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Alternative for Chromium Removal : Phytoremediation and Biosorption with Weed Plant Species in Thailand

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ABSTRACT: The alternatives for chromium (Cr) removal capacities by phytoremediation with weed plant species and biosorption with biomass are discussed. The plant species used in this research were *Cynodon dactylon*, *Vetiveria nemoralis*, *Echinochloa colonum*, *Phyllanthus reticulatus*, *Pluchea indica* and *Amaranthus viridis*. Phytoremediation experiments were prepared by adding hexavalent Cr [Cr(VI)] of 0, 100, 200 and 400 ppm initial concentrations to soil in pots at a nursery. Soil pH was also measured during the harvesting. The results showed that the leaves of *P. indica* had the highest Cr(VI) accumulation capacity of 73 mg/kg of plant on a dry weight basis on day 30 at a Cr(VI) concentration of 100 ppm. Biosorption experiments were conducted at 50 ppm initial Cr(VI) concentration and at pH levels of 2, 4, 6 and 8. Each biomass (root, stem and leaf) was added separately to the solutions. The results showed that the leaves of *P. indica* had the maximum Cr(VI) adsorption capacity of 51.3 mg/g biomass on a dry weight basis. According to these results the estimated cost of phytoremediation operation is cheaper than that of biosorption operation. Interestingly, the results from both of these remediation processes showed the leaves of *P. indica* to record the highest Cr(VI) accumulation and a maximum Cr(VI) adsorption than parts from other plants and biomasses. Thus, the cell and physical anatomy of this plant needs to be studied in greater detail in order to understand the plant attributes which led to these results.

KEYWORDS: Chromium, Phytoremediation, Biosorption, Tannery, Weed plants.

INTRODUCTION

Chromium (Cr) is found in two oxidation states in the natural environment: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Of these two forms, essentially immobile Cr(III) compounds are the predominant species in most environmental settings.[1] It is known to be less toxic than Cr(VI). Industry can and does discharge both Cr(III) and Cr(VI) into the environment. Cr is used in many industries and in particular in Thai tanning factories which has resulted in Cr contamination of soil and water. Phytoremediation and biosorption are two treatment techniques that may be used to solve or mitigate this problem.

Phytoremediation is the direct use of living plants for in-situ, or on-site remediation of contaminated soils, sludges, sediments and ground water, through contaminant removal, degradation or containment.[2,3] Phytoremediation can be used to remediate various contaminants including metals, pesticides, solvents, explosives, petroleum hydrocarbons, polycyclic aromatic hydrocarbons and landfill leachates. Phytoremediation has been studied extensively in research and small-scale demonstrations, but full-scale applications are currently limited to only a small number of projects. [4]

Biosorption is the use of dead biomass to bind and concentrate heavy metals from dilute aqueous solutions. Biomass exhibits this property by acting just as a chemical substance, as an ion exchanger of biological origin. The cell wall structure of certain algae, fungi and bacteria was found to be particularly responsible for this phenomenon. The opposite of biosorption is the metabolically driven active bioaccumulation by living cells. That is an altogether different phenomenon requiring a different approach for its exploration.[5]

The objective of this research was to evaluate the alternative between Cr removal by phytoremediation with weed plant species and biosorption with biomass. It has been discussed that the plants that are effective for use in phytoremediation would also provide effective biomass for biosorption. This research focuses

on weed plant species from phytoremediation that can be used for biosorption. Both methods can be effectively utilized for remediating Cr(VI) contaminated soil and wastewater. Moreover, the potential for alternative mitigating processes based on the relationship between phytoremediation and biosorption is one objective of the research. The important point was that these two areas have never been related even though they both rely on plants; one on a live plant and the other on a dead plant. There might or might not be a relationship between these two areas.

Materials and Methods

The experiment used plants from a tannery site. Six out of thirty four weed plant species found around the tanneries in Samutprakarn province, Thailand, were selected on the basis of their ability to accumulate total chromium (TCr). These six species, three monocot and three dicots, are widely distributed, fast growing, hardy, easy to maintain and are non-edible. Moreover, they have a short life span, high rate of propagation, and produces large quantity of biomass. The selected monocots were *C. dactylon* (L.) Pers., *V. nemoralis* (A.) Camus. and *E. colonum* (L.) Link., while *P. reticulatus* Poir., *P. indica* Less. and *A. viridis* L were the selected dicots. These plants were obtained from uncontaminated areas in the Bangprahun district, Ayutthaya province Thailand. These plant species were studied in phytoremediation and biosorption experiments.

