
40	1.29
45	1.46
50	1.68
55	1.87
60	1.99

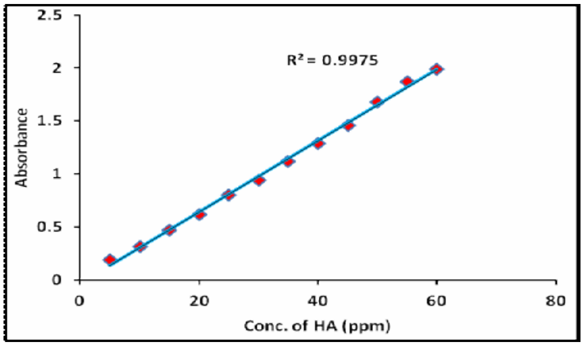

Fig. 1: HA standard calibration curve at wavelength 301 nm.

Investigation of Adsorption of Pd(II) onto Humic Acid (Binary System-1)

Adsorption can be described in several different ways depending on the requirements of the use of the data. The equilibrium based adsorption isotherms describing adsorption at the solution-solid interface is a simplest method often used to present the adsorption as a percentage of the amount of HA adsorbed per surface unit of adsorbent against a variable of interest such as pH or temperature etc. This interpretation offers the advantage of simplicity and relates the amount of adsorptive (HA) adsorbed to a surface and its concentration in the solution at constant temperature. While considering the HA-montmorillonite interactions, the adsorption of HA were examined prior to the study of ternary system by batch experiments through establishment of adsorption isotherms. The extent of adsorption of HA onto montmorillonite was predicted with reference to standard HA calibration curve (Fig. 2). It gives the amount of humic acid remaining in the solution at equilibrium thus the difference from the standard is the amount of HA adsorbed onto the solid. The adsorption of humic acid onto montmorillonite is shown in Table-2. This data indicated no perfect adsorption saturation of HA in the maximum range of HA studied. In the light of the reported work [30], montmorillonite clay is capable of attaining equilibrium in 24 h. However, in this work a plateau region has been reached after the initial increase or there is a steady increase as adsorption still occurs. Therefore, no conclusion can be drawn from this isotherm as to whether the mineral surface has reached saturation by HA. It is also reported that an increase in pH ~ 8.0 results in 50% decrease in the amount of HA adsorbed on montnorillonite [31]. As in this pH range, clay surface become negatively charged which results an increase in charge density with increasing pH. The same trend occurs with the molecules of HA, i.e., the higher the pH, greater will be the dissociation of HA functional groups and some net effect is an increase in negative charge on HA molecules. The electrostatic interactions between the charges will repel the HA from clay surfaces leading desorption of HA at higher pH. Several possible mechanisms governing the adsorption of HA on clay have been proposed [32]. These are cation bridging, water bridging and H-bond complexation. According to these, at low pH, H-bond complexation could be the dominant mechanism, at higher pH; HA molecules become more hydrophilic due to dissociation of functional groups, so cation bridging is supposed to be the more effective adsorption mechanism. However, water bridging could exist in both pH conditions. The adsorption trend seems to continue at lower concentration but as the HA concentration increases, the adsorption process slowed down. An adsorption saturation of clay particles was observed at higher concentration of HA.

Table-2: HA and Clay Interaction in Binary System-I.

HA (Conc. in ppm)	Absorbance of HA + Clay after Equilibration
5	0.06
10	0.15
15	0.23
20	0.33
25	0.62
30	0.82
35	1.03
40	1.12
45	1.44
50	1.47
55	1.71
60	1.92

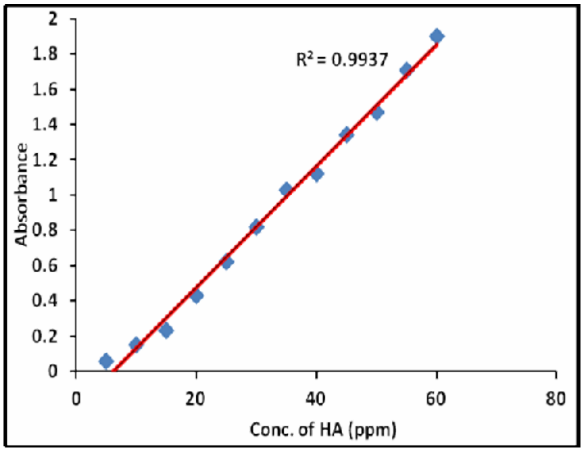

Fig. 2: Humic acid-clay interaction in binary system (I).

