International Journal of Physical Sciences Vol. 7(46), pp. 6105-6116, 9 December, 2012
Available online at http://www.academicjournals.org/IJPS
DOI: 10.5897/IJPS12.605
ISSN 1992 - 1950 ©2012 Academic Journals

Full Length Research Paper

Metallic phytoremediation and extraction of nanoparticles

Tariq Mahmood[1]*, Salman Akbar Malik[2], Syed Tajammul Hussain[1] and Shazia Aamir[3]

[1]Nano Sciences and Catalysis Division, National Centre for Physics, Quaid-i-Azam University, Islamabad 45320, Pakistan.
[2]Department of Biochemistry, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan.
[3]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan.

Accepted 26 November, 2012

The use of phytoremediation is a non-destructive method of heavy metal's removal from soils. Water hyacinth plant (*Eichhronia crassipes*), normally found in habitats around the world, and has the ability to extract heavy metals through its roots, stem, and leaves. The main aims of this study were two folds; the use of water hyacinth plant to remove metals (Lead, Pb; Copper, Cu; Zinc, Zn; Chromium, Cr; and Cadmium, Cd) from contaminated soil, and second was to use metal contaminated water hyacinth to extract metals as nanoparticles. The laboratory trials were carried out with different concentrations of heavy metals in soils. Plants were grown in metal contaminated soils ranging from 5 to 500 µg/g of soil concentrations. The heavy metals absorbed by the plants were measured with parameters like soil pH and plant fresh weight. The heavy metals were first extracted and the resultant biomass was utilized for preparation of metallic nanoparticles by a green technology route. The subsequent recovery of the heavy metal, followed by metallic nanoparticles production utilizing the contaminated biomass will add value to the use of this plant.

Key words: Water hyacinth, nanoparticles, soil, Cobalt, Nickel, Lead, Copper, Zinc, Chromium, Cadmium.

INTRODUCTION

Soil is an essential compartment of the ecosystem, contributing directly or indirectly to the general quality of life (Van Kamp et al., 2003: Marsan and Biasioli, 2010). Urban soils appear to be definitely more contaminated than their agricultural or natural surroundings (Johnson and Ander, 2008). For example, garden soils contain twice the concentration of metals Lead (Pb), Cadmium (Cd), and Zinc Zn) as corresponding agricultural soils (Schwartz et al., 1995). The risk of trace elements is usually related to their likelihood to leach to groundwater or to enter the food chain through plant uptake (Abrahams, 2002; Poggio et al., 2009; Marsan and Biasioli, 2010).

Pb had been used as antiknock and one of the major sources of pollution in cities. Other sources of Pb are car batteries, glass, radiation shields, and soldering. In recent years, electronic products and e-wastes have grown as a considerable Pb source (Terazono et al., 2006; Lincoln et al., 2007). Its manifest toxic effects (Järup, 2003; Nevin, 2007) had prompted a generalized reduction of its use. Unleaded gasoline is now in use in the vast majority of countries. However, Pb's long use and persistence in the environment has concentrated Pb in urban area's soil (Marsan and Biasioli, 2010).

Copper (Cu) is widely used for manufacturing and electrical wiring. Electronic equipment is also emerging as a source of Cu (Lincoln et al., 2007; Wong et al., 2007). Cu tends to accumulate in urban areas. In fact,

*Corresponding author. E-mail: tariqm20002000@yahoo.com. Tel: +92512077356, Fax: +92512077395.

Abbreviations: TEM, Transmission electron microscopy; **SEM,** scanning electron microscopy; **AFM,** atomic force microscopy; **DLS,** dynamic light scattering; **XPS,** X-ray photoelectron microscopy; **XRD,** X-ray diffraction; **FTIR,** Fourier transformed infra red spectroscopy; **AAS,** atomic absorption spectroscopy; **ICP-ES,** Inductively coupled plasma emission spectrometry; **DMRT,** Duncan's multiple range test; **ICP-AES,** Inductively coupled plasma atomic emission spectrometry; **MRI,** magnetic resonance imaging.

Drakonakis et al. (2007) have calculated a stock of 144 kg/capita of Cu in the City of New Haven, USA. In Sydney central city, Van Beers and Graedel (2007) estimated the Cu stock to be 520 kg/capita. Cu together with Zn, was reported to dominate (14t/year) the transfer of metals to the biosphere and sewage sludge in Stockholm, Sweden (Bergbäck et al., 2001). Spatari et al. (2005) reported that, in 1999, about 2,790 Gg of Cu were placed in landfills in North America, and according to Bertram et al. (2002), 2 kg of Cu waste per capita are produced every year in Europe (Marsan and Biasioli, 2010).

Various sources of Zn appear to concentrate in various areas. Metallurgic and galvanic industries are usually the sources of metal contamination. Apart from the waste treatment, fuel burning, in numerous alloy objects Zn is present in tires, batteries and electronic equipment (Dagan et al., 2007; Lincoln et al., 2007), and. In Sydney central city, Van Beers and Graedel (2007) assessed the Zn stock to be 420 kg/capita. A study in the city of Stockholm has calculated an emission of Zn 17t/year from street furniture, tires, and buildings (Palm and Ostlund, 1996). In the same city, 34 t Zn/year were reported to be transferred to the biosphere and sewage sludge (Bergbäck et al., 2001; Marsan and Biasioli, 2010).

Chromium (Cr) in urban areas is mainly used in the metallurgic and galvanic industry as it is employed as an alloy constituent to impart corrosion resistance. Dyes and paints also contain Cr. Emission in atmosphere may come from motor vehicle exhaust, waste incineration, and combustion of oil and coal. Frequently, however, Cr is derived from the lithogenic substrate. Soils developed from ultramafic rocks and especially serpentinites often have a high content of Cr (Adriano, 2001: Marsan and Biasioli, 2010).

There are several sources of accumulation of Nickel (Ni) and Cd in the environments. Ni and Cd extracted in the world are used in the production of Ni-Cd batteries, the rest being used for coating and plating, in pigments, and in plastics. Cd is also used in the production of automobile radiators, in manufacturing electronics components, and in photography. It is a component of tires, petrol, diesel fuel, and lubricating oils. Adriano (2001) reported an average Cd content in soils of 0.30 mg kg^{-1} (Marsan and Biasioli, 2010).

