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Adsorption and Desorption of Lead (Pb) in Sandy Soil Treated by Various Amendments

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Abstract

The ability of sandy soil to adsorb lead (Pb) to limit its dispersion in environmental compartments and its adverse effects on humans and ecological receptors depends on certain reaction parameters. The sandy soil has a low Pb retention capacity, but treatment of this soil with amendments such as bentonite, crabmeal and eggshells could significantly improve its ability to adsorb the Pb. To this end, various sorbent tests of Pb by sandy soils, soil amendments and soil+amendments have been carried out in a static mode in the laboratory. The adsorption parameters tested are: reaction time, volume/mass ratio, temperature, increasing Pb (II) concentrations, nature and type of amendment. Furthermore, it was under thermodynamic control and was endothermic in the case of an increase in adsorbed and exothermic Pb levels as they decreased. Moreover, the adsorption of Pb obeys the Langmuir model for the soil (R2=0.986), bentonite (R2=0.915) and crab meal (R2=0.790) and Freundlich for eggshells (R2=0.936). The adsorption of Pb as a function of the types and doses of amendment showed that the retention effect of Pb was very significant (p<0.0001) and that 2.5% of crab meal, compared to the minimum intakes of 10% bentonite and 20% eggshells were sufficient to adsorb the maximum Pb for soil treated with a single amendment. The application of two soil amendments showed that the amended soil adsorbed more Pb with the minimum Fe content compared to other amendments. These results show that crabmeal is an excellent biosolid for the retention of anthropogenic Pb. The desorption test demonstrates that Diethylene Triamine Pentacetic Acid (DTPA) extracted much higher amounts of freshly adsorbed Pb than those extracted with ammonium acetate. The amounts of Pb adsorbed were significantly correlated with the amounts of desorbed Pb. Adsorption and desorption are therefore important phenomena controlling the bioavailability of Pb in sandy soils.

Keywords: Sandy soil; Soil amendment; Lead; Adsorption; Desorption

Introduction

The global increase in urbanization and the demand for agriculture products has increased pressure on the soil, in particular by polluting it with releases of heavy metals such as Pb. As a result, the immediate environments in the cities, not to mention the remote regions, has evolved radically, resulting in various ecological impacts, reflecting the breakdown of biogeochemical cycles that act as regulators of natural equilibrium [1,2]. Several historical facts show that human populations have been exposed to Pb without realizing it. Indeed, Pb is a metal used by man for millennia (over 5000 years). Pb pigments were formerly used by Egyptians to cover graves. The Egyptians, the Romans, the Hebrews and the Greeks finally managed to extract the Pb intended to produce ceramics. The Romans used lead acetate to preserve their wines, which contributed more to their intoxication [3,4].

During the Industrial Revolution, the production and use of Pb was considerably enhanced by its significant release and accumulation in the environment and especially in soils. Indeed, the more improved pigments have been used in paintings since the end of the nineteenth century until recently and constitute the stepping stone of the important dispersion, still very remarkable in several coatings of the old un-rehabilitated habitat [4]. In addition, pipes in the water distribution system were a significant source of Pb by ingestion of contaminated water. The advent of organometallic compounds of Pb, including tetraethyl ($Pb(C_2H_5)_4$) in gasoline during the first half of the 20th century, exacerbated the diffusion of this metal into the atmosphere, affecting and persisting in different compartments of the environment including soils [4,5] although it is replaced by Methyltertiarybutyl ether(MTBE)in gasoline.

The research dynamic is aimed at establishing an acceptable and "eco-responsible" management of sandy soils contaminated with Pb in order to make them reusable, more productive and to reduce the vulnerability of humans and ecological receptors that incur risks toxicology, it is important to study how to stabilize the sandy soil. To this end, Pb sorption tests were carried out in static (batch) mode in order to estimate the sorption capacity of Pb by the soil. Indeed, a good understanding of the greater or less retention (adsorption-desorption) of Pb on different sites offered by the particles constituting the sandy soil is imperative to minimize the environmental consequences due to Pb [6].

Materials and Methods

Sandy marginal soil

The soil used in this study was taken from a reworked earth pile and a mineral layer of soil sieved by a pit farm to exploit the coarse fraction. This cluster of land with no vocation (here called marginal land or marginal soil) was deposited in a reclaimed soil confinement

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area on abandoned forest land. This terrain is used occasionally as a field of firing rifle by militaries. It is therefore not a specific forest floor horizon. The soil had a water pH of 5.3 and an organic content of 0.2% and contained 94% sand, 5.3% silt and 0.7% clay.

Amendments

Chicken egg shell residues were obtained from the market. Chicken eggshells have been the subject of some metal adsorption studies [7-9]. The crab meal was bought from the market, finely re-grinded using the model Fritsch Pulverisette 6 and the bentonite was also bought. The few characteristics such as grain size, surface area and water pH of the adsorbent solids used were determined before the experiment.

Analytical equipment and methods

A range of equipment was used to conduct various tests: the centrifuge CU-500 centrifuge to allow a more pronounced decantation of equilibrium mixtures, the S-4 Pioneer X-ray fluorescence spectrometer by Brukeraxs to determine the chemical composition of the adsorbent solids used, the semi-analytical scale Mettler AE 160 (whose precision extends to ten-thousand) for weighing, and the pH meter WTW Multiline P4 for the pH measurement of equilibrium solutions. In addition, analysis of adsorbed and desorbed Pb was carried out on the atomic absorption spectrophotometer (GBC 906 AA type, oxidative air-acetylene flame). Common materials such as Whatman No. 42 filter paper, beakers, funnels, centrifuge tubes, magnetic stirrer, adjustable pipette with a maximum capacity of 5 mL, automatic burette (Dispensette) containing 30 mL as well as products Chemicals for the analysis were also used.

Lead adsorption and desorption

In general, a Pb chloride or nitrate solution of Pb concentration is added to an amended or unmixed sandy soil (1 gram) and the mixture is allowed to stand for a given time corresponding to the equilibrium time. At equilibrium, the resulting mixture is filtered on Whatman No. 42 filter paper in a pill. Pb was detected on the filtrate by the atomic absorption spectrophotometer while the pH of the filtrate was measured at the pH meter. In test 5, the separated pellet of the filtrate was washed and centrifuged at the centrifuge and then subjected to the respective solutions of ammonium acetate and DTPA for the desorption of Pb was carried out as above and the Pb concentrations were measured by the same method. Various scenarios have therefore been proposed to study the relationship between the adsorbed Pb concentrations and the equilibrium time, the ratio of the reactants used, the temperature, the concentration of the Pb solution and the type of amendment. The choice of Pb concentrations was a function of the nature of the experiment.