Phytoremediation Experiment

In this experiment, soil samples were collected from 10 locations within the tannery and from 5 locations outside the tannery. Uncontaminated soil from outside the factory site, which exhibited similar properties as the contaminated soil found within the factory site, was excavated and used for these experiments. This experiment was conducted in 12-in diameter pots, each possessing a 1-in diameter drainage hole. Saucers covered with plastic bags were placed under the pots to collect drainage water and this water was later poured back into the pots daily in order to prevent the loss of TCr through leaching. Five kilograms of soil was placed in each pot. Seedlings of the plant species were planted and maintained in a nursery for 3-4 weeks in order to observe their hardiness before the Cr(VI) addition to the soil. One hundred milliliters of three different concentrations of potassium dichromate ($K_2Cr_2O_7$) aqueous solutions, 14,100, 28,300, and 56,500 mg/L, were prepared using deionized water and applied to soil in the pots, yielding the concentrations of Cr(VI) of 100, 200, and 400 ppm (mg Cr(VI)/kg soil). A lower Cr(VI) concentration of 50 ppm or 100 mL of $K_2Cr_2O_7$ solution of 7,100 mg/L, was prepared for *A. viridis* L. because Cr(VI) concentrations exceeding 50 ppm were lethal. For control pots, instead of applying potassium dichromate, 100 milliliters of water were applied. Five hundred milliliters of water were applied equally to each pot daily in the morning. One gram of 15% N, 15% P, and 15% K fertilizer was added to all pots, including the controls, every 30 days. The plants were harvested on days 30, 60, and 90. During harvesting, plant tissues were collected from each pot and analyzed for TCr concentrations. Altogether, one dicot and one monocot species that showed the highest TCr accumulation were chosen for the Cr(VI) removal mechanism process. However, the procedure of the removal mechanism experiment was similar to that of the previous section except that only a Cr(VI) concentration of 100 ppm was used because it was below the mortality concentration determined in the TCr uptake experiment. The plants were harvested after 30, 60, 90 and 120 days. After harvesting, the plants were cut into three parts, roots, stems, and leaves, and analyzed for Cr(VI), Cr(III) and TCr concentrations.

Biosorption Experiment

In this experiment, six plant species were collected from uncontaminated areas and then washed with tap water and distilled water to remove dirt and then air dried at room temperature. Roots, stems and leaves were cut and wrapped with foil and then oven-dried again at 70 °C for 2-3 days. Each part was then milled with mortar and pestle and separately screened through a 2-3 mm mesh sieve. No background TCr was found in these plant biomasses and they were used as the biosorption biomass for all experiments. In addition, two hundred milliliters of potassium dichromate ($K_2Cr_2O_7$) solutions, at 50 ppm (Cr(VI)/L) and at pH levels of 2, 4, 6 and 8 were prepared for batch experiments. Each biomass (root, stem and leaf) was added separately to the solution in dosages of 0.1, 0.25, 0.5, 1.0, 1.5 and 2 grams. Two hundred milliliters of these solutions were put into a 500 milliliter volumetric flask, which was then continuously shaken at 120 rpm. The aqueous phase was sampled and analyzed for Cr(VI) concentrations at 15, 30, 60, 120 and 180 minute intervals and then at three hour intervals until the equilibrium time was reached where there was no further change in Cr(VI) concentration. The Freundlich isotherm and the Langmuir isotherm were used to model the results. The parts of the biomass of one dicot species and one monocot species which provided the maximum Cr(VI) removal capacity were selected from the batch experiments. Acrylic columns with a diameter of 1.85 cm and a length of 20 cm were used. The biomass was prepared in the same way as in the batch experiment, weighed at 8.0 grams, and packed into

each column. Synthetic influent water containing 50 ppm of Cr(VI) was used for this experiment. Initial pH of the influent was adjusted to 2, 4, 6 or 8 for each column. The influent was continually upflow-fed into a column using perlistatic pumps (Cole Parmer Instrument Co. Model 7553-60) at empty bed contact time (EBCT) of 10, 20 and 30 min, yielding flow rates of 4, 2 and 1.3 milliliters/minute, respectively. The aqueous effluent phase was analyzed for Cr(VI) concentration.