Heavy metals are ubiquitous environmental contaminants in industrialized countries. Such metallic pollution may be easily controlled by water hyacinth (Tiwari et al., 2007; Mishra and Tripathi, 2008). Developing cost-effectiveness and environment friendly technologies for the remediation of soils and waste waters polluted with toxic substances is a topic of global interest. The value of metal accumulating plants to wetland remediation had been recently realized (Prusty et al., 2007). The concentrations of metals in plants like water hyacinth can be measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) with an ultrasonic nebulizer. It shows maximum detection limits with less chance of errors (Liao and Chang, 2004).

The phytoremediation of heavy metals from soils is emerging as a cost-effective technology (Chaney et al., 2008; El-Gendy, 2008). The aquatic plants in metallic pollution act as biological filters and biomonitors of environmental metal levels (Sujatha et al., 2001; Liao and Chang, 2004). Zhu et al. (1999) and Mahmood (2011) studied the phytoremediation of trace metals by water hyacinth. Results showed that water hyacinth is a promising candidate for the phytoremediation of metallic pollution. Pollutants removal by water hyacinth, from soil was studied by Mehra et al. (2000). They observed that the roots of water hyacinth growing in the over bank soils, are accumulating metals.

In nanotechnology, a particle is a small object that behaves as a whole unit in terms of its transport and properties. Ultra fine particles or nanoparticles are sized between 100 and 1 nm. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical, and electronic fields. There are several methods for creating nanoparticles. Nanoparticle characterization is necessary to establish the understanding and the control of nanoparticle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering (DLS), x-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). Now a day's use of nanoparticles is very common in industries. Cobalt (Co), Ni, and Iron (Fe) oxides are abundantly used in gasification and pyrolysis of plant biomass for the production of alternative fuels (Mahmood et al., 2010; Mahmood, 2011). Silver nanoparticles were synthesized by using the extract of *Eichhronia crassipes* (Water hyacinth) which is considered as one of the most notorious aquatic weeds present all over the world. The synthesized nanoparticles exhibited the size ranging from 10 to 50 nm. Fourier transformed infrared spectroscopy (FTIR) revealed that the phenolic groups present in the plant extract were responsible for the reduction of silver nitrate into silver nanoparticles and stabilization of the formed silver nanoparticles (Kiruba et al., 2012).

MATERIALS AND METHODS

In order to find out phytoremoval of Pb, Cu, Zn, Cr, and Cd from the soil, five experiments were designed. It was done to see the possible role of water hyacinth in metallic bioremediation

Study area

For the present study, Tehsil Taxila, Rawalpindi District, Punjab province, of Pakistan was chosen. Taxila is an important

Gandharan city of Takshashila (also Takkasila or Taxila). It remained as the center of one of the oldest civilization of the world that is, Gandhara. Taxila is situated at the Western Region of the Islamabad Capital Territory-Rawalpindi and on the border of the Punjab and Khyber Pakhtoonkhawa, about 30 km West-North-West of Islamabad, just off the Grand Trunk road. Taxila is situated at (Latitude: 33° 46′ 45″ N 33.779167° Longitude: 72° 53′ 15″ E 72.8875°) (Hussain et al., 2010). This study area was chosen because water hyacinth is abundantly grown here in Missa soil (Typic Ustochrept). This soil is loamy and calcareous (Ali and Higgins, 1967; Mahmood, 2011).

Sampling of soil

The 63 soil samples were collected from Taxila, Rawalpindi District, Pakistan, by following the standard sampling procedure of Ryan et al. (2001) and Mahmood (2011). The samples were air-dried, grounded and mixed thoroughly, in order to get composite samples. No metallic container was used in order to avoid metallic contamination.

Plants' propagation

Wildly grown water hyacinth plants were collected from wetlands of Taxila area. These plants were grown hydroponically as described by Zhu et al. (1999) for 5 weeks. After 5 weeks, some plants were removed from pots, washed, and weighed for fresh and dry weight. The metal content of these plants was measured by using AAS and ICP-ES as used by Mahmood (2011).

Metals' phytoremediation from soil

2 kg of soil samples were placed in labeled plastic containers. A calculated amount of $PbCl_2$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, K_2CrO_4, and $CdCl_2$. H_2O were used for artificial contamination of soil for these metals. The concentrations of Pb^{++}, Cu^{++}, Zn^{++}, Cr^{++}, and Cd^{++} varied from 5 to 500 µg/g soil. Every experiment was performed in triplicate. Deionized water (300 ml) was added in all soil samples. Then the containers were left undisturbed for two weeks. This was done to set fauna and flora of soil samples (Mahmood et al., 2010; Mahmood, 2011).

After the settlement of fauna and flora of soil according to environmental conditions, 18 plants were used for each metal (total of 90 for the five metals). These were weighted and planted in soil present in plastic containers. These plants were watered with deionized water for 10 days. After 10 days, these plants were removed from pots, washed, and weighed for fresh and dry weight. The plant samples were digested in $HClO_4$ / HNO_3 (1:2 ratio) mixture, and were analyzed for Pb^{++}, Cu^{++}, Zn^{++} Cr^{++}, and Cd^{++} at AAS and ICP-ES (Lab tam 8500) following a technique described by Liao and Chang (2004). Metal content of plants was determined in µg/g of dry weight. The data was statistically analyzed by using analysis of variance (ANOVA) and Duncan's multiple range test (DMRT) (Badr-uz-Zaman et al., 2002). The soil pH was measured before and after the experiment following a technique described by Ryan et al. (2001), Mahmood et al. (2010), and Mahmood (2011). The absorbed metal content of plant was noted (difference in metal contents that is, before and after growth in the soil).

Plants' analysis collected from contaminated soil of Taxila

Wildly grown water hyacinth plants were collected from wetlands of Taxila area. The metal content of these plants was measured by using AAS and ICP-ES (Mahmood et al., 2010; Mahmood, 2011).

Extraction of nanoparticles from metal contaminated

Wildly grown water hyacinth plants were collected from wetlands of Taxila area after drying 5 g of dried powdered, water hyacinth biomass was taken in 250 ml flask and 200 ml of 1% HNO_3 solution was added to it. The sample was shaked for 9 h on hot plate with magnetic stirrer without heating. After shaking, the solution was filtered. 50 ml of filtrate was taken in a china dish and was heated at 70°C for 21 h in oven in order to obtained dry materials. The net weight of dry material was 0.171 g, the main purpose was to solublize and extract metals from dry water hyacinth biomass. 1 g of oven dried sample was calcined at 400°C for 4 h, annelid, pulverized, and sieved. It was analyzed by XRD (Mahmood et al., 2010). Average particle size was measured by Sherrer formula as described by Mahmood (2011).