Adsorption kinetics: To determine the mechanisms by which Pb is adsorbed, the adsorbent solids studied are sandy soil, crab meal, bentonite and eggshells. Indeed, the nature of the surface and the number of active sites for sorption vary according to the type of adsorbent solid. The proportion of adsorbed Pb is the same. A mass of 2.5 g of sandy soil or amendment was respectively subjected to 1500 mL of aqueous Pb nitrate solution with a concentration of 100 ppm (in Pb) at various equilibrium times selected adsorption temperature 21-22°C (laboratory). Filtration with filter paper led to the obtaining of a filtrate which serves to detect Pb which is not adsorbed by atomic absorption spectrophotometry.

Adsorption versus Volume/Mass ratio (V/M): The evolution of the adsorbed Pb concentrations as a function of the type of SA provides information on the optimum solution/adsorbent ratio to be used in order to obtain a good adsorption yield. Therefore, keeping the mass of the above solid (soil, soil mixture+soil amendments or mixture of amendments) constant and varying the volume ratio of the Pb chloride solution (150 ppm Pb in 0.01 M $CaCl_2.2H_2O$) Per mass of SA (i.e., V/m=20, 30 and 40), the concentration of adsorbed Pb and the pH on the filtrates are measured after the equilibrium time of one week.

Adsorption as a function of temperature: The temperature may have an influence on the adsorption of Pb for a given adsorbent. Thus, 1 g of SA, to which a solution of $PbCl_2$ 200 ppm of Pb (in 0.01 M $CaCl_2.2H_2O$) was added in order to achieve a V/m ratio of 30 is allowed to stand for an equilibrium time of one week by placing them at 4°C in the refrigerator, at ambient temperature 22°C and at 40°C in an oven, respectively. The filtration of different mixtures at equilibrium makes it possible to measure the Pb concentrations as well as the pH in the respective filtrates.

Adsorption according to increasing doses of lead: This test has its basis in determining the conformity of adsorption data to the respective isotherm of Langmuir and Freundlich by considering the soil, and the various amendments as adsorbents. For this purpose, 1 g of soil, 0.25 or Pb: 10, 20, 30, 40, 50, 60, 80 and 100 ppm of Pb, results in a filtration which gives a solution which will be used to detect the concentrations of Pb non- adsorbed and measuring the pH. The translation of the percentages of Pb adsorbed as a function of the initial concentrations of Pb in the given adsorbent substance should obey the Langmuir and/or Freundlich model.

Lead adsorption and desorption according to the type of amendment: The first step consists of adsorption of Pb on 82 soil samples alone, soil amendment, soil mix+amendments and mixtures amendments between them for a 72-hour equilibrium time. Thefiltration which follows will serve to separate the filtrate from the pellet. The latter is first rinsed twice with distilled water so as to remove the excess of Pb nitrate and is then centrifuged at high speed. The pellet was mixed with extractive solutions of DTPA-TEA-$CaCl_2$ (pH=7.3). For another series of 82 samples, extraction was carried out with 1N CH_3COONH_4 ammonium acetate (pH=7.0). The respective centrifugations and filtrations after 72 hours of equilibrium make it possible to obtain filtrates for detecting concentrations of desorbed Pb.

Methods of statistical analysis

The statistical analysis of our data was done through excel. Our analysis have as cornerstone the comparison of the concentrations of Pb adsorbed by the control (soil) and those of the SA resulting from the amendment of this soil. Analysis of Variance (ANOVA) was applied and complemented by the multiple comparisons of different concentrations of Pb adsorbed by the adsorbent solids taking into account the rates of amendment. Consideration of different classification factors (type of SA and the proportion of amendment and their interaction) led to the use of ANOVA with a single classification criterion at a significance level a=0.05. Simple linear regression was also used to detect the influence of factors on each other with Pb concentration; percent change [10]. A so-called "Pearson" correlation analysis made it possible to highlight the desorbed adsorbed-Pb interdependence Pb.

Results and Discussion

Kinetics of adsorption of lead (test 1)

The adsorption of Pb by the adsorbent solids prior to contamination is influenced by the contact. The adsorption study of Pb was carried out

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by considering the time 0.5 to 1344 hours and fixing other parameters such as temperature. Moreover, knowledge of the mechanisms governing the adsorption of Pb on uncontaminated adsorbent solids is necessary to optimize the adsorption of Pb taking into account different variabilities (contact time, chemical composition, etc.). Figure 1 shows the evolution of the quantities of Pb as a function of time whereas Figures 2 and 3 shows the kinetic models inherent in the adsorption of Pb by each type of adsorbent solid. In 30 minutes, the soil adsorbed only 0.75% of Pb while the bentonite adsorbed 83.3%; the crab meal 89.55% and the eggshells 10.68% (Figure 1). At the 504th hour, the soil adsorbed 17.2%, bentonite 97.85%, while crab meal and egg shells adsorbed 100% each. It is therefore the achievement of equilibrium for most adsorbent solids except soil. At this time, the maximum Pb adsorbed for each solid is obtained. Overall, the soil adsorbs 0.75% to 17.2% of Pb; 83.3 to 97.85% for bentonite; 89.55 to 100% for crabmeal and 10.68 to 100% for eggshells.

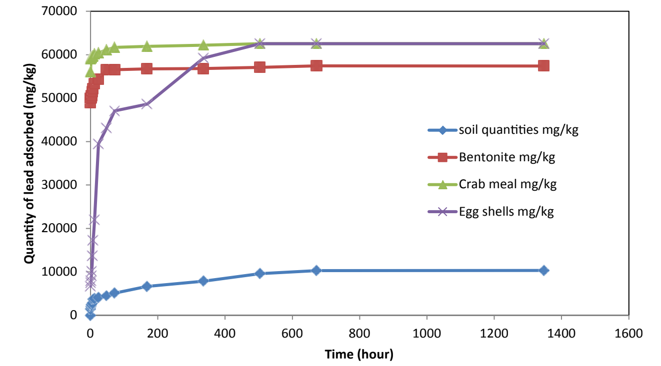

Figure 1: Quantities of lead adsorbed by sandy soil, bentonite, crabmeal and eggshell as a function of time.

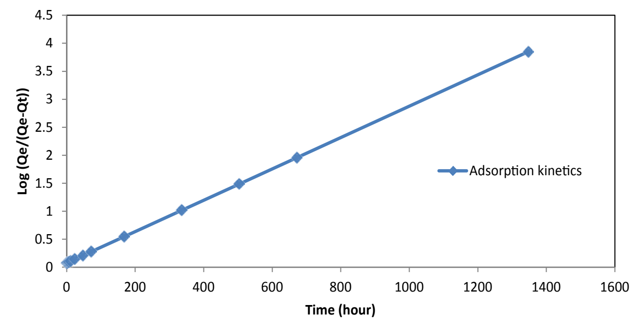

Figure 2: Adsorption kinetics of first order lead for sandy soil.

