1 # Removal of Pb^{2+} and Cd^{2+} 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 alginit, 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 alginit, 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, alginit 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.

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 0.1ug/1 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 1mg/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, alginit, 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 trails, 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_3 as matrix). A series of standard lead solutions of 5,

50   10, 50 and 100 mg Pb/l were prepared and used to test the ability of remedy agents in Pb removal.

51   Cadmium polluted water was prepared using cadmium stock solution (1000 mg Cd/l in 0.5 M HNO_3

52   as matrix). A series of standard cadmium solutions of 5, 10, 20 and 50 mg Cd/l were prepared and

53   used to test the efficiency of remedy agents in Cd removal.

54   **2.2. Remedy Agents**

55   Three remedy agents, alginit, shale, and iron oxide, were used for polluted water remediation trials.

56   These agents are common, inexpensive and easy to obtain. Besides, they could be separated easily

57   from treated water at the end of the remediation process. These agents were selected based on

58   their negatively charged surface and high adsorption capacity, which was attributed to their high

59   surface area. The important Characteristics of the remedy agents are summarized in the following

60   paragraphs.

61   **2.2.1 Alginit:** Alginit is a natural rock out of the oil shale family. It originated from fossil algae

62   biomass and pumice, descents from the mine in Gerce, Hungary. The essential ingredients of alginit

63   [15] are high of organic matter (19%), clay (54%) and lime content (22%). The clay is rich in

64   montmurillionte (52%).

65   **2.2.2 Shale**: Shale is a naturally occurring material exists in many places in Egypt at different

66   depths. It mainly consists of clay (55%). The clay is rich in Montomorillonit. Chemical analysis

67   showed that the shale contains high amount of salt, the electrical conductivity (EC) of 1:2.5 water

68   extract equals 10.63 dS/m and pH = 7.31. Sodium was the dominate cation.

69   **2.2.3. Iron Oxide (60 % Fe):** The sample of iron oxide is imported from Roseland Kazreti. The

70   Chemical composition of the iron Oxide is Fe_d (60%), Fe_o (19%), Al (0.16 mg/ kg), Zn (12.8 mg/kg)

71   and Cu (9.94mg/kg).

72   **2.3. Remediation studies**

73   Remedy agents of Alginit, shale, and iron oxide, were added to heavy metals polluted water at

74   different solid: solution ratios of 1:10000, 1:1000 and 1:100. The mixtures were then gently agitated

75   and subjected to different equilibrium periods of 1, 5 and 24 hrs. At the end of each equilibrium

76   period, the supernatant solution was obtained by centrifuging the mixtures at 3000 rpm for 10

77   minutes. Concentrations of studied heavy metals (Pb and Cd) were measured before adding the

78   remedy agent and at the end of equilibrium period as well as the pH and electrical Conductivity (Ec).

79 All trials were done in three replicates. Heavy metal removal efficiency (%) of the agents can get

80 from corresponding concentrations in solutions (mg/L) from equation:

81 ***Heavy metal removal efficiency (%) = <ins>metal conc (mg/L) Befor - metal conc. (mg/L) After</ins> * 100 eq. 1***
82 ***Conc. (mg/L) Befor***
83

84 **2.4. Analytical procedures**

85 Total concentrations of heavy metals (Pb, Cd, Ni, Co, Zn, Mn, Cu and Cr) were determined in both

86 suspended matter and clear water. Suspended matter was digested using Aqua Regia method **[16].**

87 Concentrations of Pb and Cd in polluted water as well as treated ones were determined using

88 Atomic Absorption Spectrophotometer (UNICAM, 969) **[17]**. Standard solutions were prepared from

89 mono element stock solutions containing 1000 mg/l of heavy metals. The intensity of Pb 283.3, and

90 Cd 228.8 nm spectral lines was measured. Every measurement as done three times, and then the

91 arithmetical mean and standard deviations were calculated. The pH was measured using a digital

92 Orion pH meter (model 420A). The solutions were prepared using "pure for analysis" and "chemically

93 pure" grade chemicals. All the experiments were performed at room temperature $18 \pm 2\ ℃$..

94 The electrical conductivity (EC) of the reacted solutions was measured using digital YSIEC meter

95 (model 35). Cation exchange capacity (CEC) of remedy agents were determined using ammonium

96 acetate method as described by **[18].**Specific surface area of remedy agents were determined using

97 O- phenanthroline method [19**].**

98 **2.5. Statistical analyses**

99 All statistical analyses were carried out by SAS version 9 software for all data of remediation trials.

100 R- Squared values (R^2) and Equation were considered significant (*p*-values <0.05) for the analysis of

101 variance test (ANOVA).