RESULTS

In this study there were two main objectives that is, metallic phytoremediation from soil and extraction of nanoparticles from water hyacinth already grown in contaminated soil. The results of both experiments are described respectively. The plants were grown in contaminated soil containing serial dilutions of Pb^{++}, Cu^{++}, Zn^{++} Cr^{++}, and Cd^{++}. Several parameters like plant dry weight, soil's pH change and plant's metal content were studied in these experiments. The results for each metal are described below.

Lead (Pb)

The results of pH changes in the soil contaminated by serial dilutions of 100 to 500 µg/g of Pb due to growth (biological activity) of water hyacinth are given in Figure 1. The figure shows that in absence of Pb (control) the pH increases slightly (+0.02) where as in the presence of Pb (100 to 500 µg/g) the pH decreases. The decrease in pH appears to be concentration dependent and decreases from -0.02 in case of 100 µg/g Pb to -0.18 in case of 500 µg/g Pb. Results of present study show the change in plant fresh weight of water hyacinth grown in contaminated soil as compared to control. Increase in plant fresh weight in control (0Pb) is minute as compared to those which are grown in Pb contaminated soil. Increase in plant fresh weight appears to be erratic.

Figure 2 shows phytoremoval of Pb by water hyacinth from the contaminated soil. Control (0Pb) is considered as zero than Pb's removal in µg/g of dry weight increases from 06.49 at 100 µg/g of Pb to 27.91 at 200 µg/g of Pb in the soil. Maximum phytoremoval 27.91 is obtained at 200 µg/g of Pb in the soil. Whereas, after it had slightly decreases to 24.05 at 300 µg/g of Pb but then is considerably reduced to 4.67 and 1.77 at 400 and 500 µg/g of Pb, respectively.

Summary of these results for Pb show that, maximum phytoremoval from soil is observed. In short, the phytoremoval of Pb from soil was higher in the said experiment. Water hyacinth grown in soil pH of soil

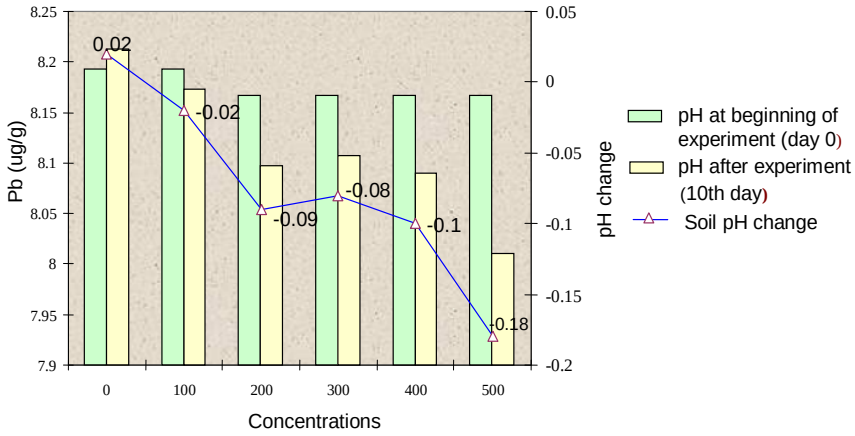


Figure 1. pH change in soil due to growth of water hyacinth.

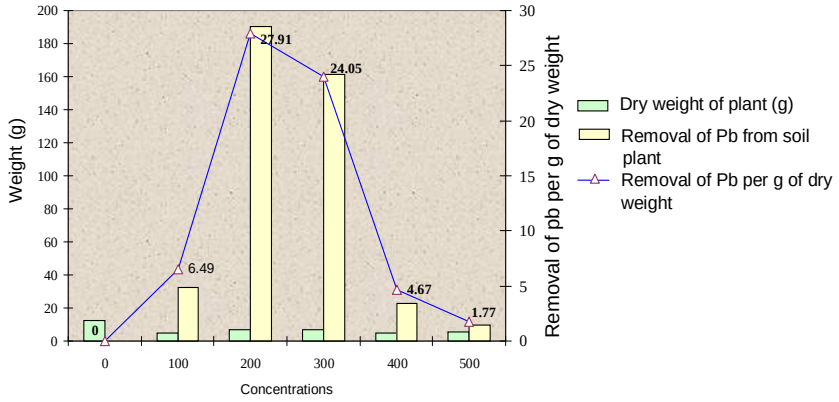


Figure 2. Study of dry weight, removal of Pb per plant and removal of Pb/g of plant dry weight.

was decreased.

Copper (Cu)

The results of pH changes in the soil contaminated by serial dilutions of 25 to 125 µg/g of Cu due to growth (biological activity) of water hyacinth were given in Figure 3. It also shows that in absence of Cu (control) the pH increases slightly (+0.010) where as in presence of Cu (25 to 125 µg/g) the pH decreases. The decrease in pH appears to be concentration dependent and increases from -0.070 in case of 25 µg/g of Cu to -0.140 in case of 100 µg/g of Cu. An abrupt change in pH is observed at 25 µg/g Cu in soil. The results showed the changes in plant fresh weight of water hyacinth grown in Cu contaminated soil as compared to control. Increase in plant fresh weight in control (with out Cu) is minute as compared to those which are grown in Cu contaminated soil.

Figure 4 shows phytoremoval of Cu by water hyacinth from the contaminated soil. When Cu (control) is considered as zero than Cu's removal in µg/g of dry weight increases from 5 to 100 µg/g of Cu in soil. Maximum phytoremoval is obtained at 100 µg/g of Cu in soil. At 125 µg/g of Cu in soil phytoremoval of Cu is decreased. Increase in Cu phytoremoval is 0.98, 1.07, 2.30, and 3.38 at 25, 50, 75, and 100 µg/g of Cu in soil, respectively.

Summary of these results for Cu showed that, maximum phytoremoval from soil is obtained (At 3.38 µg/g of dry weight for 100 µg/g of soil).

