PHYTOREMEDIATION OF LEAD POLLUTED WATER USING FIVE DIFFERENT NATURAL MATERIALS

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ABSTRACT

Pollution of the environment with toxic metals is widespread including wastewater. Lead is the most element concerning health and environment due to its accumulation potential in the food chain and also in ground water. The aim of this research was to study the adsorption ability of five different natural materials such as (Cotton stalks, Acacia, Orange peels, Rice straw and Pomegranate peels) for removal of lead ions from lead polluted solution and industrial wastewater and the effect of water remediation on the growth of sunflower plants.

Lead polluted solution (200 ppm Pb) was treated with the different portions of natural materials i.e. 0.25, 0.5 and 1 g/100 ml. Residual concentration of lead in the solution was measured after 24, 48 and 72 h. lead concentration was decreased after 72h using cotton stalks, acacia, orange peels, rice straw and pomegranate peels from 200 ppm to 1.07 (89.3%), 1.45 (85.5%), 1.20 (88%), 0.85 (91.5%) and 0.54 (94.6%), respectively. A Pot experiment under greenhouse conditions in a virgin soil was conducted in to determine the effect of water remediation on the growth of sunflower plants (*Helianthus annuus* cv. Avante) and was irrigated using industrial wastewater collected from Helwan iron and steel industries. Data indicated that irrigation with industrial wastewater inhibited seed development, reduced seed oil percentage, crude proteins percentage, increased total carbohydrates and the mobility of lead within the plant compared with the treatments of remediated water and control. It was declared that, water remediation decreased the plant hazard caused by lead present in industrial wastewater.

Key words: Remediation, wastewater, adsorption, natural material, Sunflower.

INTRODUCTION

Croplands irrigation using wastewater is regarded an important agricultural practice in many arid and semi arid regions of the world. As a consequence, heavy metals were accumulated into these irrigated lands. Furthermore, there is a concern about the potential hazard associated with the consumption of the edible crops grown in this region, because of metal phytotoxicity or transfer of the metal into the food chain. Agriculture is an economic foundation for many countries and remediation strategies must be designed to support high throughput while keeping costs to a minimum.

With improved technology, agricultural production increased every year, but more wastes are generated. Utilizing wastes for phytoremediation has attractive environmental benefits. Also, utilization of natural materials for the treatment of wastewater (containing heavy metals) is gaining more attention as a simple, effective and economic means of pollution remediation.

Ferro-Garcia *et al*. (1988) studied the adsorption of Zn, Cd and Cu ions on activated carbons obtained from agricultural by-products. **Sanciolo *et al*. (1992)** observed that removal of Cr, Ni and Zn from chromium stream electroplating wastewater by adsorbing colloid floatation. Meanwhile, **Pascucci (1993)** reported that removal of Zn ions from aqueous solution by an algal biomass. **Liu *et al*. (1999)** studied the removal of Cu, Zn, Cd and Hg ions from wastewater by chelating fiber. **Brown *et al*. (2000)** observed that the utilization of peat for the treatment of wastewater containing heavy metals is gaining more attention as a simple, effective and economical means of pollution remediation. Also, **Schneegurt *et al*. (2001)** investigated the metal binding qualities of two biomass byproducts that are commercially available in quantity and at low cost, namely 'spillage', and ground maize cobs. The biomass materials effectively removed toxic metals, such as Cu, Cs, Mo, Ni, Pb and Zn.

Abdel-Halim *et al*. (2003) studied the adsorption ability of animal bone powder, and plant powder (roots of the Nile rose plant) for removal of zinc and fluoride ions from industrial wastewater. They found that zinc ions were removed (80%) by using bone powder and (50%) by using Nile rose plant powder. **Bianchi *et al*. (2003)** observed that competitive transport of cadmium and lead through a natural porous medium, an influence of the solid/liquid interface processes. They found that contaminated ground water typically contains different metal contaminants which may compete with each other for the same adsorption sites. They conducted cadmium and lead monocomponent step column experiments to obtain adsorption isotherms on a natural aquifer material (quartz sand) in water saturated conditions. They reported conventional technologies of metals removal from contaminated waters rely on relatively expensive mineral adsorbents or chemical flocculating agents.