102 **3. RESULT AND DISSCUTION**

> **Comment [i1]:** This should be replaced by "RESULTS AND DISCUSSION"

103 Efficiency of remedy agents (shale, alginit and iron oxides) to remove Pb and Cd from synthetically

104 polluted water containing various concentrations of 5, 10 and 50 mg/l were examined using different

105 addition ratios (1:10000, 1:1000 and 1:100) of remedy agents: polluted water, at different reaction

106 periods varying between 1 to 24 hour. The results obtained were as the follows.

107 **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**.

Addition ratio	Heavy metal	5(mg/l)			R²	10(mg/l)			R²	50(mg/l)			R²	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 {$Cmol_{(c)}$/kg}	Surface area (m^2/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 alginit 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), alginit 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, alginit has higher efficiency in the removal of Pb

167 rather than Cd, which could be attributed to the relatively low CEC value (34.99 Cmol $_{(c)}$/kg) of

168 alginit (Table 2) comparing with shale (60.13 Cmol$_{(c)}$ /kg), *i.e.* low electrostatic attraction between

169 Cd and alginit surface which led to low Cd removal via exchange process. Therefore, specific

170 adsorption of Pb is more likely to be dominant on alginit 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^2	10(mg/l)			R^2	50(mg/l)			R^2	LSD (5%) for 24 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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3.3 Iron oxide

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

The efficiency of Fe-oxide in removing Cd was significantly ($LSD_{0.05}$=0.24-0.32) time dependent. As the reaction period increased, Cd concentration in the equilibrium solution decreased. High addition ratio of 1:100 was the most effective in removing Cd. At addition ratio of 1:100, iron oxide efficiently reduced the initial concentrations of 5 and 10 mg Cd/l to 0.1 and 0.4 mg/l, respectively, in a reaction period of 24 h. These concentrations (0.1 and 0.4 mg/l) were higher than the permissible level (0.01 mg/l) for irrigation water. Although, several methods have been adopted to remove heavy metals from polluted water, these methods succeeded only with water of high pH values and low concentrations of pollutants. At acidic conditions and relatively high concentrations of pollutants, the efficiency of these methods were limited. On the other hand, the techniques utilized in our research succeeded in decontaminate water of low pH values and high concentrations of Pb and Cd. Among these methods [22] stated, that waste iron (III)/chromium (III) hydroxide has been used as an adsorbent for the effective removal of Pb(II) from aqueous solution at pH greater than 7.0. The percent adsorption of Pb(II) increased with a decrease in concentration of Pb(11) and an increase in temperature. [23], suggested a process for removing

206 lead from battery industry wastewater by neutralization with NaOH, in the presence of Fe(III) salts

207 which the lead concentration of the treated effluent is below O.2 mg/l. [24], proposed a procedure

208 for purifying waters polluted with metal ions [Al(I1I), V(V), Ni(II), Cd(II), Co(II), Pb(II), Hg(II), Cr(II),

209 Sn(II),Bi(II),Zn(II),and Cu(II)], by precipitation of metals as magnetic ferrite from the alkalinized

210 solution containing iron(II) was based on the precipitation of metals as magnetic ferrite. The

211 maximal purification efficiency (99.99%) was achieved when waste water samples are treated for

212 3 hours at 50℃ and pH 10, Fe(1I)/Total metal ratio was 15.0 and different concentrations of

213 KMnO4.

214 **Table 4. Concentrations of Pb and Cd in polluted water before and after treating with iron oxide at**

215 **addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times.**

Addition ratio	Heavy metal	5(mg/l)			R2	10(mg/l)			R2	50(mg/l)			R2	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	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

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217 **3.4. Isotherm Model:**

218 Adsorption equilibrium measurements are used to determine the maximum or ultimate capacity.

219 Adsorption equilibrium data are formulated into an isotherm model. The most commonly used

220 models include Freundlich, and Langmuir isotherms [25]. The sorption data have been subjected to

221 sorption isotherms, namely, Langmuir. The equilibrium data for metal cations over the concentration

222 range from 5 to 50 mg/l at 30 C have been correlated with the **Langmuir isotherm** [26]. Langmuir

223 (1918) isotherm which models the monolayer cover age of the sorbent surface assumes that

224 sorption occurs at specific homogeneous sorption sites within the sorbent and intermolecular forces