Zinc (Zn)

The results of pH changes in the soil contaminated by serial dilutions of 50 to 250 µg/g of Zn due to growth (biological activity) of water hyacinth are given in Figure 5. The figure shows that, in absence of Zn (control) the

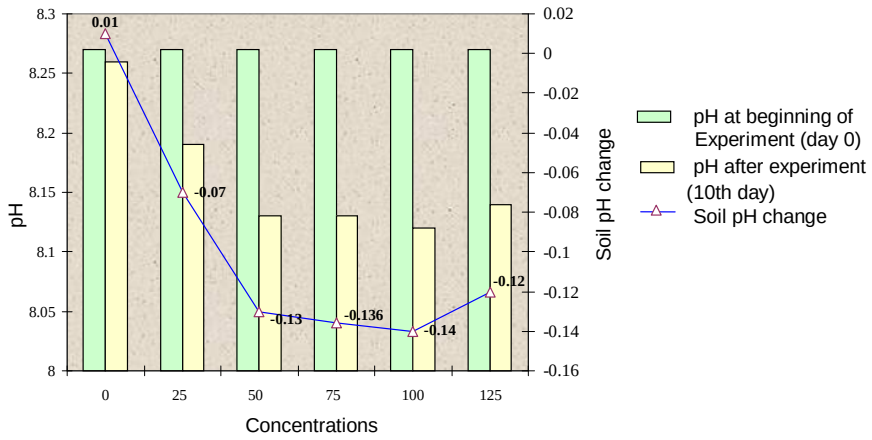


Figure 3. pH change due to growth of hyacinth.

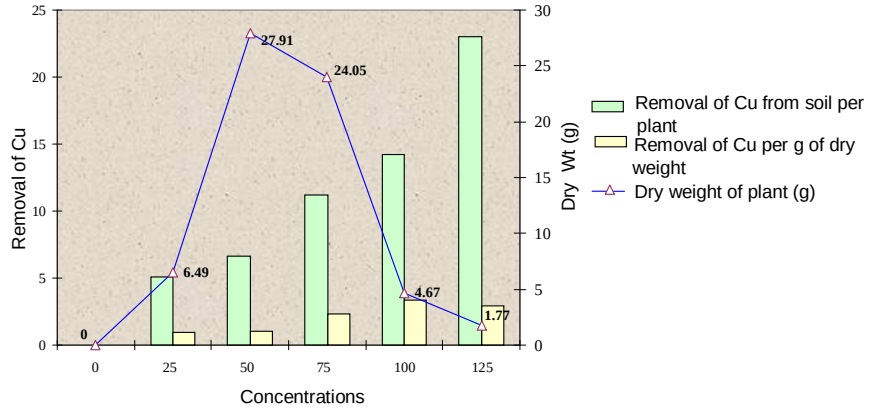


Figure 4. Study of dry weight, removal of Cu per plant and removal of Cu per g of plant dry weight.

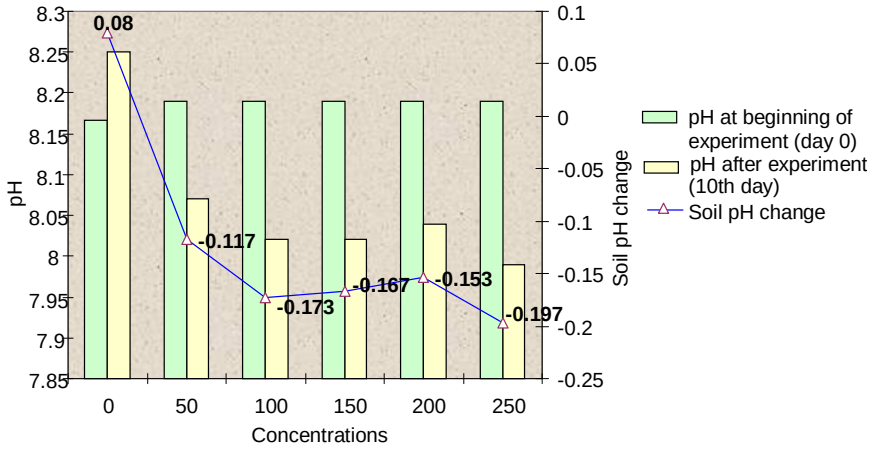


Figure 5. pH change due to growth of hyacinth.

pH increases slightly (+0.080) where as in presence of Zn (50 to 250 µg/g) the pH decreases. The decrease in pH appears not to be concentration dependent and decreases from -0.117 in case of 50 µg/g of Zn to -0.197

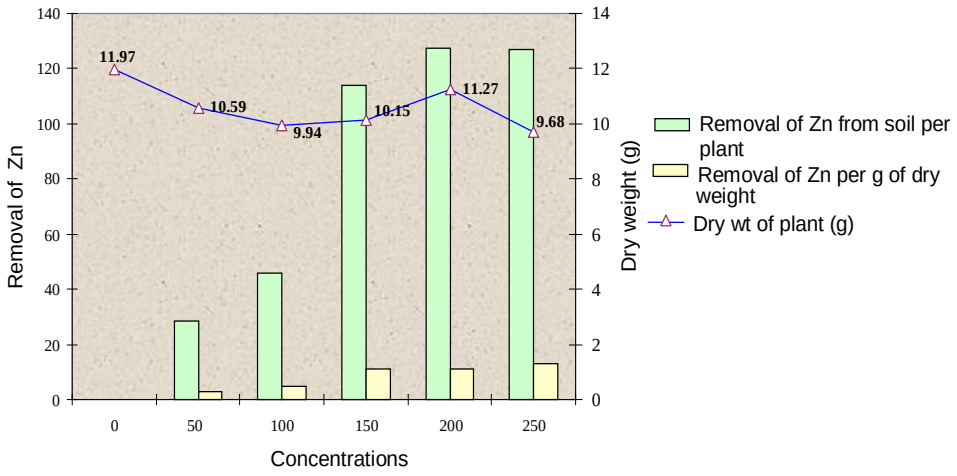


Figure 6. Dry weight, removal of Zn per plant and removal of Zn per g of plant dry weight.