Adsorption versus solution volume/adsorbent mass ratio (V/m) (test 2)

The ratio V/m makes it possible to detect the variation of the quantities of Pb adsorbed as a function of the increase in the volume of Pb solution, the mass of SA remaining equal to unity. For this purpose, 1 gram of each above solid was contacted with respectively 20, 30 and 40 ml of Pb solution containing 148 ppm of Pb in order to have the ratios 20, 30 and 40 at ambient temperature. It was in this test that the amendments were first added to the soil to improve its adsorption capacity. One or two amendments were added to the soil in precise proportions for this purpose andpH measurements were also performed at equilibrium. According to the adsorption results as a function of the V/m ratio, it should be noted that the adsorbed Pb contents vary slightly. In particular, the soil adsorbed 42.94 to 51.63% Pb, 90.12 to 93.04% for SB and 91.27 to 93% for soil+eggshell. It should be noted that the rate of adsorption of Pb by soil as a function of solution volume/soil weight ratios (20, 30 and 40) is considerably higher than the rate of adsorption of Pb by soil as a function of time of contact (test 1). This was probably due to the marked effect of the solution/soil ratio on the adsorption of Pb by soil with few metal adsorption sites (low CEC). In fact, the ratio V/m was considerably lower (20 to 40) in test 2 than in test 1 (ratio V/m=600). However, the effect of the V/m ratio on adsorption of Pb (test 2 versus test 1) was not significant in the case of the other adsorbents which possess numerous adsorption sites having a high affinity for Pb. The maximum adsorption occurs in the case of the ratio V/m equal to 30 for crab meal, eggshell, soil+bentonite, soil+eggshell, soil+crab meal, soil+crab meal+bentoniteandsoil+eggshell+crab meal. The maximum was also observed for soil and bentonite in the case of V/m equal to 40 (Figures 4-6). The equilibrium pH increases slightly with the ratio V/m for soil, soil+eggshells and (egg shells+crabmeal) as shown in Figure 7.

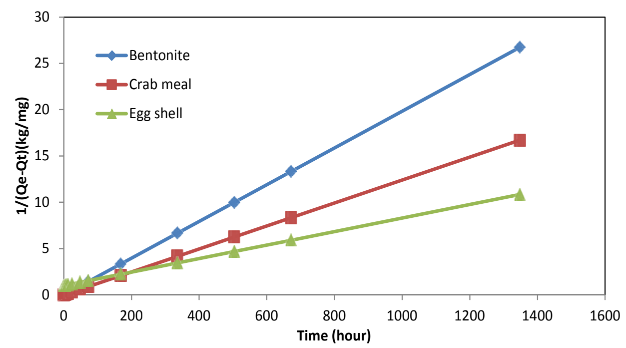

Figure 3: Kinetics of order 2 concerning the adsorption of lead by the following amendments:Bentonite, crabs meal, and eggshells (test 2).

Adsorption of lead as a function of solution temperature

The variation of temperature makes it possible to study the evolution of the system towards a new state of equilibrium. In the same manner as in section 3.2, a mixture of Pb 213.76 ppm+soil solution with or without amendment in a V/m ratio of 30 was placed under different temperature conditions of 4°C, 22°C and 40°C to evaluate its influence on adsorption of Pb. Figures 7-9 indicated that the amounts of Pb range from 11 to 13.51% for soil; 27.75 to 31.52% for the soil+bentonite combination; 98.71 to 99.2% for soil+crab meal; 20.35 to 37.06% for soil mixture+ egg shells; 97.49 to 99.16% for the combination soil+egg shells+bentoniteand 98.23 to 99.26% for the combination soil+egg

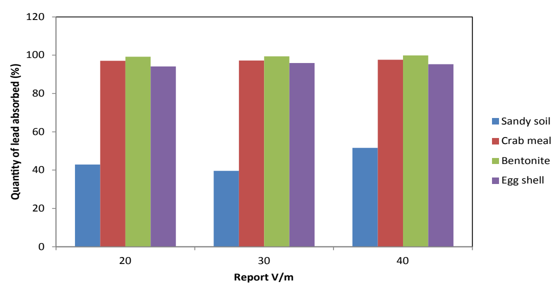

Figure 4: Quantities of lead adsorbed by non-lead-contaminated SAs as a function of the ratio V/m.

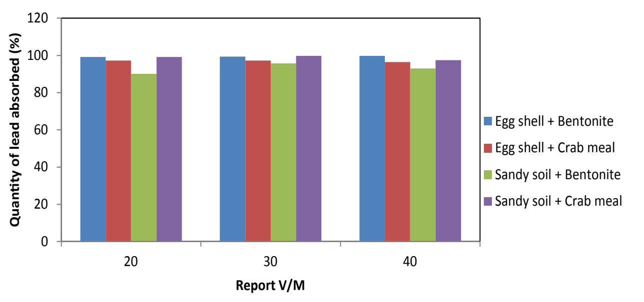

Figure 5: Quantities of lead adsorbed by soil treated by a single amendment as a function of the ratio V/m.

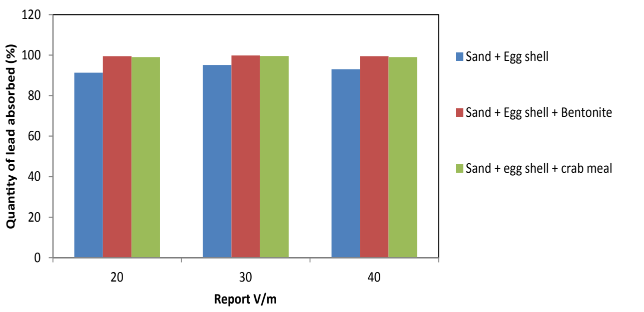

Figure 6: Quantities of lead adsorbed by soil treated by two amendments as a function of the ratio V/m.

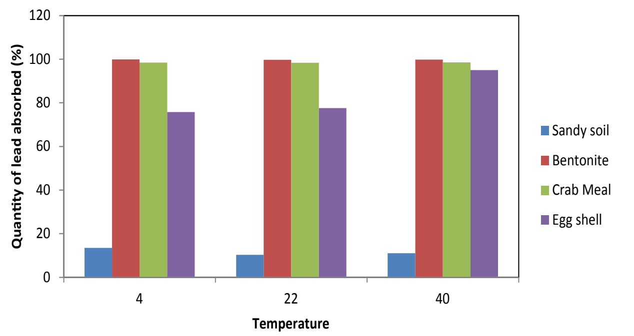

Figure 7: Quantities of lead adsorbed by adsorbent solids not contaminated with lead as a function of temperature.