Investigation of Adsorption of Pd(II) onto Montmorillonite (Binary System-II)

Both reference and batch adsorption experiments were conducted for the HA-Pb interaction study in a binary system. Adsorption was carried out under a similar condition as used for other experiments. The UV measurements corresponding to the percentage adsorption of Pb(II) onto HA with reference to control samples after equilibration period (7 days) are shown in Fig. 3. These data show that HA absorbance initially increased then decreased negligibly with increasing concentration in the range-studied. Generally, it was noted that with increasing HA concentration, metal adsorption decreased, indicates saturation for metal adsorption at higher concentration of HA. Lead interactions were studied by UV measurements of HA. The experimental data given in Table-3 indicates a decrease in optical density of HA after equilibration with Lead. The adsorption trend of Pb(II) suggests that HA has a high affinity for Pb(II) at low concentration and so on. It probably adsorbed on HA by the formation of chemical bonds with dissociated carboxyl and possibly organic hydroxyl (at higher pH) groups. In the absence of other functional groups or adsorption sites; chemical and electrostatic energy are the only components of the free energy of adsorption. It has also been reported in the literature that structure of HA molecule is unlikely to permit adsorption reactions, which have an interactional energy component. The high adsorption measured for Pb(II) on HA can be related to the strong affinity of heavy metals for carboxylic and phenolic groups of humic substances. It should be noted that Pb(II) is divalent cation and its adsorption may have consumed two carboxylic/phenolic groups of HA [32, 33].

Table-3: Lead-humic acid adsorptive interaction in binary system (II).

HA (Conc in ppm)	Absorbance of Pb(II) + HA after equilibration
5	0.009
10	0.022
15	0.052
20	0.086
25	0.108
30	0.161
35	0.193
40	0.208
45	0.25
50	0.287
55	0.31
60	0.338

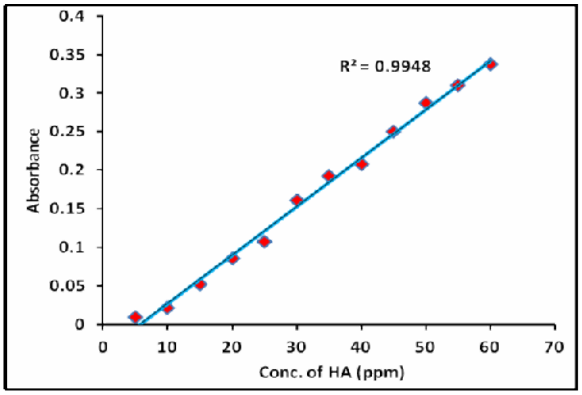

Fig. 3: Lead(II) humic acid adsorptive interaction in a binary system (II).

Investigation of Pd(II) Adsorption onto Montmorillonite Modified by Humic Acid (Binary System-III)

The interaction of metal ions with mineral components is a complex phenomenon, which has not been fully characterized to date. To investigate these, batch experiments were conducted with 0.1 g quantities of mineral suspended in a 10 cm^3 solution containing metal ions of known concentrations (50-600 mg/dm^3) in plastic bottles. Initial pH of the suspension was adjusted to the desired value (pH 6.0) using dilute HCl or NaOH solutions. Both control (without solid) and adsorption sets were prepared and equilibrated for 7 days using the procedure as stated above. It was observed that concentration of metal ions bound to the minerals was sharply increased for most dilute solutions and then decreased for higher concentrations. The Lead adsorption onto montmorillonite over different concentrations of Pb(II) indicated irreversibility behavior at low surface coverage while at higher Pb(II) concentration, partial reversibility is exhibited (Fig. 4). This suggests that high energy sites which are first to be filled are apparently also the sites which binds Pb(II) irreversibly. These data can be best described by the