Analyses and Statistics

The USEPA method; 3015A and 3052 (acid digestion/atomic absorption spectrometer) were used for the analysis of TCr.[6,7] A Perkin Elmer atomic absorption spectrometer Model AAnalyst 800 (Perkin Elmer Instruments LLC, Unberlingen, Germany) was used. For the analysis of Cr(VI), alkaline digestion of plant tissues was performed according to the USEPA method 3060A[8] and the 1,5 diphenylcarbohydrazide colorimetric method according to the USEPA method 7196A.[9] The concentration of Cr(III) was determined from the difference between measured TCr and Cr(VI) concentrations. Phytoremediation and biosorption data were also analyzed using the analysis of variance (ANOVA) and the Duncan multiple range test with orthogonal contrast. The Duncan test was used to obtain the grouping of the mean values of chromium uptake that are not significantly different among themselves. These statistical analyses were conducted through the Statistic Analysis System version 8 (Statistic Analysis System Institute Inc., Cary, North Carolina, USA).

Results and Discussion

Phytoremediation Experiment

TCr Uptake Capacities of Plants

Fig. 1 shows the mean TCr accumulation of the six plant species at different concentrations including the control and different harvesting times. The error bars represent the standard errors of the means. When only one plant out of the triplicate survived, the single TCr accumulation data point is reported with no error bar. At the Cr(VI) concentration of 200 ppm, the highest concentration that some of each of the plants tested except *A. viridis* survived, TCr accumulated in *C. dactylon* much more than in *P. indica, E. colonum, P. reticulatus* and *V. nemoralis* on day 30. The TCr accumulations in *C. dactylon, P. indica, E. colonum, P. reticulatus* and *V. nemoralis* were 451, 186, 141, 136, and 94 mg TCr/kg of plant on a dry weight basis, respectively. *A. viridis* at the Cr(VI) concentration of 50 ppm, accumulated only 8 mg/kg on day 60 while no TCr was detected in its tissues on day 30 (Fig. 1f). It should be noted that at the Cr(VI) concentration of 400 ppm, the *C. dactylon* that survived (67% of the total number tested) behaved as a TCr hyperaccumulator (TCr accumulation > 1000 mg/kg).[10] The mass balances of TCr at the end of the experiments were performed and TCr in plant, soil, and drainage water combined was > 94% of the total chromium input for all cases.

Moreover, the results showed that the TCr capacities of *C. dactylon, P. indica, P. reticulatus, E. colonum* and *V. nemoralis* were 152.1, 151.8, 101, 77 and 69 mg TCr/kg of plant on a dry weight basis on day 30 at a Cr(VI) concentration of 100 ppm, respectively. While, for *A. viridis* at the Cr(VI) concentration of 50 ppm, no TCr was detected in its tissues on day 30. Thus, Cr(VI) concentration had a significant effect on TCr uptake capacities of plants. By testing with one-way ANOVA, significant differences ($p < 0.05$) in TCr accumulation were observed among the 6 plant species.

Significant differences ($p < 0.05$, one-way ANOVA) in TCr accumulation were observed among different concentrations and the control at all harvesting times for all six species. The effect of Cr(VI) concentration was further analyzed using the Duncan multiple range test ($p < 0.05$) and the results were not the same for all six species. The numbers (1, 2, and 3) above the bars in Fig. 1 are the groups of the means that were not statistically different according to the Duncan test. For example, *C. dactylon* accumulated significantly higher TCr at the concentration of 400 ppm than at other concentrations and the control whose means were in the same group (not statistically different) although their mean TCr accumulations were quite different quantitatively. These statistical results suggest that Cr(VI) concentration tended to affect the TCr uptake capacities of the plants and that the effect was species dependent. However, the TCr uptake capacities of all plant species except *A. viridis* peaked on day 30, and decreased on days 60 and 90. The reason for the decrease could have been due to the fact that the plants had grown well and the resulting high biomass on days 60 and 90 lessened the concentrations of TCr in the plants.

The one-way ANOVA showed that, for the monocots, significant differences ($p < 0.05$) in the TCr uptake were found between *C. dactylon* and the other two species, *V. nemoralis* and *E. colonum* at all harvesting times and Cr(VI) concentrations. No statistical difference was found between the TCr uptakes by *V. nemoralis* and *E. colonum*. For the dicots, *P. reticulatus* and *P. indica* had uptakes that were not significantly different but were significantly higher than TCr uptakes by *A. viridis* at all harvesting times and Cr(VI) concentrations.