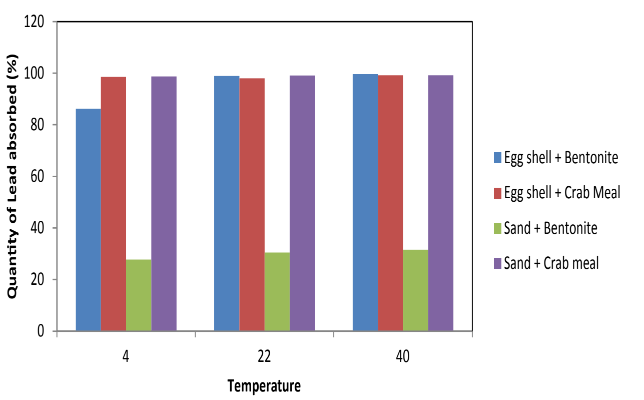

Figure 8: Quantities of lead adsorbed by soil treated by a single amendment as a function of Temperature.

shell+crab meal. The amounts of Pb adsorbed by the adsorbent solids were more or less constant when the temperature increases except for the egg shell (75.74-94.99%) and the binary mixtures of eggshells+Bentonite (86.22-99.6%) and soil+ egg shell (20.35-37.06%).

The maximum adsorption was noted for the solids bentonite, crab meal, soil+crab meal, and soil+eggshell+bentonite and soil+egg shell+crab meal as shown in Figures 7-9. Soil amendment by egg shell and bentonite improved the ability of the soil to fix Pb relative to crabmeal which gives it greater capacity as if it were acting alone as in shown in Figure 8. The treatment of sandy soils by the eggshell+bentonite and eggshell+crab meal combinations also allowed it to adsorb large concentrations as shown in Figure 9. Moreover, whether the crab meal was alone or added to the soil, the adsorption capacity involved was not affected by the rise in temperature (Figures 7 and 8). The quantities of Pb adsorbed by the ternary combinations are relatively high and are maximal respectively at ambient temperature for soil+eggshell+bentonite and at 4°C for soil+eggshell+crab meal as shown in Figure 9.

Lead adsorption based on increasing dose of lead

The adsorption of Pb is conditioned by the increasing dose of Pb in the contaminated solution. The adsorbed Pb content increased linearly with the concentration of Pb added for all the adsorbent solids except soil as shown in Figure 10. These levels increased from 348.83 mg/kg to 1069.5 mg/kg for the soil, from 2685 to 26103 mg/kg for bentonite, from 1883.1 to 29799.9 mg/kg for crab meal 887.1 to 12388.88 mg/kg for eggshell when the concentration of Pb increased from 10 to 100 ppm. This shows that bentonite and crab meal adsorb large amounts of Pb.

Adsorption and desorption of lead as a function of the nature of soil-added amendments

Adsorption of lead at 3000 mg/kg added: The graphs in Figures 11-13 shows the amounts of adsorbed Pb as a function of the percentage of added amendments alone (bentonite, crab meal and eggshells) shows that the amount of Pb adsorbed by the soil is maximum to 15% bentonite added, i.e., 2871.5 mg/kg of Pb adsorbed, 2.5% crab meal with adsorbed Pb content of 29548.4 mg/kg and 20% of eggshell added with a content of 2868 mg/kg of Pb adsorbed. Above the respective maximum quantities, the adsorption is constant in Figure 11. Crab meal is the best solid adsorbent followed by bentonite and finally eggshell. Moreover, the addition of two amendments in varying proportions also improved soil properties as in Figures 12 and 13. The contribution of eggshell+bentonite improved it more with respect to eggshell and bentonite alone (Figures 11 and 12). In the case of eggshell+crab meal application in the soil, lead adsorption was maximal with minimum crab meal content relative to that of eggshell as shown in Figure 13. The addition of eggshells and crab meal improved soil properties less than the application of crab meal alone, although economically the former has a real advantage over crabmeal alone. Moreover, the proportions of adsorbed Pb are stable while the doses of amination continue to increase. In particular, crab meal allows a more pronounced increase in adsorbed Pb compared to bentonite and chicken egg shells as shown in Figure 11.

Freshly adsorbed lead desorption: Desorption of Pb from the pellets of the adsorbent mixtures shows that the ammonium acetate extracts an average of 30.5% of Pb from the soil while the DTPA extracts 59.9%. The ammonium acetate desorbed 32.0% Pb of the soil mixture+2.5% bentonite and 39.4% of the soil mixture+20% bentonite

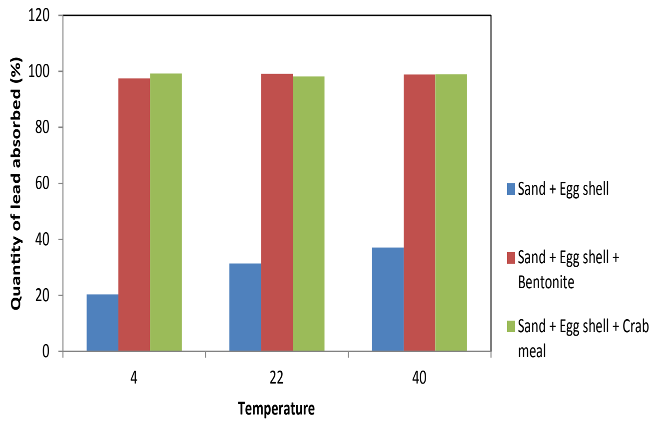

Figure 9: Quantities of lead adsorbed by soil treated by two amendments as a function of temperature.

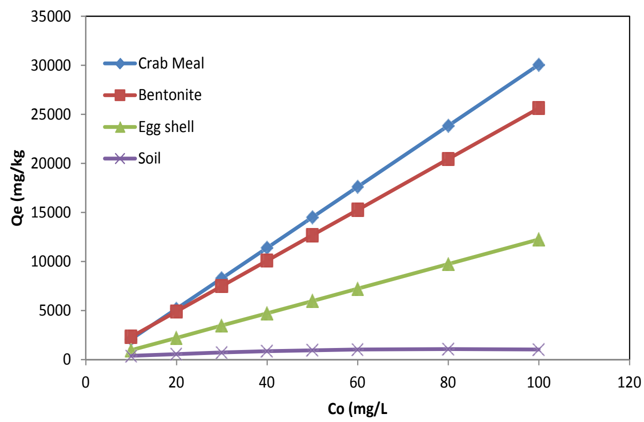

Figure 10: Quantities of lead adsorbed by uncontaminated adsorbent solids as a function of increasing lead doses.