Toth adsorption equation [34]. Montmorillonite is relatively soluble silicate clay with very high surface area, heterogeneous composition and a swelling layer structure, supposed to have three adsorption sites. The external planar surface would adsorb Pb(II) exchangeably and reversibly, since the ions are simply held on the surface by electrostatic forces. However, in reality, clay surface consist of cavities and deformities into which Pb(II) can be adsorbed possibly followed by the penetration into the octahedral sheet through a mechanism by which Pb(II) is fixed into the montmorillonite [35]. The adsorption isotherm of Pb(II) on montmorillonite exhibits a change in slope at higher lead concentration both at high and low pH value other than a fixed pH (6.0) used in these experiments. Usually, the degree of irreversibility increased with increasing pH and decrease in metal concentration. A generally accepted view is that specific adsorption of heavy metals by mineral surface is related to metal ion hydrolysis. Increasing ability of metals to form hydroxyl complexes increases their likelihood of specific adsorption, which can be related to their affinity sequences based on chemical theory [36].

Table-4: Standard Pd(II) absorbance.

Pb(II) (Conc. in ppm)	Absorbance of Pb(II) (at 301 nm)
50	0.129
100	0.244
150	0.364
200	0.486
250	0.593
300	0.735
350	0.860
400	0.983
450	1.11
500	1.22
550	1.33
600	1.44

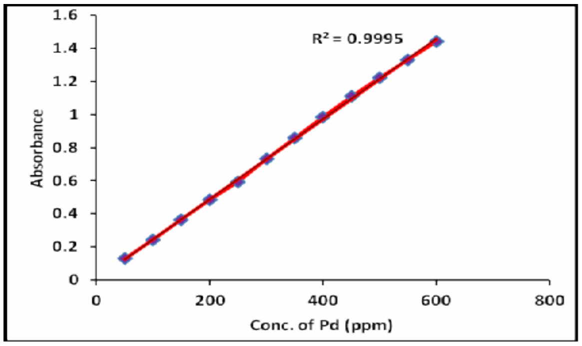

Fig. 4: Lead(II) standard calibration curve at 301nm.