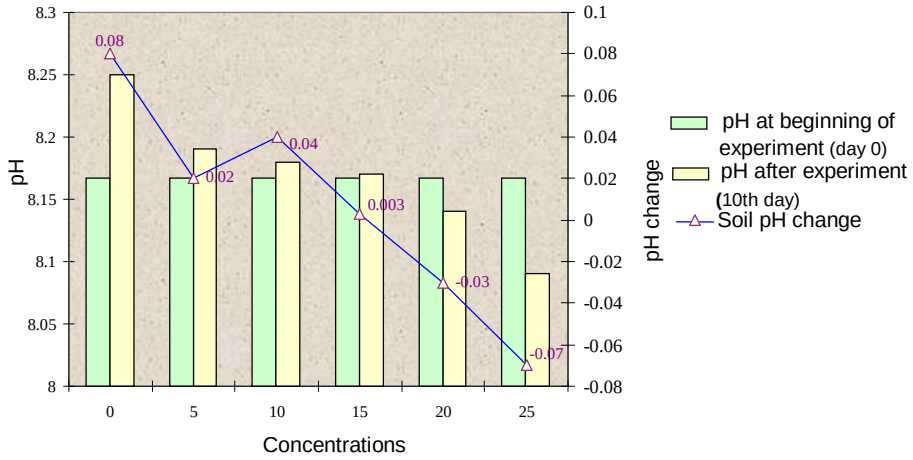


Figure 7. pH change in soil due to growth of water hyacinth.

in case of 250 µg/g of Zn. The results showed the change in fresh weight of water hyacinth grown in Zn contaminated soil as compared to the control. The fresh weight of these plants was increased except at control (0 Zn).

Figure 6 shows phytoremoval of Zn by water hyacinth from the contaminated soil. Control (0 Zn) is considered as zero than Zn's phytoremoval in µg/g of dry weight increases from 50 to 250 µg/g of zn in soil. Maximum phytoremoval is 13.11 µg/g of dry weight obtained at 250 µg/g of Zn in soil. Increase in Zn phytoremoval up to 250 µg/g of Zn from soil reveals that phytoremoval of Zn from contaminated soil may be increased as concentration of Zn soil is increased.

Summary of these results for Zn shows that maximum phytoremoval from soil was 13.11 µg/g of dry weight (for 250 µg/g). Similarly, water hyacinth grown in soil pH was significantly decreased.

Chromium (Cr)

The results of pH changes in the soil contaminated by serial dilutions of 5 to 25 µg/g of Cr due to growth (biological activity) of water hyacinth were given in Figure 7. The figure shows that in absence of Cr (control) the pH increases (+0.080) whereas in the presence of Cr (5 to 15 µg/g) the increase in pH decreases. The decrease or increase in pH appears to be concentration dependent. The decrease in pH appears not to be concentration dependent. It decreases from +0.020 (in case of 5 µg/g of Cr) to -0.070 (in case of 25 µg/g of Cr). The results showed the change in plant fresh weight of water hyacinth grown in Cr contaminated soil as compared to the control. Increase in plant fresh weight in control (0Cr) is minute, while decrease in fresh weight is more prominent in those which are grown in Cr contaminated soil.

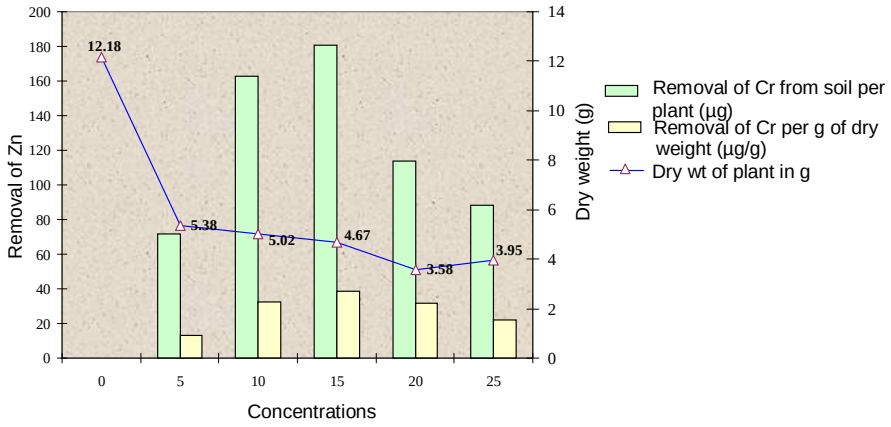


Figure 8. Dry weight, removal of Cr per plant and removal of Cr per g of plant dry weight.

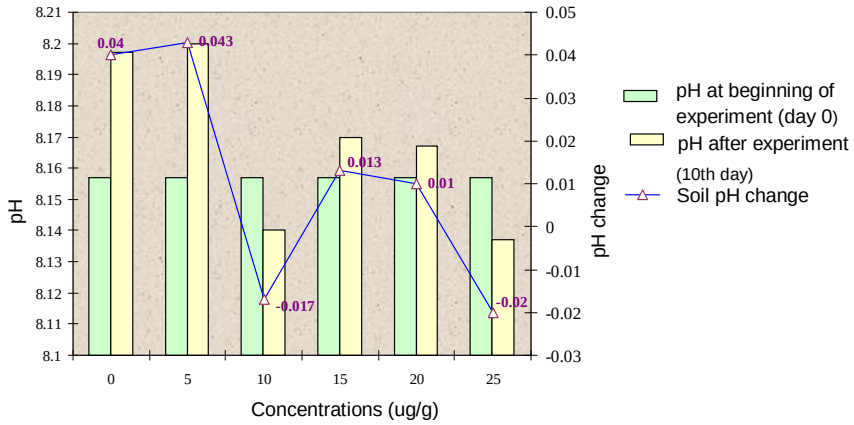


Figure 9. pH change in soil due to growth of water hyacinth.

Figure 8 shows phytoremoval of Cr by water hyacinth from the contaminated soil. Control (0Cr) is considered as zero than Cr's removal in µg/g of dry weight increases from 13.36 at 5 µg/g Cr to 38.67 at 15 µg/g Cr in soil. Maximum phytoremoval 38.67 is obtained at 15 µg/g of Cr in the soil. It decreases, from 31.78 to 22.27 at 20 to 25 µg/g of Cr respectively.

Summary of these results for Cr shows that maximum phytoremoval from soil was obtained as 38.67 µg/g of dry weight (for 15 µg/g). In short, phytoremoval of Cr from soil is good. Similarly when water hyacinth is grown in the soil, pH was significantly increased up to 15 µg/g of the soil but decreased onward.

Cadmium (Cd)

The results of pH changes in the soil contaminated by serial dilutions of 5 to 25 µg/g of Cd due to growth (biological activity) of water hyacinth were given in Figure 9. The figure shows that in the absence of Cd (control) the pH increases slightly (+0.040) whereas in the presence of Cd at 5, 15, and 20 µg/g the pH increases to 0.043, +0.013, and +0.010 respectively. This increase is decreasing with increase in concentration of Cd. The decrease in pH -0.017 and -0.020 is observed at 10 and 25 µg/g of Cd, respectively. The results showed the changes in plant fresh weight of water hyacinth grown in the contaminated soil as compared to the control. Increase in plant fresh weight in control (with out Cd) is minute as compared to those which are grown in Cd contaminated soil.