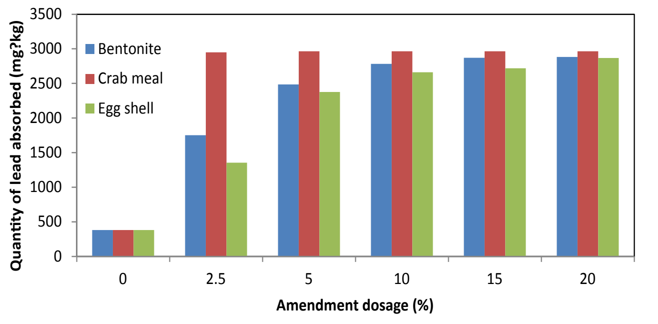

Figure 11: Quantities of lead adsorbed according to doses of soil-added amendments.

while the DTPA extracted 62.8% and 94.3% ofPb respectively. As for the soil mixture+crabmeal, ammonium acetate extracts 30.0 to 16.5% of Pb when the proportion of crab meal increased from 2.5 to 20%, while DTPA removed 88.2 to 67.2% of Pb. The soil mixture+eggshells left 28.1 to 44.8% of Pb with ammonium acetate and 82.7 to 90.6% by the DTPA. The differences between the replica values soil+bentonite (1) and soil+bentonite (2), soil+crab meal (1) and soil+crab meal (2) are due to the fact that some replicas were washed twice with bi-distilled water and others were only once when handling a very large number of samples. The concentration of Pb detected for these samples therefore include the adsorbed Pb and a portion of the added Pb entrapped in the pellets. The application of two eggshell and bentonite soil amendments allowed desorption of 22.9 to 21.4% of Pb by ammonium acetate and 84.5 to 72.6% by DTPA when studying 2, 5% to 20% of eggshell with a constant proportion of 5% bentonite. On the other hand, when the proportions of eggshells were varied in the same way as above, keeping constant the proportion of 5% for crab meal, it was observed that 30.9 to 16.8% of Pb was desorbed with ammonium acetate while 84.3 to 75.9% of Pb was desorbed by DTPA.

Discussion

The adsorption of Pb results from the transfer of Pb (II) to the surface of each SA until the dynamic equilibrium was reached between the Pb in solution and SA. From all the tests carried out above, it can be seen that the SAs contributed to reduce the quantities of Pb in the aqueous solution of Pb in given proportions depending on their chemical characteristics. This retention of Pb by soil is more effective under amendments.

Lead adsorption kinetics

The quantities of adsorbed Pb changed as a function of time. The various SAs were equilibrated in a Pb 100 ppm solution at ambient temperature and the samples were taken at different time intervals (30 min, 1 h, 2 h, 3 h, 4 h, 6 h, 8 h, 24 h, 72 h, 7 days, 14 days, 21 days, 28 days and 56 days). The results show that the Pb levels adsorbed by the soil was low in the first 30 minutes because the contact surface was not large due to the contact which becomes important over time and intermittent agitation. For other SAs (bentonite, crab meal and eggshells), adsorbed Pb levels was relatively high and adsorption stabilizes beyond 30 min. Pb levels immobilized by soil, bentonite, crab meal and eggshells increased with time according to the logarithmic model Qe=axLog (t)+b (a and b>0) and s are expressed by different mechanisms recognized by different authors as shown in Table 1. These mechanisms are pseudo-order 1 (R2=0.902) for soil, pseudo-order 2 for bentonite, crab meal and eggshells with respective coefficients of determination (R2=0.749, R2=R20, 985 and=0.915). These findings are consistent with the work of several researchers [11-17]. The low coefficient of determination for adsorption of Pb by bentonite suggests other competing mechanisms such as diffusion [14,18].

Adsorption versus Volume/Mass ratio (V/M) solution

The sorption equilibrium may vary as a function of the V/m ratio. In this context, the V/m ratios used are 20, 30 and 40. The increase in the V/m ratio from 20 to 40 has little influence on the adsorbed Pb concentrations. On the other hand, this increase in the V/m ratio seems to destabilize the complexes of Pb formed after its adsorption in the soil, soil+bentonite and soil+eggshell solids by breaking the adsorption equilibrium. Such an increase therefore solubilizes a certain proportion of these complexes of Pb. In general, the maximum adsorption of Pb was noted for solids bentonite, crab meal, eggshell+crab meal, soil+crab meal, soil+eggshell+bentonite and soil+eggshell+crab meal. Soil amendment by chicken eggshells and bentoniteimproved soil in its ability to fix Pb but its amendment by crabmeal gives it far greater capacity as if the crab meal was acting alone in the reports in Figures 4 and 6. The pH decreases with the increase of the V/m ratio for the majority of the adsorbent solids: bentonite, crab meal, eggshell+bentonite, soil+crab meal, soil+eggshell+bentonite and

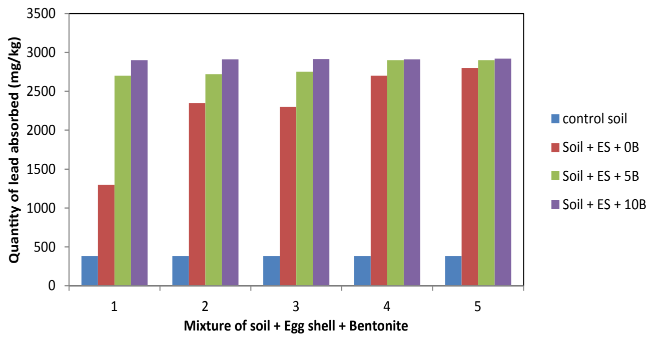

Figure 12: Quantities of lead adsorbed by soil as amended by chicken egg shells (ES) and Bentonite (B); OB, 5B and 10B respectively correspond to 0, 5 and 10% B in the mixture.

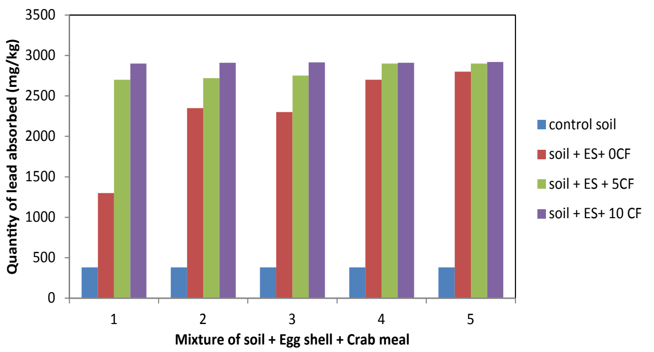

Figure 13: Quantities of lead adsorbed by soil as amended by chicken egg shells (ES) and crab meal (CF); OFC, 5FC and 10FC respectively correspond to 0, 5 and 10% FC in the mixture.

soil+eggshell+crab meal following the dissociation equilibrium in which the Pb (II) ion participates, resulting in formation of protons whose concentration is relatively high.

