

Removal of Pb²⁺ and Cd²⁺ from contaminated water using low-cost materials

ABSTRACT

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

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

Introduction

Heavy metal Release onto the water 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/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 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 $\mu\text{g/kg}$ of body weight [6]. The guideline value for lead in drinking water given by WHO is 0.01 mg/l [6].

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.

Material and methods

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, 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_3 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.

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.

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 [7] are high of organic matter (19%), clay (54%) and lime content (22%). The clay is rich in montmorillonite (52%).

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

58 **Iron Oxide (60 % Fe):** The sample of iron oxide is imported from Roseland Kazreti. The Chemical
59 composition of the iron Oxide is Fe_d (60%), Fe_o (19%), Al (0.16 mg/ kg), Zn (12.8 mg/kg) and Cu
60 (9.94mg/kg).

61 **Remediation studies**

62 Remedy agents of Alginit, shale, and iron oxide, were added to heavy metals polluted water at different solid:
63 solution ratios of 1:10000, 1:1000 and 1:100. The mixtures were then gently agitated and subjected to different
64 equilibrium periods of 1, 5 and 24 hrs. At the end of each equilibrium period, the supernatant solution was
65 obtained by centrifuging the mixtures at 3000 rpm for 10 minutes. Concentrations of studied heavy metals (Pb
66 and Cd) were measured before adding the remedy agent and at the end of equilibrium period as well as the pH
67 and electrical Conductivity (Ec). All trials were done in three replicates. Heavy metal removal efficiency (%)
68 of the agents can get from corresponding concentrations in solutions (mg/L) from equation:

$$69 \text{ Heavy metal removal efficiency (\%)} = \frac{\text{metal conc (mg/L) Befor} - \text{metal conc. (mg/L) After}}{\text{Conc. (mg/L) Befor}} * 100 \text{ eq. 1}$$

72 **Analytical procedures**

73 Total concentrations of heavy metals (Pb, Cd, Ni, Co, Zn, Mn, Cu and Cr) were determined in both suspended
74 matter and clear water. Suspended matter was digested using Aqua Regia method [8]. Concentrations of Pb
75 and Cd in polluted water as well as treated ones were determined using Atomic Absorption Spectrophotometer
76 (UNICAM, 969) [9]. Standard solutions were prepared from mono element stock solutions containing
77 1000 mg/l of heavy metals. The intensity of Pb 283.3, and Cd 228.8 nm spectral lines was
78 measured. Every measurement as done three times, and then the arithmetical mean and standard
79 deviations were calculated. The pH was measured using a digital Orion pH meter (model 420A). The
80 solutions were prepared using "pure for analysis" and "chemically pure" grade chemicals. All the
81 experiments were performed at room temperature 18 ± 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 [10]. Specific surface area of remedy agents were determined using O- phenanthroline method [11].

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).

Results and discussion

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.

Shale

The results (Table 1) showed that, although at the low addition ratio (shale: heavy metal polluted water) of 1: 10000 had no pronounced ability to remove Pb from polluted water, it was effective in removing Cd from solutions containing low concentration of 5 mg/l. Shale reduced the initial concentration from 5 to 0.55 mg Cd/l in a reaction period of one hour. As the addition ratio increased to 1:1000, the removal efficiency increased, particularly for Pb. Shale was able to reduce the initial concentration of Pb and Cd from 5 to 1.14 and 0.34 mg/l, respectively, in one hour reaction time. As the addition ratio increased to 1: 100, the efficiency greatly increased. Shale successfully reduced 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 lower than the permissible level (5 mg/l) for irrigation water [12]. The corresponding values for Cd were 0.22 and 0.74 mg/l. Although these values are much lower than the initial one, they were higher than the permissible level (0.01mg/l) for irrigation water. Shale proved efficient in the remediation of higher concentration of 20 mg Cd /l at high addition ratio of 1:100. It reduces Cd concentration from 20 to 1.5 mg /l in a matter of 2 hour reaction time. Shale has negligible ability to remove Pb and Cd from solutions containing high concentrations of 50 mg/l of Pb and Cd. In general, the obtained results showed that shale has higher efficiency to remove Cd rather than Pb. This efficiency could be attributed to high CEC

112 values of shale (Table 2) and at the same time to the character of Cd which is attracted to the negatively
113 charged sites and exist in diffuse ion swarm as exchangeable cation rather than forming inner sphere complex
114 with surface functional groups which is a characteristic of Pb.

