

# 1 Removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> from contaminated water

## 2 using environmentally safe materials

### 3 ABSTRACT

4 Heavy metals that exist in municipal wastewater can cause many problems for human hygiene and  
5 environment. Therefore, the metals need to be removed from wastewater before being used in  
6 irrigation. Materials of high surface reactivity; such as alginite, shale and iron oxide are used as  
7 potential sorbents to eliminate Pb and Cd from polluted water. In remediation studies, these  
8 materials were added to Pb and Cd polluted water at addition ratios of 1:10000, 1:1000 and 1:100  
9 (remedy agents: polluted water). The mixtures were then gently agitated and submitted to different  
10 equilibrium periods of 1, 5 and 24 h. The results showed the efficiency of tested agents (shale,  
11 alginite, and iron oxide) in the removal of Pb and Cd from polluted water containing various  
12 concentrations of 5, 10 and 50 mg/l. Shale was able to reduce Pb and Cd concentration from 5 to  
13 1.14 and 0.34 mg/l, respectively, in a reaction period of one hour. Shale, alginite and iron oxide,  
14 reduced the initial concentration of; 10 mg Pb/l to 0.98, 0.46 and 0.57 mg/l; and of 50 mg Pb/l to  
15 0.21, 6.5 and 1.68 mg/l; respectively. Shale was the most effective material in decontamination of  
16 heavy metals polluted water and it could be recommended to be used to decontaminate wastewater.  
17 This research aims to use a non expensive, environmentally safe, and efficient technique to remove  
18 heavy metals from industrial wastewater to leave them free and suitable for discharging to sanitary  
19 sewer system.

20 **Keywords:** contaminated water; remediation, heavy metals; alternative low-cost materials

## 1. Introduction

The release of heavy metals to surface and groundwater sources as a result of agricultural and industrial activities cause serious problems to the environment. The most dangerous toxic elements listed by the European Economic Community on a "Black List", were Hg and Cd, while the less dangerous substances forming the "Grey List" were Zinc, Copper, Nickel, Chromium, Lead, Selenium, Arsenic, Antimony, Molybdenum and Titanium [1]. Cadmium is present in wastewaters from metallurgical alloying, ceramics, electroplating, photography, pigment works, textile printing, chemical industries and lead mine drainage. The application of phosphate fertilizers or sewage sludge may increase cadmium levels in soil, which can cause increases in cadmium levels in crops [2]. The average cadmium content of sea water is about 0.1 µg/l or less [4]. While river water contains dissolved cadmium at concentration of < 1.1 - 13.5 ng/l, Cadmium levels of up to 5 mg/kg have been reported in river and lake sediments and from 0.03 to 1 mg/kg in marine sediments [5]. A drinking water guideline value of 0.003 mg/l has been set for cadmium by WHO. In addition, the provisional tolerable weekly cadmium intake must not exceed 7 µg/kg of body weight [6]. The guideline value for lead in drinking water given by WHO is 0.01 mg/l [6]. The optimization of water and wastewater purification processes requires the development of new operations based on low-cost raw materials with high pollutant removal efficiency. Activated carbon [7], clay minerals [8,9] biomaterials [10] zeolites [11,12] and some industrial solid wastes [13,14] have been widely used as adsorbents for adsorption of ions and organics in wastewater treatment.

The present study aimed to achieve an efficient non-expensive and environmentally safe method to decontaminate heavy metals (Pb and Cd) from polluted wastewater. Natural and non expensive materials, shale, alginite, and iron oxide, were used to decontaminate heavy metals polluted water to be suitable for discharging in drains and sanitary sewer system. At the end of remediation trials, the remedy agents can be removed easily, then recycled and utilized in manufacturing of building materials.

## 2. MATERIAL AND METHODS

### 2.1. Synthesized polluted water

Synthesized polluted water was prepared by accurate dilution of standard heavy metals solution of 1000 mg/l to known concentrations using distilled water. Lead polluted water was prepared using lead stock solution (1000 mg Pb/l in 0.5 M HNO<sub>3</sub> as matrix). A series of standard lead solutions of 5,

10, 50 and 100 mg Pb/l were prepared and used to test the ability of remedy agents in Pb removal. Cadmium polluted water was prepared using cadmium stock solution (1000 mg Cd/l in 0.5 M HNO<sub>3</sub> as matrix). A series of standard cadmium solutions of 5, 10, 20 and 50 mg Cd/l were prepared and used to test the efficiency of remedy agents in Cd removal.