Adsorption of lead as a function of the temperature of the solution

Pb adsorption as a function of temperature (4°C, 22°C and 40°C) was also studied for uncontaminated SA (soil, bentonite, crab meal, eggshell, soil+bentonite, soil+crab meal, soil+eggshell, soil+eggshell+bentonite and soil+eggshell+crab meal). The effect of temperature on adsorption of Pb was also a reflection of previous studies carried outby [19-23]. In general, adsorbed Pb increases for SA when the temperature increases from 4 to 40°C (Figures 8-10). On the other hand, this rate decreases in the same case for the SA as S and SQFC. Indeed, the adsorption in the first case is more pronounced when the temperature increases thus it is endothermic whereas it is exothermic for the second case, conclusions reported by different authors [18,22-24].

Adsorption of lead as a function of increasing lead doses

The amounts of Pb adsorbed increase with the initial concentrations of Pb added as shown in previous studies [17,25,26]. These amounts of Pb increase and do not yet reach a plateau except for the soil. Moreover, the adsorption of Pb as a function of the initial concentration follows different models, including the polynomial model for the soil and the quadratic model for other uncontaminated SAs (Figure 10). These models show that the adsorption capacity of the soil is low compared to the other adsorbent solids because the curve shapes show that the adsorption of Pb for the soil reaches equilibrium at the moment when the other adsorption curves remain linear systems. Indeed, bentonite, crabmeal and hen eggshells can absorb more lead with a concentration of Pb greater than 100 mg/L and suggest that the sites present at their respective surfaces are still active because they do not Are not saturated as found by [27].

The adsorption isotherms vary according to the type of SA uncontaminated (Table 2). The adsorption isotherm of Langmuir is suitable for the adsorption of Pb in the case of soil ($R2=0.986$), similar to those obtained by Dong et al. The balance of adsorption of Pb by crabmeal is described by the Langmuir model ($R2=0.709$) and the Freundlich model ($R2=0.790$). The same applies to bentonite ($R2=0.915$, $R2=0.906$), resulting in purely chemical interactions between the adsorbed Pb and the adsorbent surface; Lack of uniformity, energy discrepancies and no specificity of adsorption sites [18]. The Freundlich model better reflects the adsorption of Pb by the chicken egg shells ($R2=0.936$) compared to that of Langmuir ($R2=0.784$). The same results have been reported by various studies [28,29].

Adsorption and desorption of adsorbed lead as a function of the nature of soil-added amendments

Adsorption of lead at the level of 3000 mg of lead/kg added: The treatment of the data shows that raising the dose of the amendment allows the soil to absorb more Pb up to an optimum. The treatment of soil by 2.5%, 5%, 10%, 15% and 20% bentonite respectively induces adsorption of 1751.7 mg/kg, 2486.7 mg/kg, 2781.5 mg/kg, 2871.7 mg/kg and 2882.4 mg/kg of Pb relative to the control (381.56 mg/kg). An intake of the same proportions of crab meal produced adsorption of 2948.4 mg/kg, 2964.1 mg/kg, 2964.7 mg/kg, 2963.9 mg/kg and 2964.8 mg/kg Pb and 2.5%, 5%, 10%, 15% and 20% chicken eggshells on average permit the adsorption of 1353.9 mg/kg, 2375.4 mg/kg, 2661.7 mg/kg, 2718.8 mg/kg and 2868 mg/kg of Pb respectively compared to the control (381.56 mg/kg). This level of adsorbed lead increases with the nature of the adsorbent solid: 12.72% (soil) "98.2% (eggshell) <99.39% (bentonite)=99.39% (crab meal).

The effect of the type of amendment and its dose is highly significant for all treatments ($p<0.0001$). This indicates that adsorption is a simultaneous function of the type and dose of a given amendment. Comparison of the doses of eggshells shows that the intakes of 2.5, 5 and 10% are significantly different, whereas the 10% improvement was not different from 15%. Moreover, the addition of 20% of egg shells allows greater adsorption of Pb. This is also true for bentonite, although the percentages 10 and 15% on one hand and 15% and 20% on the other hand, have no different effects on the respective adsorption capacities of the soil. In the case of crab meal, a contribution of 2.5% was sufficient to reach the maximum of adsorption, since from 2.5% the effects are not significantly different. The combination of amendments such as egg shell and in particular egg shell+crab meal in varying proportions also improved the adsorption capacity of Pb by soil ($p<0.0001$). Considering the increasing proportions of eggshell in ternary mixtures, adsorption of Pb was more noticeable in the case of the addition of a smaller amount of crab meal compared to that of bentonite. Combinations of SA amendments adsorbedPb in descending order:(soil+10% eggshell+10% crab meal) ~ (soil+15% eggshell+10% crab meal) ~ (soil+20% eggshell+10%)>(soil+2,5% eggshell+10% crab meal) ~ (soil+5% egg shell+10% bentonite) ~ (soil+15% egg shell+10% bentonite). Lead adsorption was more pronounced in the case of crab meal because its main constituent, chitin, is a polysaccharide consisting of carboxylate, phenolate and carbonyl groups. These chemical groups allow the soil to have more adsorbent sites for Pb (II) retention than

Type of SA	Qe (mg/Kg)	Adsorption as a function of time		Adsorption Kinetics	
		R^2	Characteristic equation	Pseudo order	R^2
Soil	Qe=1256.9 Log(t)+846.15	0.952	Log Qe/(Qe-Qt)=0.0028(t)+0.0763	1	0.902
Bentonite	Qe=1268,3 Log(t)+49645	0.928	1/(Qe-Ql)=5E-6(t)+0.0003	2	0.749
Crab meal	Qe=667.841 Log(t)+58375	0.885	1/(Qe-Qt)=8E-6(t)+0.0003	2	0.985
Egg shell	Qe=8940.4 Log(t)+3940.9	0.949	1/(Qe-Qt)=8E-7(t)+IE-5	2	0.915

Table 1: Models and kinetics of adsorption of lead by soil and amendments.