Ternary Interactions (Three Component System) Humic Acid-Lead-Montmorillonite

The term adsorption refers to all phenomena at the solid-solution interface including physical adsorption, chemical adsorption, charge transfer, ion and ligand exchange etc. However, in three component systems, it is extremely difficult to separate adsorption reactions from those occurring in solution phase (complexation or precipitation). To know the interactions among metal-humic acid-solid, batch experiments (reference and Pb-adsorption sets) were conducted to examine the distribution of Pb(II) between montmorillonite and supernatant in the presence of humic acid concentration ranging from 5.0 to 60 mg/dm^3. Set 'A' was processed to ensure HA adsorption occurring as previously observed in other adsorption isotherm (binary system) experiments and set 'B' to observe the distribution of Pb(II) in three component system. Initially, HA-solid (contacted) samples were equilibrated for 7 days and their absorbance was measured. Then set B samples containing HA-solid-Pb were equilibrated for 7 days and were filtered using standard procedure for UV and pH measurements. MES buffer solution was used as a baseline for the absorbance measurements. Experimental data was recorded in Table-5 and Fig. 5. The pH measurement shows no measurable change from the initially fixed pH of HA before and after physical contact with montmorillonite over the experimental period. The decrease in adsorption of Pb(II) on HA in three component system indicates no occlusion mechanism that can be conceivably operated because of the structure of HA. This is contrary to the observations that minerals coated with HA have a higher capacity in the adsorption of metal ions. These finding agreed well with the previously reported results [37]. According to possible mechanism, below the iso-electric point, mineral surface is supposed to be positive and that of HA is negatively charged that makes adsorption possible by the phenomena of electrostatic interactions. However, above the iso-electric point both HA and minerals are negatively charged. So average electrostatic repulsion would be expected (although some localized attraction may still occur on the surface) which could explain the reduction of HA adsorption with increasing pH [38]. Despite the fact that repulsive interactions are operative between HA and mineral surfaces, HA is being sorbed onto the minerals, suggesting the involvement of other binding mechanisms including any localized electrostatic interactions. These mechanisms are likely to include ligand exchange, where surface or edge-OH_2- or -OH groups exchange with anionic groups on the HA or a surface complexation mechanism between the mineral $-OH_2^+$ groups and humic groups [39]. Both these specific binding mechanisms require the uptake of protons or the expulsion of hydroxyl groups. Many other factors including hydrophobic binding, hydrogen binding, cation bridging, Vander Waal's interactions and electrostatic repulsion between adsorbed and un-adsorbed HA might have played some role in adsorption phenomenon. It is has also been reported that decrease in adsorption may be due to blocking of the adsorptive surfaces and cation exchange capacity of montmorillonite in the; presence of HA through its polar adsorption on mineral surface. Therefore, adsorption will be minimal because of the extended electrical double layers surrounding both clay and HA. Another reason of reduction in adsorption may be the interaction of HA with Lead, as it is expected that HA might have complexed the metal ions existing in both soluble and insoluble complexes. Increase in the removal of Pb(II) at higher pH is apparently due to the higher concentration of $Pb(OH)^+$ and Pb(II) present in reaction mixture, thus, one can conclude an increase in adsorption at higher pH (> 6.0) may be due to greater reactivity of $Pb(OH)^+$ than Pb(II). In the same way HA adsorption onto montmorillonite is also minimum at pH more than 6.0, so effect of HA and Pb(II) adsorption by montmorillonite is pH dependent [40].

The data analyses reveal that amount of lead remaining in the solution increases with increasing HA concentration in the solution. Therefore, with an increase in the amount of HA in the solution phase the amount of Pb(II) sorbed onto the solid surface is decreased. This trend may be explained by the redistribution of the Lead between the solid/solution phase HA i.e., as more HA present in the solution phase, more Pb(II) will be in the solution. Thus, more adsorption of Pb(II) at low HA concentration and low adsorption at higher concentration of HA can be described in a ternary system. This indicates that Pb(II) follows the HA distribution between the: mineral and the solution phase. However, results show that at low concentrations of HA, the predicted values are different than observed for Pb(II) adsorption but at higher HA concentration; the predicted and observed values are comparable. Hence it can be said that at low HA concentration, the mineral surface exert an effect on Pb(II) adsorption and vice-versa. Conversely at high HA concentration where the mineral surface is saturated with HA, the Pb(II) seems to distribute between the mineral-bound and the solution phase HA. This may be due to the modification of inorganic surface made by mineral-bounded humic substances and this change the nature and complexing sites of minerals for contaminants [41]. The data indicate that the ratio of the bounded / free HA is correlated with the ratio of the bounded/free Pb(II) over the linear range studied. From the gradient, an apparent 'enhancement' value can be determined for the relationship between the bounded/free ratio for HA and lead radionuclide. If the HA and Pb(II) distribution between the solid and solution phase were the same, then the 'enhancement value' would be approximately equal to one. Fig. 5, gives the enhancement values (Y = 1.30) for a ternary system described here in. These values indicated that metal was adsorbed even in the presence of HA coated solid particles. For convenience, the adsorption phenomena can be simply expressed as;

$$1.30 = [Pb(II)]_{bound}/ [Pb(II)]_{free} * [HA]_{free}/ [HA]_{bound}$$

This value (1.30) is greater than unity, indicating more adsorption of lead onto minerals in the presence of HA at low concentration and so on. Two possible hypotheses have been proposed to explain the difference between the observed Pb(II) distribution and HA predicted Pb(II) distribution as well as enhancement between the $[HA]_{min}$./$[HA]_{soln}$. and $[Pb(II)]_{min}$. /$[Pb(II)]_{soln}$. ratios:

a) The HA sorbed on solid has a greater affinity for Pb(II) than that of solution phase.
b) The mineral surface still exert an effect on the Pb(II) even when saturated with HA.