## **2.2. Remedy Agents**

Three remedy agents, alginite, shale, and iron oxide, were used for polluted water remediation trials. These agents are common, inexpensive and easy to obtain. Besides, they could be separated easily from treated water at the end of the remediation process. These agents were selected based on their negatively charged surface and high adsorption capacity, which was attributed to their high surface area. The important Characteristics of the remedy agents are summarized in the following paragraphs.

**2.2.1 Alginite:** Alginite is a natural rock out of the oil shale family. It originated from fossil algae biomass and pumice, descends from the mine in Gerce, Hungary. The essential ingredients of alginite [15] are high of organic matter (19%), clay (54%) and lime content (22%). The clay is rich in montmorillonite (52%).

**2.2.2 Shale:** Shale is a naturally occurring material exists in many places in Egypt at different depths. It mainly consists of clay (55%). The clay is rich in Montmorillonit. Chemical analysis showed that the shale contains high amount of salt, the electrical conductivity (EC) of 1:2.5 water extract equals 10.63 dS/m and pH = 7.31. Sodium was the dominate cation.

**2.2.3. Iron Oxide (60 % Fe):** The sample of iron oxide is imported from Roseland Kazreti. The Chemical composition of the iron Oxide is Fe<sub>d</sub> (60%), Fe<sub>o</sub> (19%), Al (0.16 mg/ kg), Zn (12.8 mg/kg) and Cu (9.94mg/kg).

## **2.3. Remediation studies**

Remedy agents of Alginite, shale, and iron oxide, were added to heavy metals polluted water at different solid: solution ratios of 1:10000, 1:1000 and 1:100. The mixtures were then gently agitated and subjected to different equilibrium periods of 1, 5 and 24 hrs. At the end of each equilibrium period, the supernatant solution was obtained by centrifuging the mixtures at 3000 rpm for 10 minutes. Concentrations of studied heavy metals (Pb and Cd) were measured before adding the remedy agent and at the end of equilibrium period as well as the pH and electrical Conductivity (Ec).

All trials were done in three replicates. Heavy metal removal efficiency (%) of the agents can get from corresponding concentrations in solutions (mg/L) from equation:

$$\text{Heavy metal removal efficiency (\%)} = \frac{\text{metal conc (mg/L) Befor} - \text{metal conc. (mg/L) After}}{\text{Conc. (mg/L) Befor}} * 100 \text{ eq. 1}$$

## 2.4. Analytical procedures

Total concentrations of heavy metals (Pb, Cd, Ni, Co, Zn, Mn, Cu and Cr) were determined in both suspended matter and clear water. Suspended matter was digested using Aqua Regia method [16]. Concentrations of Pb and Cd in polluted water as well as treated ones were determined using Atomic Absorption Spectrophotometer (UNICAM, 969) [17]. Standard solutions were prepared from mono element stock solutions containing 1000 mg/l of heavy metals. The intensity of Pb 283.3, and Cd 228.8 nm spectral lines was measured. Every measurement as done three times, and then the arithmetical mean and standard deviations were calculated. The pH was measured using a digital Orion pH meter (model 420A). The solutions were prepared using “pure for analysis” and “chemically pure” grade chemicals. All the experiments were performed at room temperature  $18 \pm 2$  °C..

The electrical conductivity (EC) of the reacted solutions was measured using digital YSIEC meter (model 35). Cation exchange capacity (CEC) of remedy agents were determined using ammonium acetate method as described by [18]. Specific surface area of remedy agents were determined using O- phenanthroline method [19].

## 2.5. Statistical analyses

All statistical analyses were carried out by SAS version 9 software for all data of remediation trials. R- Squared values ( $R^2$ ) and Equation were considered significant ( $p$ -values <0.05) for the analysis of variance test (ANOVA).

# 3. RESULT AND DISSCUTION

Efficiency of remedy agents (shale, alginite and iron oxides) to remove Pb and Cd from synthetically polluted water containing various concentrations of 5, 10 and 50 mg/l were examined using different addition ratios (1:10000, 1:1000 and 1:100) of remedy agents: polluted water, at different reaction periods varying between 1 to 24 hour. The results obtained were as the follows.