225 decrease rapidly with the distance from the sorption surface. The model is also based on the

226 assumption that all the sorption sites are energetically identical and sorption occurs on a structurally

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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.
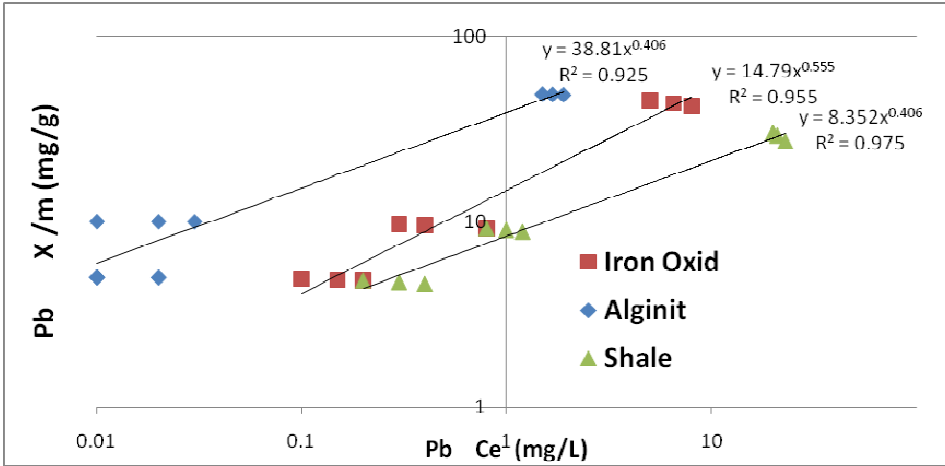

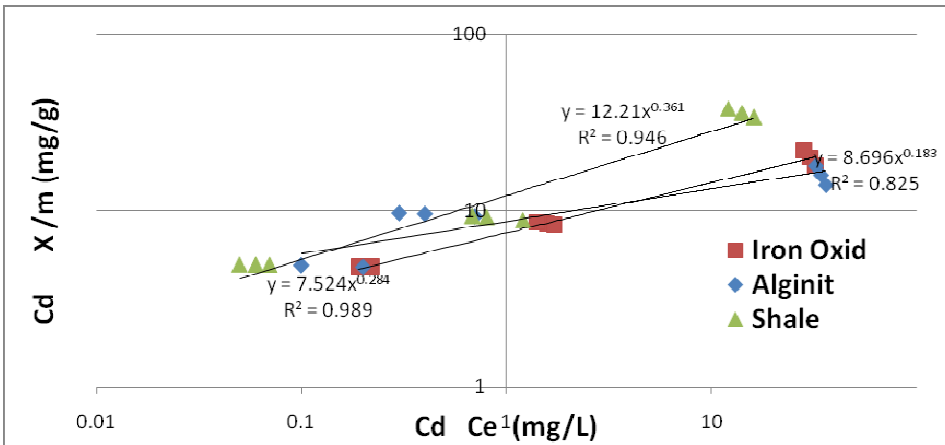**Fig. 3 Freundlich plots for Lead ions adsorption onto different Additive.**

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

4. CONCLUTION

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

258 increased from 1:10000 – 1:100. Among all tested agents, shale had the highest efficiency for the

259 removal of Cd. It had high potential ability to remediate higher concentration of 20 mg Cd /l at

260 addition ratio of 1:100. However, shorter equilibrium period of 1 hour was more effective than the

261 higher one of 24 h. Alginit proved high efficiency in removing Pb and Cd from polluted water

262 when added at high ratio of 1:100. Unlike shale, alginit had higher removal efficiency for Pb rather

263 than Cd. Iron oxide had potential efficiency in removing Pb from polluted water only at high

264 addition ratio of 1:100. This efficiency was shown even for high Pb concentration of 50 mg/l. In a

265 reaction period of 24 hour, it eliminated Pb from solutions of initial concentration of 5 and 10,

266 mg/l, while reducing the concentration of 50 to a level (1.67 mg/l) lower than irrigation water

267 permissible level (5 mg/l). The Langmuir model described the sorption data with R2 values

268 ranged from 0.92 to 0.98 with lead and cadmium, while Freundlich and Langmuir isotherm,

269 suggesting that adsorption intensity is favorable at high concentrations but much less at lower

270 concentrations. The sorption data of different sorption isotherms, Langmuir and Freundlich were

271 suitable to describe the adsorption equilibrium measurements to determine the maximum or

272 ultimate capacity.

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