The aim of the present investigation was to study the adsorption ability of five different natural materials such as (Cotton stalks, Acacia, Orange peels, Rice straw and Pomegranate peels) for removal of lead ions from lead polluted solution and industrial wastewater and the effect of remediated water on the growth of sunflower plants.

MATERIALS AND METHODS

1. Laboratory experiment

Metal solution preparation

Metal solution was prepared from lead nitrate (200 ppm Pb). The concentration of lead in the final solution was determined by Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS Perkin Elmer).

Natural material preparation

Five different natural materials i.e. cotton stalks, acacia, orange peels, rice straw and pomegranate peels were air dried and then broken manually to reach the weight of 0.25, 0.5 and 1 g/100 ml then were soaked in 200 ppm Pb solutions. The residual concentration in metal solution was measured after soaking for 24, 48 and 72 h by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS Perkin Elmer) at Soils, Water and Environ. Res. Inst., ARC.

2. Pots experiment

Ten seeds of sunflower (*Helianthus annus*) were germinated in pots each containing 15 Kg non-contaminated virgin soil. Plants were periodically irrigated with three different types of water i.e. tap water or industrial wastewater collected from Helwan steel and iron industrial or industrial wastewater treated with mixture cotton stalks, rice straw and pomegranate peels. Four and a half months later, plants flowered and gave fruit. Plants were then harvested and all plants were briefly washed and divided into leaves, shoots and seeds and dried at 60 ºC.

Plant analysis

Lead was determined in dry ground shoot according to **Piper (1950)**, while wet digestion procedure was performed by adding 10 ml concentrated sulfuric acid to 0.5g dry sample and heated. After digestion, the solution was left till cooling and then 0.5 ml of perchloric acid was added and heated until obtaining clear solution. Later, the digested solution was transferred and up to 50 ml in volumetric flask using de-ionized water D.D.H_2O. Lead in digested solution was measured by ICP-MS.

Determination of crude protein

Total nitrogen was determined by micro-Kjeldahl method according to **A.O.A.C. (1980).** Crude protein was calculated by multiplying the values of total nitrogen by 5.30 for sunflower shoots.

Determination of total lipids

Total lipids were determined in seeds of dry samples according to the method of **A.O.A.C. (1980).**

Total hydrolysable carbohydrates determination

The total hydrolysable carbohydrates were determined in dry leaves using phenol-sulfuric acid method as described by **Dubios *et al*. (1956).**

RESULTS AND DISCUSSION

Results in Fig. 1a indicate that cotton stalks, acacia, orange peels, rice straw and pomegranate peels at 0.25g/100 ml decreased lead concentration from 200 ppm to 12.6 ppm (93.7%), 28.43 ppm (85.8%), 47.23 ppm (76.39%), 31.46 ppm (84.27%) and 38.94 ppm (80.5%) within 24 hours, respectively. After 48 hours, lead levels were decreased to 7.51 ppm (96.2%), 45.52 ppm (77.2%), 32.5 ppm (83.8%), 20.65 ppm (89.7%) and 16 ppm (92%), respectively. Moreover, after 72 hr, lead levels were decreased to 5.97 ppm (97%), 51.7 ppm (74.1%), 26.18 ppm (86.9%), 16.14 ppm (91.9%) and 12.47 ppm (93.8%), respectively. it was clearly shown that cotton stalks was more effective for lead removal than rice straw and Pomegranate peels, respectively.

Curves represented in Fig.1b show that cotton stalks, acacia, orange peels, rice straw and pomegranate peels (0.5g/100 ml) decreased lead concentration from 200 ppm to 8.99 ppm (95.5%), 27.93 ppm (86%), 31.84 ppm (84%), 24.27 ppm (87.9%) and 35.22 ppm (82.4%) within 24 hours, respectively. On other hand lead levels after 48 hours were 6.29 ppm (96.9%), 61.18 ppm (69.4%), 30.77 ppm (84.6%), 22.75 ppm (88.6%) and 21.25 ppm (89.38%), respectively. After 72 hours, more decline in lead levels was observed where it reached 3.57 ppm (98.2%), 54.94 ppm (72.5%), 37.21 ppm (81.4%), 19.37 ppm (90.3%) and 18.67 ppm (90.7%), respectively. It was evident that lead removal was most effective with cotton stalks and rice straw followed by Pomegranate peels.