## 3.1 Shale

108 The results (Table 1) showed that, although at the low addition ratio (shale: heavy metal polluted  
109 water) of 1: 10000 had no pronounced ability to remove Pb from polluted water, it was effective in  
110 removing Cd from solutions containing low concentration of 5 mg/l. Shale reduced the initial  
111 concentration from 5 to 0.55 mg Cd/l in a reaction period of one hour. As the addition ratio increased  
112 to 1:1000, the removal efficiency increased, particularly for Pb. Shale was able to reduce the initial  
113 concentration of Pb and Cd from 5 to 1.14 and 0.34 mg/l, respectively, in one hour reaction time. As  
114 the addition ratio increased to 1: 100, the efficiency greatly increased. Shale successfully reduced  
115 the initial Pb concentration of 5 and 10 to 0.4 and 0.7 mg/l, in a reaction period of 1 hour which were  
116 lower than the permissible level (5 mg/l) for irrigation water [20]. The corresponding values for Cd  
117 were 0.22 and 0.74 mg/l. Although these values are much lower than the initial one, they were  
118 higher than the permissible level (0.01mg/l) for irrigation water. Shale proved efficient in the  
119 remediation of higher concentration of 20 mg Cd /l at high addition ratio of 1:100. It reduces Cd  
120 concentration from 20 to 1.5 mg /l in a matter of 2 hour reaction time. Shale has negligible ability to  
121 remove Pb and Cd from solutions containing high concentrations of 50 mg/l of Pb and Cd. In  
122 general, the obtained results showed that shale has higher efficiency to remove Cd rather than Pb.  
123 This efficiency could be attributed to high CEC values of shale (Table 2) and at the same time to the  
124 character of Cd which is attracted to the negatively charged sites and exist in diffuse ion swarm as  
125 exchangeable cation rather than forming inner sphere complex with surface functional groups which  
126 is a characteristic of Pb.

127      **Table 1. Concentrations of Pb and Cd in polluted water before and after treating with shale at addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times.**

| 128            |             |         |      |       |                |          |      |       |                |          |       |       |                |                 |
|----------------|-------------|---------|------|-------|----------------|----------|------|-------|----------------|----------|-------|-------|----------------|-----------------|
| Addition ratio | Heavy metal | 5(mg/l) |      |       | R <sup>2</sup> | 10(mg/l) |      |       | R <sup>2</sup> | 50(mg/l) |       |       | R <sup>2</sup> | LSD(5%) for 24h |
|                |             | 1(h)    | 5(h) | 24(h) |                | 1(h)     | 5(h) | 24(h) |                | 1(h)     | 5(h)  | 24(h) |                |                 |
| 1:10000        | Pb          | 4.11    | 4.20 | 4.18  | 0.8450         | 8.10     | 7.70 | 9.24  | 0.8364         | 40.30    | 38.70 | 45.04 | 0.8422         | 0.26            |
| 1:10000        | Cd          | 0.55    | 3.80 | 3.40  | 0.8465         | 8.80     | 5.40 | 9.20  | 0.9408         | 46.50    | 33.00 | 52.36 | 0.9202         | 0.22            |
| 1:1000         | Pb          | 1.14    | 1.14 | 1.68  | 0.9735         | 2.70     | 2.60 | 4.40  | 0.9553         | 32.70    | 32.70 | 39.77 | 0.9735         | 0.30            |
| 1:1000         | Cd          | 0.34    | 1.11 | 1.43  | 0.8793         | 5.00     | 3.00 | 4.40  | 0.9113         | 41.50    | 28.80 | 50.00 | 0.911          | 0.26            |
| 1:100          | Pb          | 0.40    | 0.40 | 0.20  | 0.9735         | 0.70     | 0.51 | 0.98  | 0.9640         | 14.50    | 15.30 | 21.59 | 0.9964         | 0.32            |
| 1:100          | Cd          | 0.22    | 0.21 | 0.07  | 0.9893         | 0.74     | 0.77 | 0.68  | 0.8607         | 17.80    | 13.60 | 14.00 | 0.9976         | 0.31            |

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133 Table 2. Cation exchange capacity (CEC) and surface area of remedy agents.

| Remedy Agent | CEC {Cmol <sub>(c)</sub> /kg} | Surface area<br>(m <sup>2</sup> /g) |
|--------------|-------------------------------|-------------------------------------|
| Shale        | 60.13                         | 165                                 |
| Alginit      | 34.99                         | 81                                  |
| Iron oxide   | 7.49                          | 150                                 |