The proper modeling could be used to get further information on the theory stated above. It is to be considered whether the inclusion of the Pb(II)/mineral as well as HA/mineral adsorption can explain the metal distribution in the system and hence validate the hypotheses 'b' above.

Table-5: Adsorptive interaction of lead(II) and clay (montmorillonite) in binary system (III).

Pb(II) (Conc. of in ppm)	**Absorption of Pb(II) + Clay (after equilibration)**
50	**0.110**
100	**0.133**
150	**0.143**
200	**0.141**
250	**0.146**
300	**0.156**
350	**0.155**
400	**0.162**
450	**0.169**
500	**0.176**
550	**0.179**
600	**0.183**

Table-6: UV measurement of ternary system containing Pb(II), clay and humic acid at 301 nm.

HA (Conc. in ppm)	**Absorbance of Pb(II) + Clay + HA (after equilibration)**
5	**0.08**
10	**0.096**
15	**0.12**
20	**0.145**
25	**0.12**
30	**0.32**
35	**0.456**
40	**0.433**
45	**0.572**
50	**0.735**
55	**0.772**
60	**0.91**

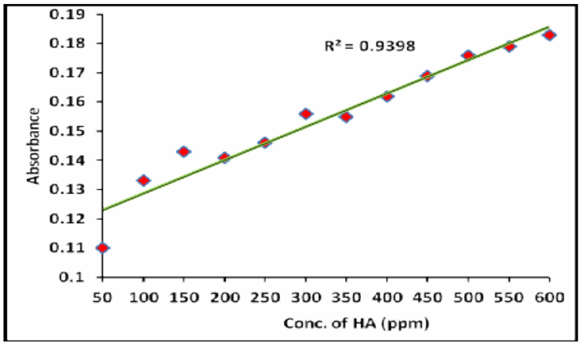

Fig. 5: Adsorption of Pb(II) onto montmorillonite in the presence of HA in ternary system

Conclusion

The removal of heavy metals a from aqueous solution by clay minerals at a given pH is influenced markedly by speciation of the metal ions concerned, Metal adsorption processes are strongly influenced by the natural organic matter contents in the system. The effect of HA on the adsorption of Pb(II) onto montmorillonite depends on its concentration in the solution i.e. metal adsorption decreases with increasing concentration of HA in the solution. The HA was found to enhance the metal adsorption capacity of mineral surfaces in ternary system. The pH 6.0 is supposed to be ideal for adsorption of Pb(II) on montnorillonite. In the presence of HA a decrease in adsorption of Pb(II) in a ternary system was observed which may be due to the blocking of adsorptive surfaces and reduction of cation exchange capacity by the clay in the presence of HA through its polar adsorption on mineral surface. The interaction of HA with Pb(II) also contribute to the reduction in metal removal by montmorillonite. It was concluded that Pb(II) will remain in solution without being adsorbed by the minerals in the presence of high concentration of HA. The adsorption of Pb(II) on coated minerals indicated great affinity for metal ions than that of solution phase may be due to tunneling effect of minerals. The adsorption mechanism of Pb(II) is may be clue to bridging between the adsorption sites on montmorillonite and HA molecules. Results also show that organic coating significantly effect on the mineral surface properties that cause the reduction in pollutant mobility. The presence of dissolved humic substances in water is a positive factor that cause retardation of pollutants and delay their arrival to environment.

Acknowledgements

The authors are highly acknowledged to Higher Education Commission (HEC) Pakistan, for financial support.

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