Cr Removal Mechanisms Experiment

Fig. 2 shows the Cr(VI), Cr(III), and TCr accumulation in roots, stems, and leaves of *C. dactylon* and *P. indica* on

days 30, 60, 90, and 120 at the Cr(VI) concentration of 100 ppm. Similar to Fig. 1, the data with no error bar resulted from the cases where only one plant out of the triplicate survived. *C. dactylon* and *P. indica* accumulated Cr(VI) and Cr(III) in roots throughout the experimental period. The accumulation of both Cr forms reached the highest values in roots on day 30, and gradually decreased on days 60, 90, and 120.

C. dactylon showed accumulation in stems until day 60, but no accumulation in the leaves. *P. indica* accumulated Cr in stems and leaves until day 60. On days 90 and 120, Cr did not disappear from the stems of *C. dactylon* and the stems and leaves of *P. indica* but were diluted by plant growth (with minimal or no Cr uptake) to the levels that were lower than the detection limit (about 30 mg/kg for TCr). It should be noted that the TCr levels in the stems of *C. dactylon* and *P. indica* were close to 30 mg/kg on day 60. The TCr level of about 50 to 75 mg/kg in the leaves of *P. indica* on day 60 was diluted by a factor of 2.1 between days 60 and 90. The translocation of both Cr forms from the roots to the above ground parts of the plants suggests that phytoaccumulation is the main removal mechanism.

The accumulation of TCr on day 30 in roots, stems and leaves of *C. dactylon* were 62, 40, and 0 mg/kg corresponding to 51%, 49% and 0% of the TCr mass uptake, respectively. For *P. indica*, TCr accumulated in roots, stems, and leaves on day 30 at 180, 86, and 90 mg/kg or 27%, 38%, and 35% of the TCr mass uptake, respectively. Accumulations of Cr(III) in *C. dactylon*