Figure 10 shows phytoremoval of Cd by water hyacinth from the contaminated soil. When control (0Cd) is considered as zero then Cd's removal is increased to 0.2319, 0.4119, 0.4483, 1.1178, and 1.9150 µg/g of dry weight at 5, 10, 15, 20, and 25 µg/g of Cd in the soil, respectively. Maximum phytoremoval is obtained at 25 µg/g of Cd in the soil. Figure 10 shows that with the increase in concentration of Cd, phytoremoval may increase up to a large extent.

Summary of these results for Cd shows that maximum

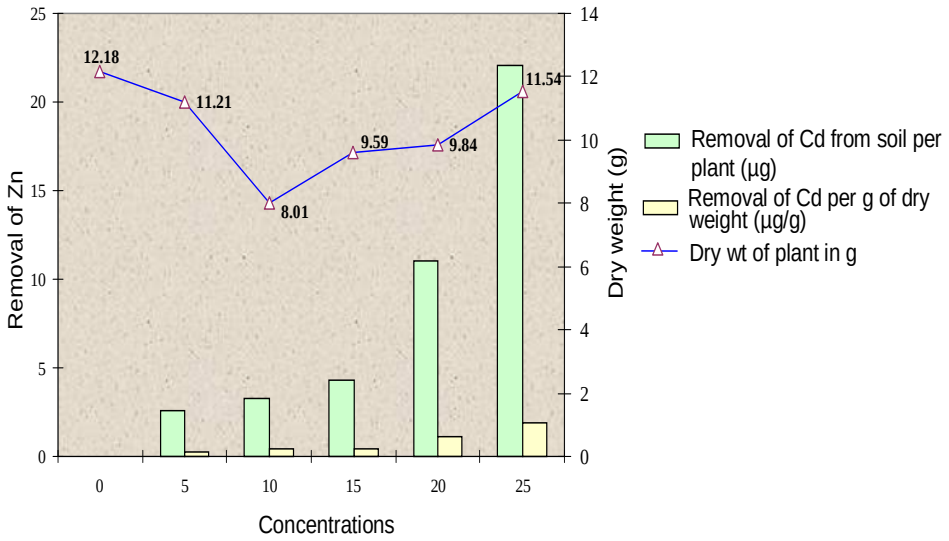


Figure 10. Dry weight, removal of Cd per plant and removal of Cd per g of plant dry weight.

phytoremoval from soil was obtained as 1.915 at 25 µg/g.

Extraction of nanoparticles from hyacinth

Elemental concentrations of some metals in water hyacinth were measured with ICP-AES (Mahmood et al., 2010). Results of analysis show that plant contains 56 ± 0.81 Co, 1218 ± 1.63 Fe, 10 ± 0.81 Ni, and 190 ± 7.9 Pb, respectively in µg/g of dry plant.

The XRD showed that sharp peaks were obtained as given in Figure 11. The metals absorbed in the plant were converted to nitrates and became soluble in water. On heating, these metals were converted into oxides as shown in Figure 11. The occurrence of metals as oxides in water hyacinth was also verified by previous studies (Li and Thornton, 2001; Mahmood, 2011). Sherror formula was used for the calculation of the particle size of the oxides of Pb, Co, Ni, and Fe. The peaks show that they are in crystallite shape with variable size but average particle size is 22.872 nm.

DISCUSSION

Two main objectives of these experiments were to find phytoremediation/phytoaccumulation of Pb^{++}, Cu^{++}, Zn^{++} Cr^{++}, and Cd^{++} from the soil by water hyacinth and extraction of nanoparticles from metal contaminated wildly grown water hyacinth biomass. In this study plants were grown in artificially contaminated soil containing variable additions of said metals. Several parameters were studied in these experiments. The results for each metal were individually discussed as well as the extraction of nanoparticles.

Lead (Pb)

Water hyacinth was grown in artificially contaminated soil containing serial dilutions of Pb 100 to 500 µg/g of soil. The fresh weight of these plants was increased as compared to the control (0Pb). Increase in fresh weight shows that Pb favors growth of water hyacinth (Qian et al., 1999). The pH of soil is increased (Figure 1). This increase in pH shows that the mechanisms other than acidification, such as ion exchange and roots exudation, may be responsible for the increased in heavy metal uptake in plants (Kashem and Singh, 2002). Nitrogen containing organic compounds due to microbial activities change into NH_3 (Sooknah, 2001; Mahmood et al., 2009), this ammonia (NH_3) may be able to increase pH. Figure 2 explains dry weight and removal of Pb/g of soil. This shows that water hyacinth is useful for the removal of Pb from contaminated soil. Removal of metals from soil is verified by Kashem and Singh (1999). Summary of discussion for Pb shows that maximum phytoremoval from soil is 27.91 µg/g (for 200 µg/g).

Copper (Cu)

In plants, Cu is a structural element of various enzymes, and it is involved in carbohydrate and nitrogen metabolism. Normal plant concentrations of Cu range from 5 to 20 µg/g dry weight; above this value Cu can be toxic, affecting the uptake or the metabolic displacement of other important ions, such as Fe, causing chlorosis and inhibiting root growth (Mengel and Kirkby, 2001).

High concentrations of Cu were reported for *Larrea tridentata* (Gardea-Torresdey et al., 1999). Although the concentration of Cu in the leaf material, 493 µg/g dry weights is not high enough for the plant to be considered a hyperaccumulator, the authors found that the47% of the Cu contained in the plant was found in the upper parts. The same pattern was observed for Cd (61%) and Ni (55%).

Water hyacinth was grown in artificially contaminated soil containing 25 to 125 µg/g of Cu. The fresh weight of these plants is decreased as compared to the control (0Cu). Decrease in fresh weight shows that it is may be due to osmotic potential and decrease in moisture content. The pH of soil is decreased (Figure 3). This decrease in pH shows that it may be due to activities of *Thiobacillus* bacteria (Mahmood et al., 2009). The Figure 3 shows decrease in pH as compared to the control. The Figure 4 shows the dry weight and phytoremoval of Cu µg/g of plant dry weight. Maximum removal of Cu is 3.38 µg/g of dry weight at 100 µg/g of Cu in soil. It is decreased after 100 µg/g. Therefore this method is useful for the phytoremoval of Cu pollution in soil. Removal of Cu from soil is verified by Kashem and Singh (1999).