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138 The results (Table 1) showed that the efficiency of shale in removing Pb and Cd from  
 139 polluted water was higher at shorter equilibrium period of one hour rather than longer ones which  
 140 could be attributed to the release of exchangeable cations initially existing in the interlayer of clay  
 141 minerals, then replacing Pb and Cd readily exchanged to the surface. So that, higher reaction  
 142 time of 24 h is not recommended for shale. Similar trails have been done [21] using alkali-treated  
 143 oil shale ash as adsorbent to remove lead and cadmium ions from aqueous solutions. They  
 144 reported that adsorption of lead and cadmium ions by the modified oil shale ash depended on  
 145 adsorbent concentration, ash particle size, contact time and pH of solution. At initial concentration  
 146 of an aqueous solution of 10mg/L and that of the adsorbent 5g/L, 91% of lead and cadmium ions  
 147 was removed from the solution. These results proved lower efficiency when modified oil shale  
 148 ash was compared with the shale sample utilized in our research.

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150 **3.2 Alginit**

151 The lowest addition ratio of 1:10000 was not effective even for low concentration of 5 mg Pb/l.  
 152 The higher addition ratio of 1:1000 (Table 3) was effective only for relatively low concentration of  
 153 5mg /l, which is considerably reduced to 0.52 mg/l in a reaction time of 24 h. The efficiency of  
 154 alginit in remediation of Pb polluted water increased as the addition ratio increased. Addition ratio

155 of 1:100 significantly eliminates Pb from polluted water containing 5 and 10 mg Pb/l in a reaction  
156 time of 24h, Pb concentration in the previous solutions reduced to 0.21 and 0.46 mg/l,  
157 respectively. For water highly polluted with 50 mg Pb /l, addition ratio of 1:100 was able to reduce  
158 Pb to concentration (6.5 mg/l) little higher than the permissible level.

159 Regarding Cd, addition ratios of 1:10000 and 1:1000, gave low efficiency in removing Cd from  
160 polluted water. However, addition ratio of 1:100 proved more efficient in eliminating Cd from  
161 polluted water. It reduces the initial Cd concentrations of 5 and 10 to 0.21 and 1.57 mg/l,  
162 respectively. The results showed that, removal of Cd by alginite was time dependent since the  
163 changes in pollutant concentrations with time were significant ( $LSD_{0.05}$  ranged from 0.20 – 0.33).  
164 Based on Cd permissible level for irrigation water (0.01 mg/l), alginite showed low efficiency in Cd  
165 removal. It works only with low Cd concentration at high addition ratio of 1:100. Based on these  
166 results, it could be concluded that, unlike shale, alginite has higher efficiency in the removal of Pb  
167 rather than Cd, which could be attributed to the relatively low CEC value ( $34.99 \text{ Cmol}_{(c)}/\text{kg}$ ) of  
168 alginite (Table 2) comparing with shale ( $60.13 \text{ Cmol}_{(c)}/\text{kg}$ ), *i.e.* low electrostatic attraction between  
169 Cd and alginite surface which led to low Cd removal via exchange process. Therefore, specific  
170 adsorption of Pb is more likely to be dominant on alginite surface than the exchange process

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172      **Table 3. Concentrations of Pb and Cd in polluted water before and after treating with alginit at addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times**

| Addition ratio | Heavy metal | 5(mg/l) |      |       | R <sup>2</sup> | 10(mg/l) |       |       | R <sup>2</sup> | 50(mg/l) |       |       | R <sup>2</sup> | 173<br>LSD<br>(5%)<br>for 24<br>h |
|----------------|-------------|---------|------|-------|----------------|----------|-------|-------|----------------|----------|-------|-------|----------------|-----------------------------------|
|                |             | 1(h)    | 5(h) | 24(h) |                | 1(h)     | 5(h)  | 24(h) |                | 1(h)     | 5(h)  | 24(h) |                |                                   |
| 1:10000        | Pb          | 5.00    | 4.73 | 4.70  | 0.8733         | 10.00    | 9.50  | 9.50  | 0.8018         | 40.10    | 40.80 | 40.30 | 0.9985         | 0.26                              |
| 1:10000        | Cd          | 5.00    | 5.00 | 5.00  | Nd             | 8.90     | 10.00 | 5.50  | 0.8483         | 47.40    | 46.50 | 39.60 | 0.9967         | 0.32                              |
| 1:1000         | Pb          | 1.85    | 1.2  | 0.52  | 0.8843         | 9.01     | 8.10  | 9.68  | 0.9117         | 40.20    | 39.70 | 38.50 | 0.9352         | 0.20                              |
| 1:1000         | Cd          | 2.80    | 4.40 | 3.20  | 0.9691         | 9.10     | 8.00  | 5.20  | 0.9872         | 50.00    | 48.90 | 50.00 | 0.9859         | 0.33                              |
| 1:100          | Pb          | 0.04    | 0.21 | 0.21  | 0.8803         | 0.40     | 0.42  | 0.46  | 0.9868         | 19.80    | 17.90 | 6.50  | 0.9990         | 0.31                              |
| 1:100          | Cd          | 0.29    | 0.23 | 0.21  | 0.2845         | 2.00     | 1.70  | 1.57  | 0.9307         | 47.40    | 39.90 | 30.00 | 0.9233         | 0.31                              |

