Removal Pb^{2+} and Cd^{2+} from contaminated water by alternative low-cost materials

ABSTRACT

Heavy metals that exist in municipal wastewater can cause many problems for human hygiene and environment. Therefore, it should be removed from wastewater before being used in irrigation. Materials of high surface reactivity; alginit, shale and iron oxide are used as a potential sorbents to eliminate Pb and Cd from polluted water. In remediation trials, 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 submited to different equilibrium periods of 1, 5 and 24 h. The results proved the efficiency of tested agents (shale, alginit, and iron oxide) to remove Pb and Cd from polluted water contain 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, alginit and Fe-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

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 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.

Material and methods

Synthesized polluted water

Synthesized polluted water was prepared by accurate diluting 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 solution 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, alginit, shale, and iron oxide, were used for polluted water remediation trials. These agents are common, inexpensive and easily to be obtained. 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 attributed to their high surface area. The important Characteristics of the remedy agents are summarized in the following paragraphs.

Alginit: Alginit is a natural rock out of the oil shale family. It originated from fossil algae biomass and pumice, descents from the mine in Gerce, Hungary. The essential ingredients of alginit [14] are high content of organic matter (19%), clay (54%) and lime content (22%). The clay is rich in montmurillionte (52%).

Shale: Shale is a naturally occurring material exists in many places in Egypt at different depths. It is mainly consists of clay (55%). The clay is rich in Montomorillonit. 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.

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

Remediation trials

Remedy agents of Alginit, 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 submit 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.

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 **[15].** Concentrations of Pb and Cd in polluted water as well as treated ones were determined using Atomic Absorption Spectrophotometer (UNICAM, 969) (APHA, 1998). The pH was measured using digital Orion pH meter (model 420A).

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 **[16].**Specific surface area of remedy agents were determined using O- phenanthroline method [17]**.**

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, alginit and iron oxides) to remove Pb and Cd from synthetically polluted water contain 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 h. The obtained results are displayed as the following.

Shale

The results (Table 1) showed that, although the low addition ratio (shale: heavy metal polluted water) of 1: 10000 proved no efficiency to remove Pb from polluted water, it was effective in removing Cd from solutions containing low concentration of 5 mg/l. Shale reduces the initial concentration from 5 to 0.55 mg Cd/l in a reaction period of one hr. 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 h 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 hr which were lower than the permissible level (5 mg/l) for irrigation water [18]. 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 efficiency to remediate 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 h reaction time. Shale proved no potential efficiency to remove Pb and Cd from solutions contain 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 values of shale (Table 2) and at the same time to the character of Cd which is attracted to the negatively charged sites and exist in diffuse ion swarm as exchangeable cation rather than forming inner sphere complex with surface functional groups which is a character of Pb.

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**	**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**

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

The results (Table 1) showed that the efficiency of shale in removing Pb and Cd from polluted water was higher at shorter equilibrium period of one h rather longer ones which could be attributed to the release of exchangeable cations initially exist in the interlayer of clay minerals, then replacing Pb and Cd readily exchanged to the surface. So that, higher reaction time of 24 h is not recommended for shale. Similar trails have been done **[20]** using alkali-treated oil shale ash as adsorbent to remove lead and cadmium ions from aqueous solutions. They reported that adsorption of lead and cadmium ions by the modified oil shale ash depended on adsorbent concentration, ash particle size, contact time and pH of solution. At initial concentration of an aqueous solution of 10mg/L and that of the adsorbent 5g/L, 91% of lead and cadmium ions was removed from the solution. These results proved lower efficiency of the modified oil shale ash comparing with the shale sample utilized in our research

Alginit

The lowest addition ratio of 1:10000 was not effective even for low concentration of 5 mg Pb/l. The higher addition ratio of 1:1000 (Table 3) was effective only for relatively low concentration of 5mg /l, which is considerably reduced to 0.52 mg/l in a reaction time of 24 h. The efficiency of alginit in remediation of Pb polluted water increased as the addition ratio increased. Addition ratio of 1:100 significantly eliminates Pb from polluted water contain 5 and 10 mg Pb/l in a reaction time of 24h, Pb concentration in the previous solutions reduced to 0.21 and 0.46 mg/l, respectively. For water highly polluted with 50 mg Pb /l, addition ratio of 1:100 was able to reduce Pb to concentration (6.5 mg/l) little higher than the permissible one.

Regarding Cd, addition ratios of 1:10000 and 1:1000, showed low efficiency to remove Cd from polluted water. However, addition ratio of 1:100 proved high efficiency in eliminating Cd from polluted water. It reduces the initial Cd concentrations of 5 and 10 to 0.21 and 1.57 mg/l, respectively. The results show that, removal of Cd by alginit was time dependent since the changes in pollutant concentrations with time was significant ($LSD_{0.05}$ ranged from 0.20 – 0.33). Based on Cd permissible level for irrigation water (0.01 mg/l), alginit showed low efficiency in Cd removal. It works only with low Cd concentration at high addition ratio of 1:100. Based on these results, it could be concluded that, unlike shale, alginit has higher efficiency to remove Pb rather than Cd, which could be attributed to the relatively low CEC value (34.99 $Cmol_{(c)}$/kg) of alginit (Table 2) comparing with shale (60.13 $Cmol_{(c)}$ /kg), *i.e.* low electrostatic attraction between Cd and alginit surface which lead to low Cd removal via exchange process. On the other hand, alginit surface contains both organic and inorganic functional groups due to its high contents of both organic matter (19%) and smectite mineral (54%). Therefore, specific adsorption of Pb is more likely to be dominant on alginit surface than the exchange process

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**

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 no efficiency remove Pb even from water polluted with low concentrations of 5 mg/l. As the addition ratio increased to 1:1000, iron oxide works 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 h. Iron oxide has potential efficiency in removing Pb from polluted water only at high addition ratio of 1:100. This efficiency was extended 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 h, it eliminates Pb from solutions of initial concentration of 5 and 10, which the concentrations reduced to undetectable value (Table 4). Also, it reduced the concentration of 50 mg Pb/l to 1.67 mg/l which 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, Fe-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 was limited. On the other hand, the techniques utilized in our research succeeded to decontaminate water of low pH values and high concentrations of Pb and Cd. Among these methods, **[21]**, stated that the 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. **[22],** 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 O.2 mg/l. **[23]**, proposed a procedure for purifying waters polluted with metal ions [Al(I1I), 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 3hours at 50°C and pH 10, Fe(1I)/Total metal ratio was *15.0* and different concentrations of $KMnO_4$.

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)			R^2	10(mg/l)			R^2	50(mg/l)			R^2	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

Conclusion

All remedy agents, shale, alginit and iron oxides, proved potential efficiency to remove 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 has highest efficiency to remove Cd. It proved high potential ability to remediate higher concentration of 20 mg Cd /l at addition ratio of 1:100. However, shorter equilibrium period of 1 h was effective than 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 has higher efficiency to remove Pb rather than Cd. Iron oxide has potential efficiency in removing Pb from polluted water only at high addition ratio of 1:100. This efficiency was extended even for high Pb concentration of 50 mg/l. In a reaction period of 24 h, it eliminates Pb from solutions of initial concentration of 5 and 10, while reduces the concentration of 50 to a level (1.67 mg/l) lower than irrigation water permissible level (5 mg/l).

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