Fig 1

Figure 1c show that cotton stalks, acacia, orange peels, rice straw and pomegranate peels (1g/100 ml) decreased lead from 200 ppm to 8.62 ppm (95.7%), 38.02 ppm (80.9%), 24.74 ppm (87.6%), 28.08 ppm (85.9%) and 30.81 ppm (84.6%) within 24 hours, respectively. Moreover, lead levels after 48 hours, were 6.63 ppm (96.7%), 52.59 ppm (73.70%), 23.27 ppm (88.4%), 14.79 ppm (92.6%) and 20.71 ppm (89.6%), respectively. Also, there was more decrements after 72 hours, since lead levels were 3.55 ppm (98.2%), 41.78 ppm (79.1%), 28.08 ppm (85.6%), 11.39 ppm (94.3%) and 15.43 ppm (92.3%), respectively. It was concluded that lead removal was most effect with cotton stalks and rice straw followed by pomegranate peels. On the other hand, acacia showed little effect at 48 hours followed by decrease in lead level at 72 hours. This enhancement of lead level at 72hr can be attributed to the change in lead solution pH.

To compare the efficiency of studied five different types of natural materials with respect to 200 ppm lead concentration and their interaction with time, data represented in Table 1 show that all five natural materials at ratios of 0.25, 0.5 and 1 g/100 ml were significantly different ($p \leq 0.05$). It was concluded from present data that lead removal was highest for cotton stalks and rice straw followed by Pomegranate peels. Generally removal of lead using natural materials can be attributed to surface adsorption by some organic compounds such as (Lignin) which may be bound to metal.

Gharaibeh, ***et al*****. 1998** reported that the removal of dissolved metals by plant tissues has been examined using a variety of biomasses that represent byproducts from other commercial processes. It was found that trace concentrations of Pb and Zn were successfully removed from solution by processed solid residue of olive mill products.

Meanwhile**, Muratak (1998)** used aquatic plants for removal of heavy metals from water and industrial wastewater. **Brown** ***et al*****. 2000** stated that the utilization of peat and other biomass materials for the treatment of wastewater containing heavy metals is gaining more attention as a simple effective and economical means of pollution remediation**.**

Data in Tables 2 and 3 represent the application of water remediation on growth, dry weight, crude protein percentage, total lipids percentage, total carbohydrates and accumulation metal of sunflower plants. The aim of this analysis was to investigate the metabolic responses of sunflower plant to high metal concentration by elucidating the eventual processes responsible for the sequestration and detoxification of heavy metals. Data indicated that irrigated with industrial wastewater inhibited seed development, reduced seed oil percentage, reduced crude proteins percentage, increased total carbohydrates and the mobility of lead within the plant were increased compared with the treatments of remediation water and control.

Figure 2 show that there were gradual decrements in sunflower shoots dry weight average as a result of industrial wastewater irrigation compared to remediated water irrigation and control and it reached 8.71 g/pot while 16.0 g/pot and 14.4 g/pot for remediated water and control, respectively.

Table 1. Concentration of lead residue in lead solution (200 ppm) after treatment with natural materials