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### 178 3.3 Iron oxide

179 Table (4) shows the concentration of Pb and Cd in polluted water before and after treating with  
180 iron oxide at addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times. At the lowest  
181 addition ratio of 1:10000, iron oxide proved not efficient in the removal of Pb even from water  
182 polluted with low concentrations of 5 mg/l. As the addition ratio increased to 1:1000, iron oxide  
183 worked well with low Pb concentration of 5 mg /l and reduced the initial concentration to 0.67  
184 mg/l. However, for water polluted with higher Pb concentration of 10 mg/l, the efficiency dropped,  
185 in which the initial concentration reduced to be 3.5 mg/l in a reaction time of 24 hour. Iron oxide  
186 can be potentially efficient in removing Pb from polluted water only at high addition ratio of 1:100.  
187 This efficiency increased even for high Pb concentration of 50 mg/l. Also the removal efficiency  
188 increased significantly ( $R^2=0.888$ ) as the reaction time increased. In a reaction time of 24 hour, it  
189 eliminated Pb from solutions of initial concentration of 5 and 10, with the concentrations reduced  
190 to undetectable value (Table 4). Also, it reduced the concentration of 50 mg Pb/l to 1.67 mg/l  
191 where is lower than the permissible level (5 mg/l) for irrigation water.

192 The efficiency of Fe-oxide in removing Cd was significantly ( $LSD_{0.05}=0.24-0.32$ ) time dependent.  
193 As the reaction period increased, Cd concentration in the equilibrium solution decreased. High  
194 addition ratio of 1:100 was the most effective in removing Cd. At addition ratio of 1:100, iron oxide  
195 efficiently reduced the initial concentrations of 5 and 10 mg Cd/l to 0.1 and 0.4 mg/l, respectively,  
196 in a reaction period of 24 h. These concentrations (0.1 and 0.4 mg/l) were higher than the  
197 permissible level (0.01 mg/l) for irrigation water. Although, several methods have been adopted to  
198 remove heavy metals from polluted water, these methods succeeded only with water of high pH  
199 values and low concentrations of pollutants. At acidic conditions and relatively high  
200 concentrations of pollutants, the efficiency of these methods were limited. On the other hand, the  
201 techniques utilized in our research succeeded in decontaminate water of low pH values and high  
202 concentrations of Pb and Cd. Among these methods [22] stated, that waste iron (III)/chromium  
203 (III) hydroxide has been used as an adsorbent for the effective removal of Pb(II) from aqueous  
204 solution at pH greater than 7.0. The percent adsorption of Pb(II) increased with a decrease in  
205 concentration of Pb(II) and an increase in temperature. [23], suggested a process for removing

lead from battery industry wastewater by neutralization with NaOH, in the presence of Fe(III) salts which the lead concentration of the treated effluent is below 0.2 mg/l. [24], proposed a procedure for purifying waters polluted with metal ions [ Al(III), V(V), Ni(II), Cd(II), Co(II), Pb(II), Hg(II), Cr(II), Sn(II),Bi(II),Zn(II),and Cu(II)], by precipitation of metals as magnetic ferrite from the alkalinized solution containing iron(II) was based on the precipitation of metals as magnetic ferrite. The maximal purification efficiency (99.99%) was achieved when waste water samples are treated for 3 hours at 50°C and pH 10, Fe(II)/Total metal ratio was 15.0 and different concentrations of KMnO<sub>4</sub>.