115 **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)				R ²	10(mg/l)			R ²	50(mg/l)			R ²	116 LSD(5%) for
		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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121 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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126 The results (Table 1) showed that the efficiency of shale in removing Pb and Cd from polluted
 127 water was higher at shorter equilibrium period of one hour rather than longer ones which could be
 128 attributed to the release of exchangeable cations initially existing in the interlayer of clay minerals, then
 129 replacing Pb and Cd readily exchanged to the surface. So that, higher reaction time of 24 h is not
 130 recommended for shale. Similar trails have been done [13] using alkali-treated oil shale ash as adsorbent to
 131 remove lead and cadmium ions from aqueous solutions. They reported that adsorption of lead and cadmium
 132 ions by the modified oil shale ash depended on adsorbent concentration, ash particle size, contact time and
 133 pH of solution. At initial concentration of an aqueous solution of 10mg/L and that of the adsorbent 5g/L,
 134 91% of lead and cadmium ions was removed from the solution. These results proved lower efficiency
 135 when modified oil shale ash was compared with the shale sample utilized in our research

136 *Alginit*

137 The lowest addition ratio of 1:10000 was not effective even for low concentration of 5 mg Pb/l. The higher
 138 addition ratio of 1:1000 (Table 3) was effective only for relatively low concentration of 5mg /l, which is
 139 considerably reduced to 0.52 mg/l in a reaction time of 24 h. The efficiency of alginit in remediation of Pb
 140 polluted water increased as the addition ratio increased. Addition ratio of 1:100 significantly eliminates Pb

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

144 Regarding Cd, addition ratios of 1:10000 and 1:1000, gave low efficiency in removing Cd from polluted
145 water. However, addition ratio of 1:100 proved more efficient in eliminating Cd from polluted water. It
146 reduces the initial Cd concentrations of 5 and 10 to 0.21 and 1.57 mg/l, respectively. The results showed
147 that, removal of Cd by alginite was time dependent since the changes in pollutant concentrations with time
148 were significant ($LSD_{0.05}$ ranged from 0.20 – 0.33). Based on Cd permissible level for irrigation water (0.01
149 mg/l), alginite showed low efficiency in Cd removal. It works only with low Cd concentration at high
150 addition ratio of 1:100. Based on these results, it could be concluded that, unlike shale, alginite has higher
151 efficiency in the removal of Pb rather than Cd, which could be attributed to the relatively low CEC value
152 (34.99 $Cmol_{(c)}/kg$) of alginite (Table 2) comparing with shale (60.13 $Cmol_{(c)}/kg$), *i.e.* low electrostatic
153 attraction between Cd and alginite surface which led to low Cd removal via exchange process. Therefore,
154 specific adsorption of Pb is more likely to be dominant on alginite surface than the exchange process

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156 Table 3. Concentrations of Pb and Cd in polluted water before and after treating with alginat 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	157 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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162 ***Iron oxide***

163 Table (4) shows the concentration of Pb and Cd in polluted water before and after treating with iron oxide
164 at addition ratios of 1:10000, 1:1000 and 1:100 for different reaction times. At the lowest addition ratio of
165 1:10000, iron oxide proved not efficient in the removal of Pb even from water polluted with low
166 concentrations of 5 mg/l. As the addition ratio increased to 1:1000, iron oxide worked well with low Pb
167 concentration of 5 mg /l and reduced the initial concentration to 0.67 mg/l. However, for water polluted
168 with higher Pb concentration of 10 mg/l, the efficiency dropped, in which the initial concentration reduced
169 to be 3.5 mg/l in a reaction time of 24 hour. Iron oxide can be potentially efficient in removing Pb from
170 polluted water only at high addition ratio of 1:100. This efficiency increased even for high Pb concentration
171 of 50 mg/l. Also the removal efficiency increased significantly ($R^2=0.888$) as the reaction time increased.
172 In a reaction time of 24 hour, it eliminated Pb from solutions of initial concentration of 5 and 10, with the
173 concentrations reduced to undetectable value (Table 4). Also, it reduced the concentration of 50 mg Pb/l to
174 1.67 mg/l where is lower than the permissible level (5 mg/l) for irrigation water.