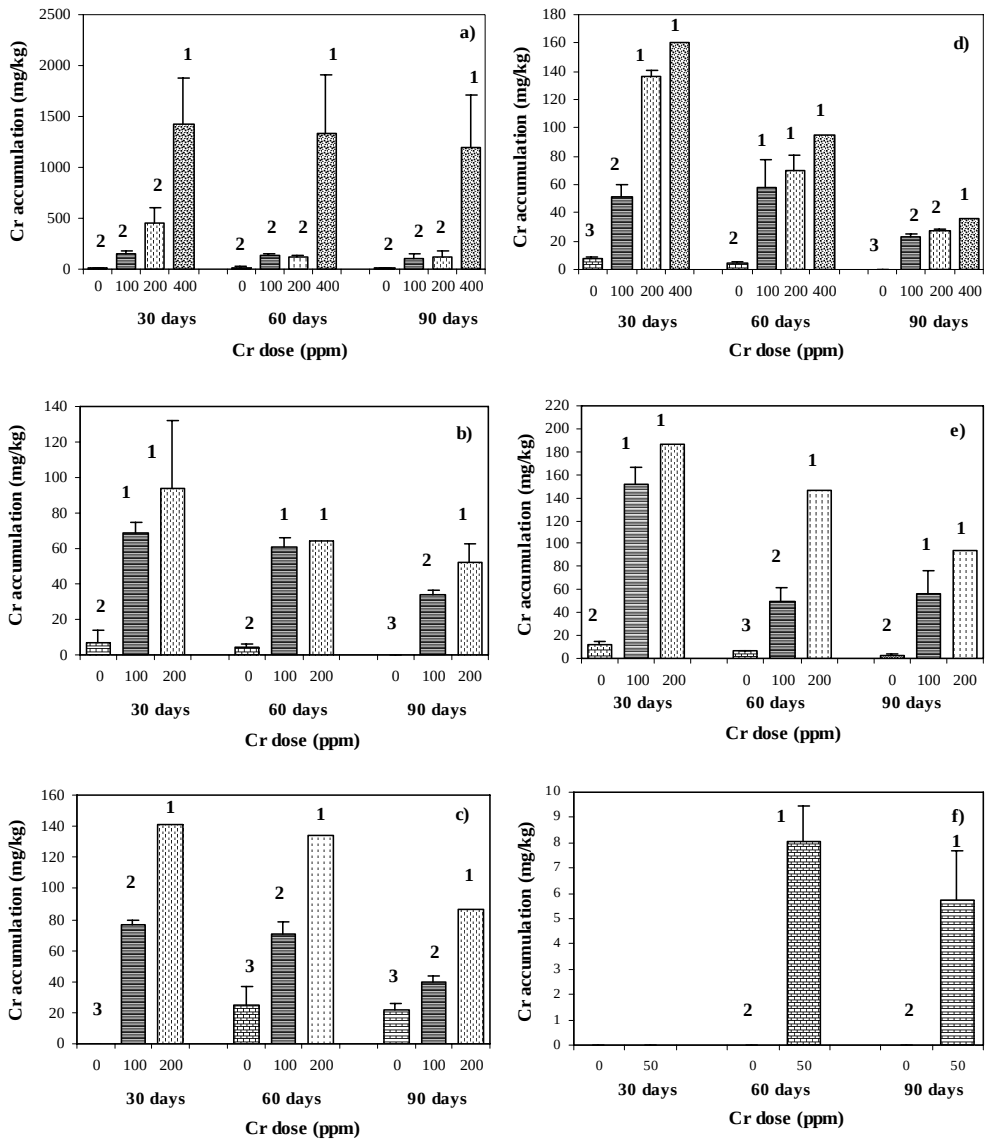

Fig 1. TCr accumulation in six plant species: a) *C. dactylon* (L.) Pers., b) *V. nemoralis* (A.) Camus., c) *E. colonum* (L.) Link, d) *P. reticulatus* Poir., e) *P. indica* Less., and f) *A. viridis* L.

were observed along with the accumulation of Cr(VI) in all cases at comparable levels or slightly to moderately less than the levels of Cr(VI) accumulation. While Cr(VI) accumulation increased from roots to leaves for *P. indica*, the results were the opposite for Cr(III). Less and least accumulations of Cr(III) in stems and leaves of *P. indica* suggests that the plant has less ability to translocate Cr(III) compared to Cr(VI).

The finding that *C. dactylon* accumulated the highest Cr(III) and Cr(VI) in roots (24 and 38 mg/kg) on day 30 agrees with the result of a previous study by Arteaga.[11] They reported that *Larrea tridentata* (Creosote bush) could highly accumulate TCr in roots. The difference in the TCr accumulation in plant tissues of *L. tridentata* was probably due to the difference in the molecular components of the tissues. Roots and stems contain more cellulose and hemicellulose than leaves, which consist of mostly proteins; therefore, roots and stems have more hydroxyl groups which can coordinate with Cr and assist its uptake inside their tissues better than in leaves.[12]

The more favorable accumulation of Cr(VI) in the leaves of *P. indica* at 73 mg/kg on day 30 was expected. ANRCP[13] summarized that dicots such as buckwheat and rutabaga absorbed more Cr through their roots and transported more Cr to the above ground parts than did monocots such as corn and barley. The difference in the TCr accumulation in different tissues was reportedly due to the differences in the rooting patterns, transpiration rates and metabolisms between monocot and dicot species.

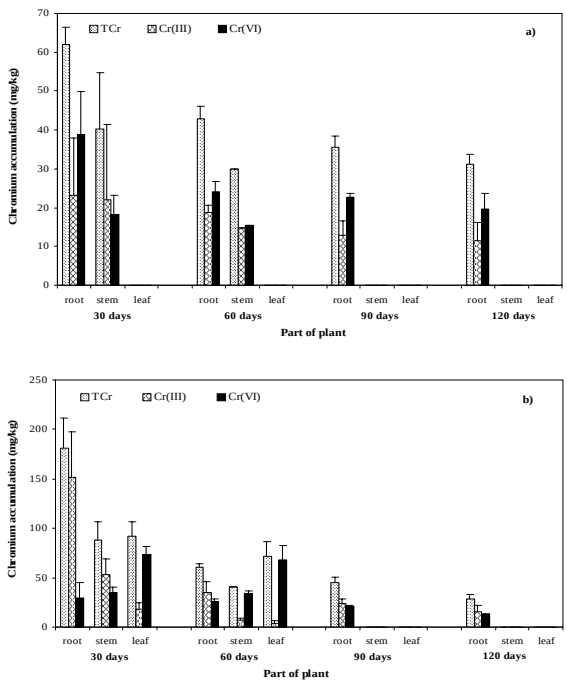

Fig 2. Cr(VI), Cr(III) and TCr accumulation in roots, stems and leaves of a) *C. dactylon* (L.) Pers. and b) *P. indica* Less.