Type of SA	Qe (mg/Kg)	Adsorption as a function of initial concentration		Adsorption isotherm	
		R^2	Adsorption model	Characteristic equation	R^2
Soil	Qe=-0.14 (Co)2+22.67 (Co)+173.73	0.974	Langmuir	Ll/Qe=0.0113 (Ce)+0.0008	0.986
Bentonite	Qe=258.91 (Co)-62.39	0.953	Langmuir	1/Qe=0.0004 (Ce)+9E-6	0.915
Bentonite	Qe=258.91(Co)-62,39	0.953	Freundlich	LogQe=0.8516 Log(Ce)+3.4787	0.906
Crab meal	Qe=310.82 (Co)-023,8	0.99	Freundlich	LogQe =-1.1041 Log(Ce)+ 4.1308	0.835
Egg shell	Qe=125.37 (Co)-285.6	0.999	Freundlich	LogQe=1.5231 Log(Ce)+2.218	0.919

Table 2: Models and balance of adsorption of lead by soil and amendments.

in the case of egg shells and bentonite as reported by other researchers [30-35]. Moreover, the presence of phosphorus and sulfur in the crab meal would suggest Pb precipitation reactions. Several authors have reported that the addition of phosphates to soil contaminated with Pb contributes to the precipitation of Pb, in particular by forming lead phosphate [36]. As for the soil mixture+eggshell, the quantities of Pb adsorbed are quite high. Numerous studies have confirmed the adsorption of metals on the surface of carbonates contained in soils, particularly on calcite [37-39]. concluded that the carbonates contained in forest soil indirectly influence the adsorption of Pb by creating alkaline conditions leading to its precipitation as lead carbonate. They postulated that high calcite content favors precipitation of Pb. There is also a link between the amounts of Pb adsorbed and the pH of the soil samples. The pH values of the added amendments are higher than the pH of the soil. As a result, the addition of the amendments contributes to increasing the pH of the soil and, consequently, the number of negative sites and the adsorption of Pb. Ref. [15,40,41] reported that the number of negative sites increases with pH resulting in more pronounced Pb adsorption.

Desorption of freshly adsorbed lead: The extractions of Pb make it possible to simulate its solution in accordance with different physicochemical conditions prevailing in the natural environment. For this purpose, reagents such as ammonium acetate and OTPA were used. Indeed, the use of these extractives tests the soil's ability to make metals bioavailable. The total concentration of Pb in the SA, the total number of sites and the nature of ligands are essential conditions governing desorption, as shown by [42]. Desorption of pellets from filtration of equilibrium solutions of the adsorbent solids used ammonium acetate solutions (pH=7.0) And OTPA at pH=7.3. The adsorbent solids alone: soil, bentonite, crab meal and egg shells allowed Pb to be desorbed by ammonium acetate in a decreasing order as follows: 30.5% (soil)>28.5 (eggshell)>15.8% (bentonite)>6.1% (crab meal). As for desorption of Pb by OTPA, the desorbed Pb levels decreased as follows: 75.2% (Q)>63.1% (B)>59.9 (S)>47.8%. For the mixture of soil+eggshell+bentonite, when the proportions of egg shell and bentonite increased, it was observed that desorption of Pb decreased.

The data analysis on the desorption of Pb shows that as the soil+soil mixture fixes more Pb, it also allows to be desorbed by reagents such as ammonium acetate and OTPA as observed by other researchers [43]. When the soil was modified by bentonite and eggshells, the desorbed rates was not significantly different and was lower than those desorbed in soil modified by crabmeal. In addition, there are large correlations between adsorbed anddesorbed quantities of Pb: R2=0.961 (ammonium acetate) and 0.998 (DTPA) for egg shells; R2=0.883 (ammonium acetate) and 0.954 (DTPA) for bentonite and R2=0.700 (ammonium acetate) and 0.821 (DTPA) for crabmeal.

DTPA is responsible for desorption of a higher proportion of Pb relative to ammonium acetate for all lead-contaminated SAs. The carboxyl, carbonyl and amine functional groups of DTPA served as adsorbent sites for the Pb already adsorbed on the sites of the adsorbent solids. Moreover, semi-developed formula of DTPA shows that it is a polydenic ligand comprising five carboxylic groups and three amino teeth capable of sequestering two moles of Pb ion per mole of DTPA whereas one mole of ammonium acetate precipitates only one mole of Pb resulting in a large exchange of Pb (II) cations between the complexes formed in the soil and the different chemical groups of the DTPA. Indeed, the dissociation constants of the DTPA complexes with Pb are greater than those of the complexes of Pb present in the soil. These results were also found by [44,45].

Moreover, the stability of the complexes depends on the pH. At basic pH, precipitation of Pb compounds in the form of oxides, hydroxides, carbonates and phosphates or their complexes may compete with adsorption [22,36]. In general, the desorbed contents show that at neutral pH, ammonium acetate makes desorb less Pb than DTPA. This indicates a greater stability of the DTPA-Pb (II) complexes at this pH than those formed in the SA.

Conclusion

The adsorption of Pb in soil samples is important and depends on several factors: metal contact time with soil, initial Pb concentration added, amount and type of amendment and pH. The adsorption of Pb was complete after 8 weeks of contact with crab meal and eggshells while it was low for the soil. This study have shown that adsorption of Pb is a first-order mechanism in the case of soil only, second order for each of the other adsorbent solids such as bentonite, crab meal and eggshells. The adsorbed Pb content increases with the initial concentration of Pb. This evolution makes it possible to know the extent the Pb can be adsorbed. In case of soil modification in given proportions, the adsorption rate of Pb becomes higher for bentonite and in particular for crabmeal. The eggshell+bentonite and eggshell+crab meal combinations provide essentially Pb adsorption rates comparable to those of bentonite and crab meal. Crab meal is therefore an excellent natural biosolid for the immobilization of anthropogenic Pb in an acidic sandy soil compared with bentonite and eggshells. The adsorbed Pb levels increase with pH depending on the type and amount of amendment used to treat the soil until it stabilizes at an optimum. Desorption of Pb from the SAs by ammonium acetate and DTPA shows that the adsorbed levels of Pb and those desorbed are closely related. The higher the adsorbed Pb, the more desorbed the Pb. Although the adsorption of Pb is accentuated by the treatment of sandy soil by incorporation of biosolid, desorption of Pb adsorbed by the chemical solutions of which the chelating agents at pH 7 are also important. Adsorption and desorption therefore control the bioavailability of Pb in sandy soil.