175 The efficiency of Fe-oxide in removing Cd was significantly ($LSD_{0.05}=0.24-0.32$) time dependent. As the
176 reaction period increased, Cd concentration in the equilibrium solution decreased. High addition ratio of
177 1:100 was the most effective in removing Cd. At addition ratio of 1:100, iron oxide efficiently reduced the
178 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.
179 These concentrations (0.1 and 0.4 mg/l) were higher than the permissible level (0.01 mg/l) for irrigation
180 water. Although, several methods have been adopted to remove heavy metals from polluted water, these
181 methods succeeded only with water of high pH values and low concentrations of pollutants. At acidic
182 conditions and relatively high concentrations of pollutants, the efficiency of these methods were limited.
183 On the other hand, the techniques utilized in our research succeeded in decontaminate water of low pH
184 values and high concentrations of Pb and Cd. Among these methods [14] stated, that waste iron
185 (III)/chromium (III) hydroxide has been used as an adsorbent for the effective removal of Pb(II) from
186 aqueous solution at pH greater than 7.0. The percent adsorption of Pb(II) increased with a decrease in
187 concentration of Pb(II) and an increase in temperature. [15], suggested a process for removing lead from
188 battery industry wastewater by neutralization with NaOH, in the presence of Fe(III) salts which the lead
189 concentration of the treated effluent is below 0.2 mg/l. [16], proposed a procedure for purifying waters

190 polluted with metal ions [Al(III), V(V), Ni(II), Cd(II), Co(II), Pb(II), Hg(II), Cr(II),
 191 Sn(II),Bi(II),Zn(II),and Cu(II)], by precipitation of metals as magnetic ferrite from the alkalized solution
 192 containing iron(II) was based on the precipitation of metals as magnetic ferrite. The maximal purification
 193 efficiency (99.99%) was achieved when waste water samples are treated for 3 hours at 50°C and pH 10,
 194 Fe(II)/Total metal ratio was 15.0 and different concentrations of KMnO_4 .

195 **Table 4. Concentrations of Pb and Cd in polluted water before and after treating with iron**
 196 **oxide 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
		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	0.85
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	0.92
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	0.87
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	0.96
1:100	Pb	0.27	Nd	Nd	0.402	0.20	0.28	Nd	0.815	29.01	15.80	1.68	0.88
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	0.88

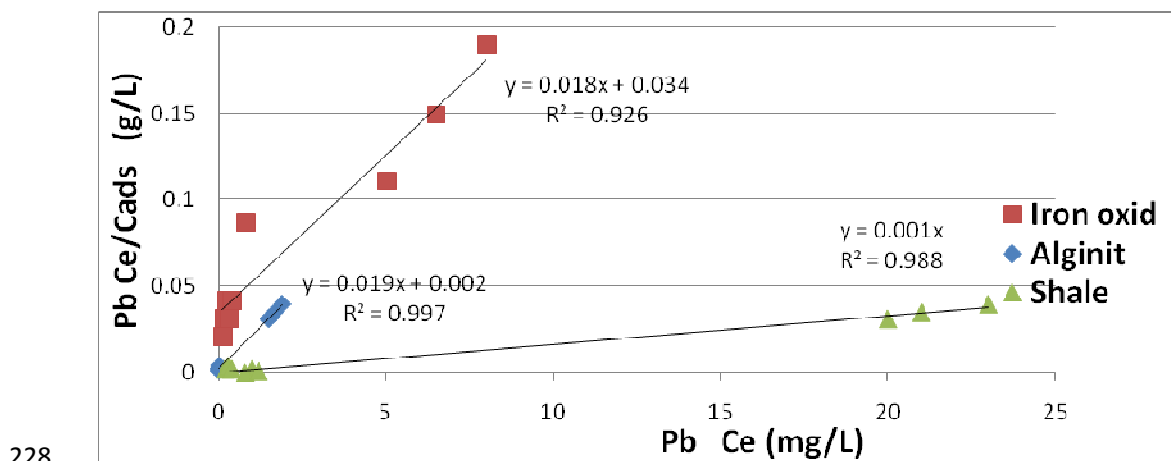
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210 Isotherm Model:

211 Adsorption equilibrium measurements are used to determine the maximum or ultimate capacity.
 212 Adsorption equilibrium data are formulated into an isotherm model. The most commonly used
 213 models include Freundlich, and Langmuir isotherms [17]. The sorption data have been subjected to
 214 sorption isotherms, namely, Langmuir. The equilibrium data for metal cations over the
 215 concentration range from 5 to 50 mg/l at 30 C have been correlated with the Langmuir isotherm
 216 [18]. Langmuir (1918) isotherm which models the monolayer cover age of the sorbent surface
 217 assumes that sorption occurs at specific homogeneous sorption sites within the sorbent and
 218 intermolecular forces decrease rapidly with the distance from the sorption surface. The model is
 219 also based on the assumption that all the sorption sites are energetically identical and sorption
 220 occurs on a structurally homogeneous sorbent [19–20]. The equilibrium data for each metal cation
 221 Cd and Pb over the concentration range from 5 to 50 mg/L at 25° ±0.1 C have been correlated with
 222 the Langmuir:

$$223 \quad C_e/C_{ads} = 1/Qb + C_e/Q \quad \text{eq. 2}$$

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



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

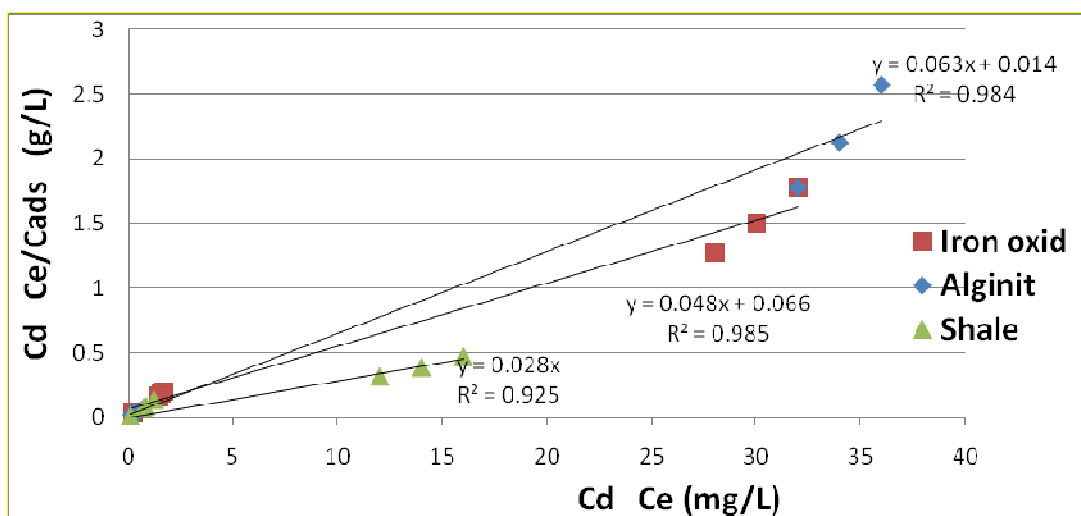


Fig. 2 Langmuir plots for Cadmium ions adsorption onto different Additive

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. Alginit proved high efficiency in removing Pb and Cd from polluted water when added at high ratio of 1:100. Unlike shale, alginit 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).

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