**Table 4. Concentrations of Pb and Cd in polluted water before and after treating with iron oxide at addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times.**

| Addition ratio | Heavy metal | 5(mg/l) |      |       |       | 10(mg/l) |       |       |       | 50(mg/l) |       |       |       | LSD (5%) for 24h |
|----------------|-------------|---------|------|-------|-------|----------|-------|-------|-------|----------|-------|-------|-------|------------------|
|                |             |         |      |       | R2    |          |       |       | R2    |          |       |       | R2    |                  |
|                |             | 1(h)    | 5(h) | 24(h) |       | 1(h)     | 5(h)  | 24(h) |       | 1(h)     | 5(h)  | 24(h) |       |                  |
| 1:10000        | Pb          | 2.76    | 5.00 | 5.00  | 0.851 | 10.10    | 10.00 | 10.00 | 0.906 | 42.60    | 10.78 | 44.04 | 0.853 | 0.25             |
| 1:10000        | Cd          | 4.50    | 2.60 | 3.00  | 0.984 | 0.30     | 10.40 | 8.00  | 0.850 | 47.10    | 52.80 | 42.00 | 0.926 | 0.25             |
| 1:10000        | Pb          | 2.76    | 2.60 | 0.67  | 0.991 | 9.60     | 8.53  | 3.50  | 1.000 | 42.60    | 39.82 | 44.83 | 0.879 | 0.29             |
| 1:10000        | Cd          | 3.70    | 2.00 | 2.00  | 0.842 | 2.10     | 9.20  | 8.80  | 0.796 | 49.80    | 49.20 | 49.40 | 0.962 | 0.24             |
| 1:100          | Pb          | 0.27    | Nd   | Nd    | 0.402 | 0.20     | 0.28  | Nd    | 0.815 | 29.01    | 15.80 | 1.68  | 0.888 | -                |
| 1:100          | Cd          | 0.70    | 0.34 | 0.10  | 0.790 | 4.00     | 2.40  | 0.40  | 0.915 | 38.80    | 44.00 | 34.00 | 0.880 | 0.32             |

### 3.4. Isotherm Model:

Adsorption equilibrium measurements are used to determine the maximum or ultimate capacity. Adsorption equilibrium data are formulated into an isotherm model. The most commonly used models include Freundlich, and Langmuir isotherms [25]. The sorption data have been subjected to sorption isotherms, namely, Langmuir. The equilibrium data for metal cations over the concentration range from 5 to 50 mg/l at 30 C have been correlated with the Langmuir isotherm [26]. Langmuir (1918) isotherm which models the monolayer coverage of the sorbent surface assumes that sorption occurs at specific homogeneous sorption sites within the sorbent and intermolecular forces decrease rapidly with the distance from the sorption surface. The model is also based on the assumption that all the sorption sites are energetically identical and sorption occurs on a structurally

homogeneous sorbent [27–28]. The equilibrium data for each metal cation Cd and Pb over the concentration range from 5 to 50 mg/L at  $25 \pm 0.1$  °C have been correlated with the Langmuir:

$$C_e/C_{ads} = 1/Qb + C_e/Q \quad \text{eq. 2}$$

Where  $C_e$  is the equilibrium concentration of metal in solution,  $C_{ads}$  is the amount of metal ions sorbed per unit mass onto Alginit, Iron Oxid and Shale. A linear plot is obtained when  $C_e/C_{ads}$  is plotted against  $C_e$  over the entire concentration range of metal ions investigated Figs. 1 and 2. The Langmuir model effectively described the sorption data with all  $R^2$  values > 0.9.