natural material	Weight of natural material (g)	Time of socking (h)			MWx MP	MP
		24	48	72		
Cotton stalks	0.25/100ml	12.6^{u}	7.51^{x}	5.97^{y}	8.64^{j}	7.06^{e}
	0.5/100ml	8.99^{w}	6.29^{y}	3.57^{z}	6.28^{k}	
	1/100ml	8.62^{w}	6.63^{xy}	3.55^{z}	6.26^{k}	
	MPxMt	10.02^{i}	6.81^{j}	4.36^{k}		
Acacia	0.25/100ml	28.43^{m}	45.52^{e}	51.72^{c}	41.89^{c}	44.68^{a}
	0.5/100ml	27.93^{m}	61.18^{a}	54.94^{b}	48.02^{a}	
	1/100ml	38.02^{h}	52.59^{c}	41.78^{f}	44.13^{b}	
	MPxMt	31.46^{d}	53.10^{a}	49.48		
Orange peels	0.25/100ml	47.23^{d}	32.48^{j}	26.18^{n}	35.29^{d}	30.77^{b}
	0.5/100ml	31.84^{jk}	30.77^{l}	37.21^{jk}	31.64^{e}	
	1/100ml	24.74^{o}	23.27^{p}	28.08^{m}	25.36^{f}	
	MPxMt	34.60^{c}	28.84^{e}	28.86^{e}		
Rice straw	0.25/100ml	31.46^{kl}	20.65^{q}	16.14^{s}	22.75^{g}	20.99^{d}
	0.5/100ml	24.27^{o}	22.75^{p}	19.37^{r}	22.13^{h}	
	1/100ml	28.08^{m}	14.79^{t}	11.39^{v}	18.08^{i}	
	MPxMt	27.93^{f}	19.39^{g}	15.63^{h}		
Pomegranate peels	0.25/100ml	38.94g	16s	12.47^{u}	22.47gh	23.28^{c}
	0.5/100ml	35.22^{i}	21.25^{q}	18.67^{r}	25.05^{f}	
	1/100ml	30.81^{l}	20.71	15.43	22.32^{gh}	
	MPxMt	34.99^{c}	19.32^{g}	15.52^{h}		
Main of time		27.80^{a}	25.49^{b}	22.77^{c}		

Means in the vertical row with different superscripts are significantly different ($p \leq 0.05$)

L.S.D: MP= Mean of plant: 0.294

MT= Mean of time: 0.228

MW= Mean of weight: 0.2276

MWx MP= Mean of plant × Mean of weight: 0.509

MPxMT= Mean of plant ×mean of time: 0.509

MTxMW= Mean of time ×Mean of weight: 0.39

MTxMWxMP= Mean of time ×Mean of weight ×Mean of plant: 0.882

Table 2: Effect of irrigation with industrial wastewater, remediated wastewater and tap water on some chemical analysis of sunflower plant

Treatment	Dry weight (g/pot)	Crude protein%	Total lipid%	Total carbohydra-tes%
Before remidiation	8.71^{b}	5.04^{b}	32^{c}	26.72^{a}
After remidiation	16^{a}	8.84^{a}	40^{a}	13.34^{b}
Control	14.4^{a}	8.04^{a}	33.8^{b}	16.55^{b}
LSD at 0.05	2.78	2.39	0.32	5.86

Means in the vertical row with different superscripts are significantly different ($p \leq 0.05$)

Fig. 2,3

Table 3: Effect of irrigation with wastewater industrial, remediation water and fresh water on availability of lead (ppm) of sunflower plant

Treatment	Lead (ppm)
Before remediation	13.83[a]
After remediation	5.77[b]
Control	7.33[b]
LSD at 0.05	2.77

Means in the vertical row with different superscripts are significantly different ($p \leq 0.05$)

In contrast, ratio of crude protein content in shoots showed a 62.7% decrement with industrial wastewater irrigation compared with remediated water samples and control with no significant between control and remediated water irrigation (Fig. 3).

As shown in Figure 4, significant increases was observed in total lipid percentages with remediated water irrigation treatments and control, compared with the irrigated with industrial wastewater, since total lipid percentages at remediated water irrigation treatment was 40% and with control 33.8%. Furthermore, there were significant decrements in total lipid percentages (32%) when irrigated with industrial wastewater treatment.

It was observed that the ratio of total carbohydrates content in leaves increased by 38.06 and 50.07% when irrigated with industrial wastewater compared to irrigation with remediated water and control (Fig.5).

Contamination of soil by industrial wastewater irrigation affects the accumulation of Pb content significantly **(**Figure 6**).** Irrigation with industrial wastewater increased metal level to 13.83 mg/kg Pb.

Lead accumulation in plants is often accompanied by induction of variety of cellular changes and some of them directly or indirectly contribute to lead tolerance capacity of the plant. Moreover, toxicity symptoms which are seen in the presence of excessive amounts of metal may be due to a range of interactions at the cellular/molecular level (fig 7). Also, toxicity may be resulted from the binding of metal to sulphydryl groups in proteins, leading to an inhibition of activity or disruption of structure, from the displacing of an essential element resulting in deficiency effects.