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References

1. Street-Perrott FA, Barker PA (2008) Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. Earth Surface Processes and Landforms 33: 1436-1457.
2. Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, et al. (2011) Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Frontiers in Ecology and the Environment 9: 53-60.
3. Jarup L (2003) Hazards of heavy metal contamination. British Medical Bulletin 68: 167-182.
4. Tabrizi SJ, Langbehn DR, Leavitt BR, Roos RA, Durr A, et al. (2009) Biological and clinical manifestations of Huntington's disease in the longitudinal TRACK-HD study: cross-sectional analysis of baseline data. The Lancet Neurology 8: 791-801.
5. Patnaik P (2010) Handbook of environmental analysis: chemical pollutants in air, water, soil and solid wastes. CRC Press.
6. Prueb A (1997) Action values for mobile (NH4NO3-extractable) trace elements in soils based on the German national standard DIN 19730. Les Colloques de l'INRA, pp: 415-423.
7. Vangronsveld J, Herzig R, Weyens N, Boulet J, Adriaensen K, et al. (2009) Phytoremediation of contaminated soils and groundwater: lessons from the field. Environmental Science and Pollution Research 16: 765-794.
8. Arends IWCE (2014) Chemistry of Biofuels and Biofuel Additives from Biomass. Biomass as a Sustainable Energy Source for the Future: Fundamentals of Conversion Processes: 547.
9. Cheshomi A, Eshaghi A, Hassanpour J (2017) Effect of lime and fly ash on swelling percentage and Atterberg limits of sulfate-bearing clay. Applied Clay Science 135: 190-198.
10. World Health Organization (2014) Global status report on noncommunicable diseases.
11. Chaturvedi PK, Seth CS, Misra V (2006) Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). Chemosphere 64: 1109-1114.
12. Inglezakis VJ, Stylianou MA, Gkantzou D, Loizidou MD (2007) Removal of Pb (II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents. Desalination 210: 248-256.
13. Montinaro S, Concas A, Pisu M, Cao G (2008) Immobilization of heavy metals in contaminated soils through ball milling with and without additives. Chemical Engineering Journal 142: 271-284.
14. Xu H, Yang L, Wang P, Liu Y, Peng M (2008) Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite. J Environ Manage 86: 319-328.
15. Dong D, Zhao X, Hua X, Liu J, Gao M (2009) Investigation of the potential mobility of Pb, Cd and Cr (VI) from moderately contaminated farmland soil to groundwater in Northeast, China. Journal of Hazardous Materials 162: 1261-1268.
16. Fonseca B, Maio H, Quintelas C, Teixeira A, Tavares T (2009) Retention of Cr (VI) and Pb (II) on a loamy sand soil: kinetics, equilibria and breakthrough. Chemical Engineering Journal 152: 212-219.
17. Wan MW, Kan CC, Rogel BD, Dalida ML (2010) Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. Carbohydrate Polymers 80: 891-899.
18. Gupta SS, Bhattacharyya KG (2008) Immobilization of Pb (II), Cd (II) and Ni (II) ions on kaolinite and montmorillonite surfaces from aqueous medium. J Environ Manage 87: 46-58.
19. Yadava KP, Tyagi BS, Singh VN (1991) Effect of temperature on the removal of lead (II) by adsorption on china clay and wollastonite. Journal of Chemical Technology and Biotechnology 51: 47-60.
20. Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials 97: 219-243.
21. Zhou D, Zhang L, Zhou J, Guo S (2004) Cellulose/chitin beads for adsorption of heavy metals in aqueous solution. Water Research 38: 2643-2650.
22. Cappuyns V, Swennen R (2008) The application of pH stat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. Journal of Hazardous Materials 158: 185-195.
23. Xiong C (2009) Sorption of lead (II) in aqueous solution on chitin. Asian Journal of Chemistry 21: 6005.
24. Singh SP, Ma LQ, Hendry MJ (2006) Characterization of aqueous lead removal by phosphatic clay: equilibrium and kinetic studies. Journal of Hazardous Materials 136: 654-662.
25. Harter RD, Naidu R (2001) An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Science Society of America Journal 65: 597-612.
26. Abate G, Masini JC (2005) Influence of pH, ionic strength and humic acid on adsorption of Cd (II) and Pb (II) onto vermiculite. Colloids and Surfaces A: Physicochemical and Engineering Aspects 262: 33-39.
27. Christophi CA, Axe L (2000) Competition of Cd, Cu, and Pb adsorption on goethite. Journal of Environmental Engineering 126: 66-74.
28. Arunlertaree C, Kaewsomboon W, Kumsopa A, Pokethitiyook P, Panyawathanakit P (2007) Removal of lead from battery manufacturing wastewater by egg shell. Songklanakarin Journal of Science and Technology 29: 857-868.
29. Park HJ, Jeong SW, Yang JK, Kim BG, Lee SM (2007) Removal of heavy metals using waste eggshell. Journal of Environmental Sciences 19: 1436-1441.
30. Tipping E, Hurley MA (1992) A unifying model of cation binding by humic substances. Geochimica et cosmochimica acta 56: 3627-3641.
31. Ge Y, Murray P, Hendershot WH (2000) Trace metal speciation and bioavailability in urban soils. Environ Pollution 107: 137-144.
32. An HK, Park BY, Kim DS (2001) Crab shell for the removal of heavy metals from aqueous solution. Water Research 35: 3551-3556.
33. Kim DS (2003) The removal by crab shell of mixed heavy metal ions in aqueous solution. Bioresource technology 87: 355-357.
34. Krishnan KA, Sheela A, Anirudhan TS (2003) Kinetic and equilibrium modeling of liquid-phase adsorption of lead and lead chelates on activated carbons. Journal of Chemical Technology and Biotechnology 78: 642-653.
35. Rana MS, Halim MA, Safiullah S, Mollah MM, Azam MS, et al. (2009) Removal of heavy metal from contaminated water by biopolymer crab shell chitosan. Journal of Applied Sciences 9: 2762-2769.
36. Kabata-Pendias A (2010) Trace elements in soils and plants. 3rd edn. CRC Press, USA.
37. Zachara JM, Cowan CE, Resch CT (1991) Sorption of divalent metals on calcite. Geochimica et Cosmochimica Acta 55: 1549-1562.
38. Hong SC, Kim MS, Chung JG (2002) Adsorption characteristics of Pb (II) on calcite-type calcium carbonate by batch and continuous reactors. Journal of Industrial and Engineering Chemistry 8: 305-312.
39. Sipos P, Nemeth T, Mohai I, Dodony I (2005) Effect of soil composition on adsorption of lead as reflected by a study on a natural forest soil profile. Geoderma 124: 363-374.
40. Aualiitia TU, Pickering WF (1987) The specific sorption of trace amounts of Cu, Pb, and Cd by inorganic particulates. Water, Air & Soil Pollution 35: 171-185.

41. Nowack B, Kari FG, Krüger HG (2001) The remobilization of metals from iron oxides and sediments by metal-EDTA complexes. Water, Air & Soil Pollution 125: 243-257.

42. Bolger JA (2000) Semi-quantitative laser-induced breakdown spectroscopy for analysis of mineral drill core. Applied Spectroscopy 54: 181-189.

43. Peld M, Tonsuaadu K, Bender V (2004) Sorption and desorption of Cd^{2+} and Zn^{2+} ions in apatite-aqueous systems. Environmental Science & Technology 38: 5626-5631.

44. Cooper EM, Sims JT, Cunningham SD, Huang JW, Berti WR (1999) Chelate-assisted phytoextraction of lead from contaminated soils. Journal of Environmental Quality 28: 1709-1719.

45. Yapici T, Fasfous II, Zhao J, Chakrabarti CL (2009) Effects of various competing ligands on the kinetics of trace metal complexes of Laurentian Fulvic Acid in model solutions and natural waters. Analytica Chimica Acta 636: 6-12.

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