Zinc (Zn)

Zn is an essential element necessary for plant development intervening in carbohydrate and protein metabolism, enzyme and plant hormone activities. Normal concentrations of Zn in the environment are in the range of 17 to 160 µg/g and bioavailability is dependent on pH (Mengel and Kirkby, 2001). In plants, Zn is normally found in concentrations of 20 µg/g dry weight (Jones, 2003). However, high concentrations of Zn in the order of 150 to 200 µg/g dry weight are toxic to most plant resulting in chlorotic and necrotic leaves and retarded growth of the plants (Mengel and Kirkby, 2001; Jones, 2003). Water hyacinth was grown in artificially contaminated soil containing Zn 50 to 250 µg/g of the soil. The fresh weight of these plants is increased as compared to the control (0Zn). Increase in fresh weight shows that Zn favors the growth of water hyacinth. Zn plays a vital role in plant and animal nutrition. It is mobilized in the earth crust by various types of mechanisms (Dara, 1993). Nitrogen containing organic compounds due to microbial activities change into NH_3 (Sooknah, 2001), this NH_3 may be able to increase pH (Figure 5) (Mahmood et al., 2009). Figure 6 explains dry weight, and phytoremoval of Zn in µg/g of dry weight.

The increase in fresh weight in said experiments is verified by Lu et al. (2004). All these results are verified by Kashem and Singh (1999, 2001, 2002), Wang et al. (2002), Das (2004), Tyagi and Covillard (1987), Yan and Viraraghavan (2003), Ingole and Bhole (2000), and Ntengwe (2005). Zn levels are high in cells of hyacinth and are increased in cell walls. Little quantities of Zn are found in external granular form in water hyacinth (Vesk et al., 1999).

Chromium (Cr)

Water hyacinth is grown in artificially contaminated soil containing 5 to 25 µg/g Cr. The fresh weight of these plants is decreased as compared to control (0Cr). Decrease in fresh weight shows that it is may be due to osmotic potential and decrease in moisture content. The pH of soil is increased (Figure 7). This increase in pH shows that mechanisms other than acidification, such as ion exchange and roots exudation, may be responsible for the increased heavy metal uptake in plants (Kashem and Singh, 2002). Nitrogen containing organic compounds due to microbial activities change into NH_3 (Sooknah, 2001; Mahmood et al., 2009), this NH_3 may be able to increase pH. Figure 8 explains dry weight and removal of Cr per g of plant dry weight. Maximum removal of Cr is 38.67 µg/g of dry weight at 15 µg/g of soil. It is decreased after 15 µg/g of Cr in soil. Therefore this method is useful for the phytoremoval of Cr from the soil. Removal of Cr from soil is verified by Kashem and Singh (1999). Phytoremediation process is faster in the earlier stages of the experiment after which it slows down probably due to reduction in the initial concentration of metals like Cr (Singh and Sinha, 2011).

Cadmium (Cd)

Cd is a non essential element and may be taken up by plants because of the chemical similarities it has with Zn. It is found in low concentrations in the environment. Normal concentrations in non contaminated soil are lower than 1 µg/g of soil (Mengel and Kirkby, 2001). Sources of Cd contamination are the electroplating industry, plastics, and batteries (Jones, 2003). Cd is toxic at very low concentrations; for example, in leaf tissue at concentrations of 0.05 to 0.2 µg/g dry weight, toxicity is evident by symptoms of chlorosis, reddish veins, and petioles, brown, stunted roots and deterioration of the xylem tissue (Jones, 2003). As mentioned above, certain plants can tolerate and/or accumulate high concentrations of metals. Li et al. (2006) described a genotype of *Thlaspi caerulescens,* a known Zn and Cd hyperaccumulator, capable of accumulating 1800 µg/g of Cd and 18000 µg/g of Zn (dry shoot tissue); this genotype showed the highest Zn/Cd ratio. As soil Cd concentrations tend to be much lower than Zn concentrations, a high ratio of Zn: Cd concentrations in hyperaccumulating plants allow a more efficient removal of Cd from the soil.

Water hyacinth was grown in artificially contaminated soil containing 5 to 25 µg/g Cd. The fresh weight of these plants is decreased as compared to control (0Cd).

Change in fresh weight shows that it may be due to osmotic potential and decrease in moisture content. The pH of soil is increased. This increase in pH showed that mechanisms other than acidification, such as ion exchange and roots exudation, may be responsible for the increased in heavy metal uptake in plants (Kashem and Singh, 2002). Nitrogen containing organic compounds due to microbial activities change into NH_3 (Sooknah, 2001; Mahmood et al., 2009), this NH_3 may be able to increase pH. Figure 9 shows the pH changes and it explains increase in pH as compared to control with an exception of increase at 10 and 25 µg/g of Cd. At high pH phytoremoval of Cd is verified by Kashem and Singh (2001). Figure 10 shows dry weight and phytoremoval of Cd µg/g of plant dry weight. Maximum Cd removal is 1.915 µg/g dry weights at 25 µg/g of soil. This method is useful for the phytoremoval of Cd from contaminated soil. Removal of metals from soil is verified by Kashem and Singh (1999).

The phytoremediation efficiency of water hyacinth may be improved by periodically harvesting plants, which removes trace elements from the site and mining toxicity of phytoaccumulated trace elements to wildlife. The trace elements accumulated in plant tissue may be recovered for commercial use (Zhu et al., 1999). If the major goal of the phytoremediation process is to remove the maximum amount of elements in the shortest time possible then the selection should be based on the element accumulation in harvestable tissues as well as known information on plant densities (Qian et al., 1999).

Extraction of nanoparticles from metal contaminated plant

This study proposes a solution by extracting such dissolved heavy metals from a polluted soil using aquatic plants. The organism used for the study is the aquatic plant *E. crassipes* (Water hyacinth). Water hyacinth plants can extract and accumulate large quantities of various heavy and toxic metals such as Pb, Cu, Zn, Cr and Cd, Ni, Fe, and Co. This study also proposes extracting of heavy metals to either recycle or dispose off safely then to use the resultant biomass for the preparation of nanoparticles such as silver, which is used in medicines, electronics and other industries as described by Al-Akeel et al. (2010). Silver nanoparticles were synthesized by using extract of *E. crassipes* (Kiruba et al., 2012).