Gadallah (1996) stated that in general, wastewater-treated plants showed a lower transpiration rate than the control (tap water). Leaf relative water content of plants grown in the detergent and oil factory wastewater was significantly lower than that of control samples. The physicochemical analysis of the wastewater was often above the standard limits for irrigation water for agricultural land. **Tedeschi *et al*. (1997)** found that the biggest depletion of sunflower yield occurred under irrigation with the highest salt concentration, however dry matter accumulation was reduced as salinity levels increased. **El-Zaher *et al*. (2004)** obtained results which indicated that the percentage of reduction in seed and oil yield decrease when sunflower plants were subjected to water stress.

It can be concluded from the present study that cotton stalks and rice straw followed by Pomegranate peels at 1 g/100 ml after soaking for 72 hours is the most effective successful treatment for removal of lead and could be beneficial to agricultural practices, and the usage of this considerable amount of agricultural waste for lead removal.

Fig. 4,5, 6

Fig. 7

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المعالجة النباتية للرصاص فى الماء الملوث بإستخدام خمس مواد طبيعية مختلفة

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يعد تلوث البيئة بالمعادن السامة منتشرا أنتشاراً واسعا وغالبا ما يشمل ماء الصرف. ويعتبر الرصاص أكثر المعادن سمية بالنسبة للصحة العامة والبيئة نتيجة تراكمه فى سلسلة الغذاء وأيضا فى الماء الأرضى. وكان الغرض من هذا البحث هو دراسة مدى مقدرة إدمصاص والتخلص من عنصر الرصاص من كلاً من محلول الرصاص وماء الصرف الصناعى عن طريق خمس مواد طبيعية مختلفة مثل حطب القطن، الصمغ العربى، قشر البرتقال، قش الأرز، قشر الرومان وتأثير معالجة ماء الصرف الصناعى على نمو نباتات زهرة الشمس.

يعد هذا البحث جزءاً من الدراسة التى تلقى الضوء على القدرة الإدمصاصية عبر خمس أنواع مختلفة من مواد نباتية طبيعية مثل حطب القطن، الصمغ العربى، قشر البرتقال، قش الأرز، قشر الرومان من المحلول المعدنى (٢٠٠ جزء فى المليون من الرصاص). تم معالجة المحلول المعدنى بواسطة تركيزات مختلفة من المواد الطبيعية تحت الدراسة (٠.٢٥، ٠.٥ و١ جرام لكل ١٠٠ مللتر). تم قياس التركيز المتبقى للرصاص فى المحلول المعدنى وذلك بعد ٢٤، ٤٨ و٧٢ ساعة. وقد إنخفض تركيز الرصاص بعد ٧٢ ساعة بإستخدام حطب القطن، الصمغ العربى، قشر البرتقال، قش الأرز، قشر الرومـان وذلك من ٢٠٠ جزء فى المليون إلى ١.٠٧ جزء فى المليون (٨٩.٣%)، ١.٤٥ جزء فى المليون (٨٥.٥%)، ١.٢٠ جزء فى المليون (٨٨%)، ٠.٨٥ جزء فى المليون (٩١.٥%) و٠.٥٤ جزء فى المليون (٩٤.٦%)؛ على التوالى.

وقد أظهرت الفروق المعنوية بالنسبة للتفاعل الداخلى بين الفترة وإزالة الرصاص، مدى منطقية كل المواد الطبيعية المختبرة. وقد أجريت تجربة أصص تحت ظروف الصوبة الزراعية فى بيئة طبيعية وذلك لتقدير تأثير إزالة الرصاص على نمو نباتات زهرة الشمس التى تم ريها بإستخدام ماء الصرف الصناعى لمصانع حلوان للحديد والصلب، ماء الصرف الصناعى المعالج بواسطة أحسن ثلاث مواد طبيعية السابق ذكرها (حطب القطن، قش الأرز، قشر الرومان)، والماء العذب ككنترول. وقد أوضحت النتائج أن الرى بإستخدام ماء الصرف الصناعى يثبط نمو التطورى للبذرة، مع خفض نسبة الزبت، النسبة المئوية للبروتين الخام، مع رفع نسبة الكربوهيدرات الكلية وحركة الرصاص عبر النبات مقارنة بالرى بإستخدام ماء الصرف الصناعى المعالج والكنترول.