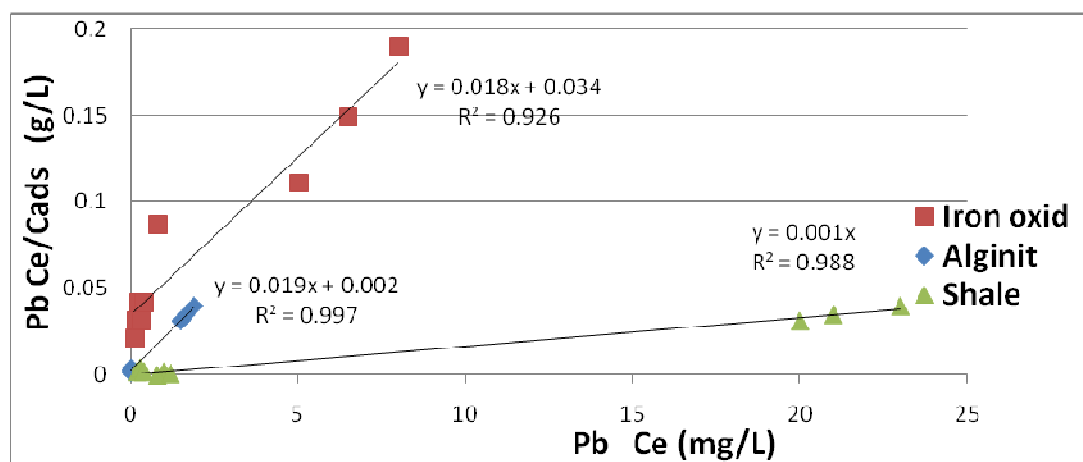


Fig. 1 Langmuir plots for Lead ions adsorption onto different Additive

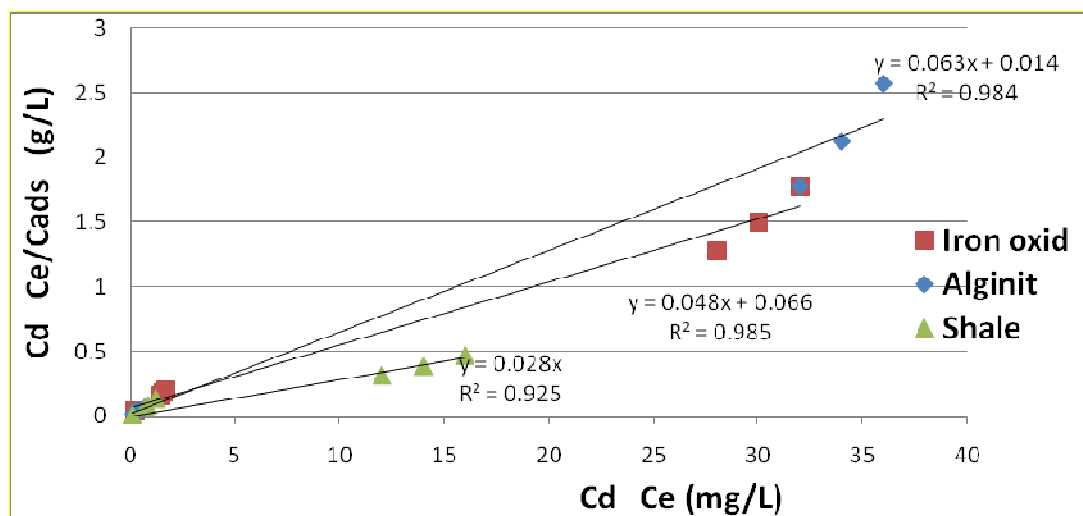


Fig. 2 Langmuir plots for Cadmium ions adsorption onto different Additive

The equilibrium data for each metal cation over the concentration range from 5 to 50 mg/L at  $30 \pm 0.1$  °C has been correlated with the Freundlich isotherm, [25, 29, and 30].:

$$\text{Log } C_{ads} = \text{Log } K + 1/n \text{ Log } C_e \quad \text{eq. 3}$$

Where  $C_e$  is the equilibrium concentration in mg/l and  $C_{ads}$  shows that the adsorption seems to follow the Freunlich isotherm model as well as the Langmuir isotherm. A linear plot is obtained when  $\log C_e$

is plotted against  $\log C_{ads}$  over the entire concentration range of metal ions investigated and the values of  $K$  and  $n$  can be calculated from the intercept and the slope of this straight line, respectively (Figs. 3, 4). The result shows that all metals under investigation have a numerical value of  $1/n < 1$ ; value of  $n$  is greater than unity, suggesting that adsorption intensity is favorable at high concentrations but much less at lower concentrations.