Al-Akeel et al. (2010) suggested that for the ability of grasses to manufacture metallic nanoparticles, an extract of a common grass *Fetsuca* sp was used. Manufacture of silver nanoparticles; was faster in *Fetsuca* sp than in *Medicago Arabica*. These experiments may be repeated to test the ability of water hyacinth to prepare metallic nanoparticles (Elmachliy et al., 2011). Water hyacinth metal contaminated extract may be used for the preparation of nanoparticles by using metal nitrates. Our results are supported by this idea. The results of our findings showed that plant contains Pb, Fe, Ni, and Co in appropriate amount. On treatment with nitric acid metals converted into nitrates while on heating these nitrates are converted into oxides. These were verified by XRD results.

Pb oxide nanoparticles were prepared by nitrates and characterized through XRD. Under optimum conditions, uniform, and homogeneous nanostructured Pb oxide with particle size 20 to 40 nm were also studied by Karami et al. (2008). Ni nanoparticles were prepared from nitrate. The size, morphology, and crystallinity of Ni nanoparticles were also investigated and strong Ni peaks, in powder XRD patterns, indicated that Ni nanoparticles are easier to be oxidized (Wang et al., 2004). Co oxide (Co_3O_4) nanoparticle was synthesized by thermal treatment of the precursor obtained through mechanochemical reaction of $Co(NO_3)_2 \cdot 6H_2O$ with NH_4HCO_3. The Co_3O_4 nanoparticles were characterized by XRD and TEM. Effect of calcinations temperature on Co_3O_4 crystal size was discussed by Yang et al. (2004). All these evidences are proving authenticity of our procedure. Fe oxide nanoparticles prepared by our technique have important applications in industries. Applications of Fe oxide nanoparticles include terabit magnetic storage devices, catalysis, sensors, and high-sensitivity biomolecular magnetic resonance imaging (MRI) for medical diagnosis and therapeutics. Figure 11 explains XRD spectrum of plant biomass. The obtained nanoparticles were characterized by XRD and may be used in industries.

Conclusions

Water hyacinth shows good phytoremediation/removal of Pb, Cu, Zn, Cr, and Cd from Missa soil of Taxila Pakistan. The major advantages of the developed technology over conventional treatment methods include: low cost, high efficiency, and minimization of chemical and low biological sludge. No additional nutrient is needed, cheapest generation of biomass, high possibility of metal recovery, and raw material is locally available. Metals (Pb, Co, Fe, and Ni) contaminating water hyacinth is a serious threat to the environment, so the conversion of absorbed metals into useful nanoparticles solved the said problem. After the conversion of absorbed metals into useful nanoparticles, solid residue of water hyacinth is rich in N, P, and proteins which can be used as biofertilizer.

ACKNOWLEDGEMENT

The authors are grateful for the support of Prof. Dr. Khalid Saifullah Khan of Pir Mehr Ali Shah Arid Agriculture University, Rawalpindi, Pakistan for the guidance and technical support.

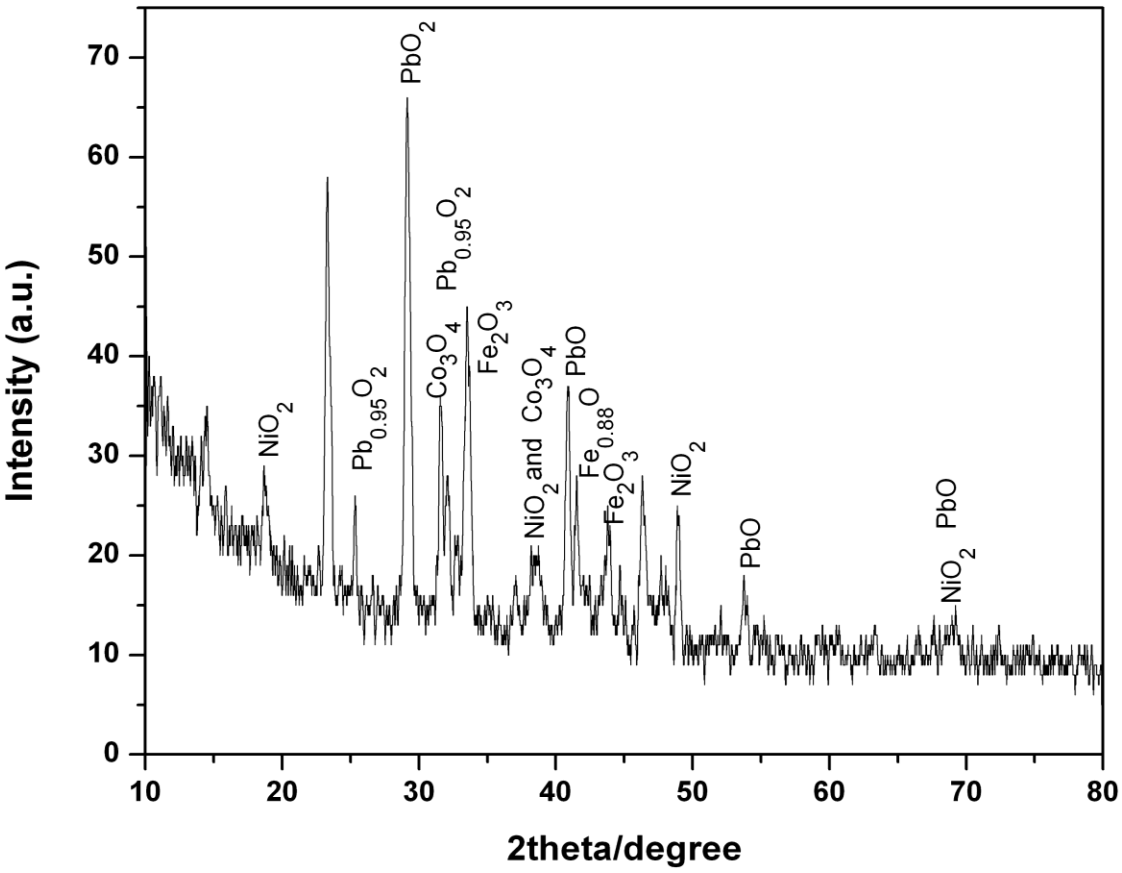


Figure 11. The XRD spectrum of material extracted from hyacinth.

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