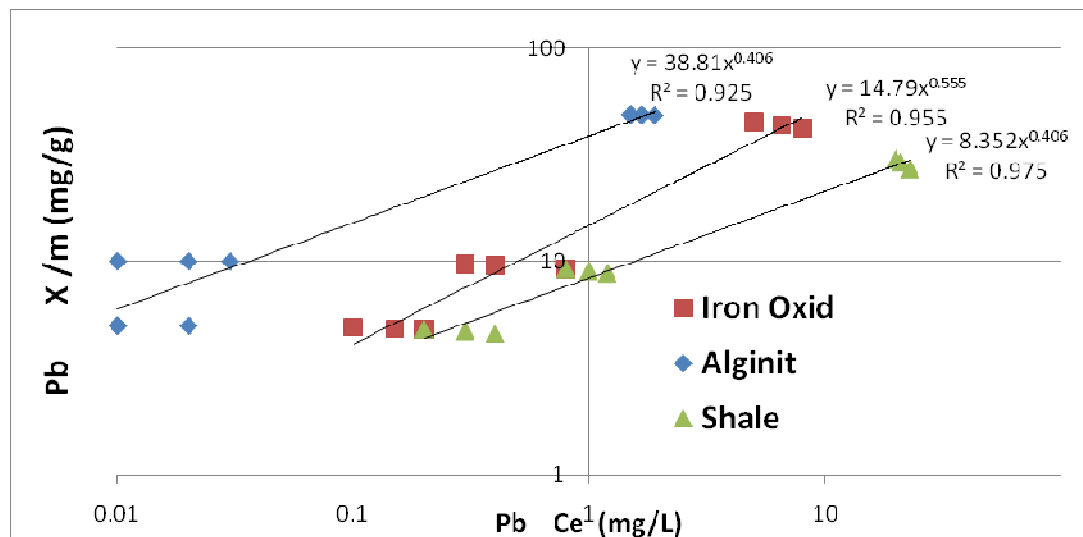


Fig. 3 Freundlich plots for Lead ions adsorption onto different Additive.

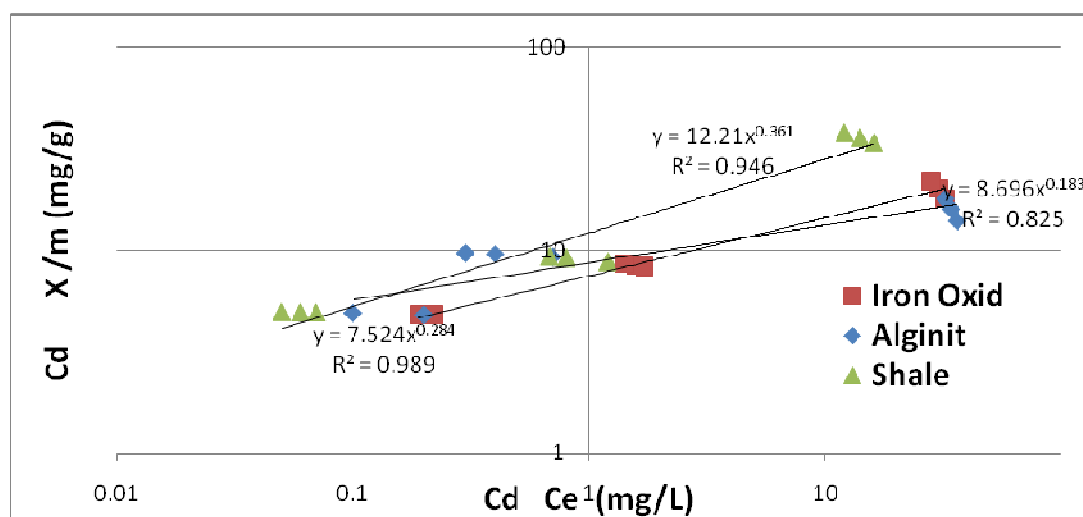


Fig. 4 Freundlich plots for Cadmium ions adsorption onto different Additive.

#### 4. CONCLUSION

All remedy agents, shale, alginit and iron oxides, proved potentially efficient in the removal of Pb and Cd from water polluted of wide range of Pb and Cd varied between 5 to 50 mg/l. Generally, their efficiency increased as the addition ratio between remedy agents and polluted water

increased from 1:10000 – 1:100. Among all tested agents, shale had the highest efficiency for the removal of Cd. It had high potential ability to remediate higher concentration of 20 mg Cd /l at addition ratio of 1:100. However, shorter equilibrium period of 1 hour was more effective than the higher one of 24 h. Alginite proved high efficiency in removing Pb and Cd from polluted water when added at high ratio of 1:100. Unlike shale, alginite had higher removal efficiency for Pb rather than Cd. Iron oxide had potential efficiency in removing Pb from polluted water only at high addition ratio of 1:100. This efficiency was shown even for high Pb concentration of 50 mg/l. In a reaction period of 24 hour, it eliminated Pb from solutions of initial concentration of 5 and 10, mg/l, while reducing the concentration of 50 to a level (1.67 mg/l) lower than irrigation water permissible level (5 mg/l). The Langmuir model described the sorption data with R<sup>2</sup> values ranged from 0.92 to 0.98 with lead and cadmium, while Freundlich and Langmuir isotherm, suggesting that adsorption intensity is favorable at high concentrations but much less at lower concentrations. The sorption data of different sorption isotherms, Langmuir and Freundlich were suitable to describe the adsorption equilibrium measurements to determine the maximum or ultimate capacity.

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