Biosorption Experiment

Type of Biomass

Fig. 3a shows the Cr(VI) adsorption capacities of the leaves of the six plant species at a pH of 2, biomass mass of 0.1, 0.25, 0.5, 0.75, 1 and 2 gram and an equilibrium time of 24 hours. The leaves of the dicot species of *P. reticulatus*, *P. indica* and *A. viridis* showed maximum Cr(VI) adsorption capacities of 53, 45 and 36.4 mg/g, respectively, at biomass mass of 0.1 gram. These were greater than the adsorption capacities of the leaves of the monocot species of *E. colonum, C. dactylon* and *V. nemoralis*, which yielded maximum Cr(VI) adsorption capacities of 36.6, 33.9 and 27.5 mg/g, respectively, at

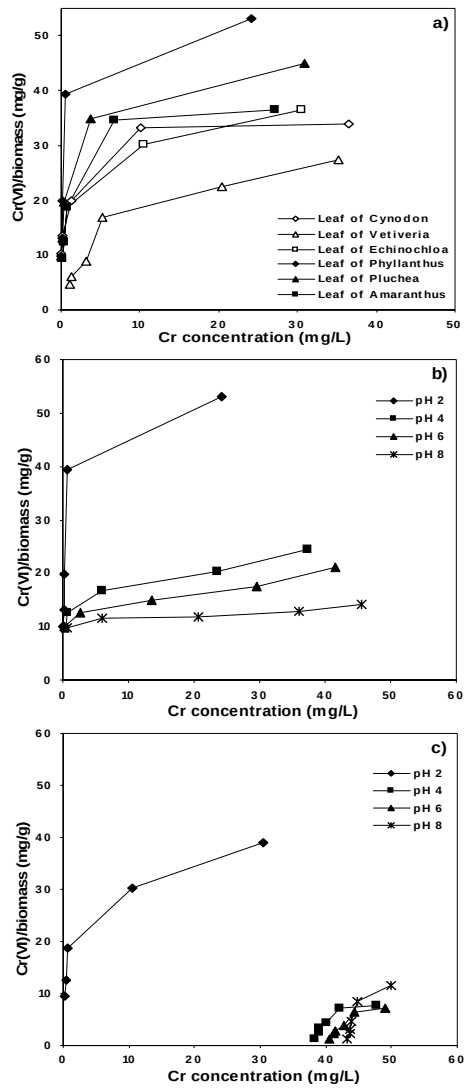

Fig 3. Isotherm for leaves of plant species at the maximum Cr(VI) adsorption capacity: a) at pH of 2, b) Leaves of *P. reticulatus* and c) Leaves of *E. colonum*.

biomass mass of 0.1 gram.

Effect of pH

Fig. 3b and Fig. 3c show the isotherm of dicot and monocot species which recorded the maximum Cr(VI) adsorption capacities, at biomass mass of 0.1, 0.25, 0.5, 0.75, 1 and 2 grams. Fig. 3b shows that the leaves of *P. reticulatus* had maximum Cr(VI) adsorption capacities of 53, 25.1, 21.4 and 12 mg/g, respectively, at biomass mass of 0.1 gram and pH levels of 2, 4, 6 and 8. Fig. 3c shows that the leaves of *E. colonum* had maximum Cr(VI) adsorption capacities of 36.6, 7.7, 7.3 and 11.6 mg/g, respectively, at biomass mass of 0.1 gram and pH levels of 2, 4, 6 and 8. However, these results show that the Cr(VI) removal efficiency decreased as pH increased.

The adsorption of metal ions depends on the pH level of the contaminated solution because acidity strongly influences the electrostatic binding of these ions to corresponding functional groups of OH^-, COO^-, –COOH or $–NH_2$, etc. Sudha[14] found that the *Rhizopus* biomass serves as a matrix of –COOH and $–NH_2$ groups, which in turn take part in the binding of metal ions. At low pH levels, Cr(VI) is mostly found in $HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$. Thus, the increased binding of Cr(VI) ions can be explained as being due to electrostatic binding to positively charged groups, such as amino and carboxyl groups in plant cell walls.[12,15]

Effect of Various Parts of Plants

These results showed that the type of plant part used (root, stem or leaf) for six plant species (eighteen types of biomass) had affected Cr(VI) adsorption capacities. Of the three parts, leaves were found to adsorb most effectively. Gardea-Torresdey[12] summarized that the three different biomass types (roots, stems and leaves) all had different Cr(VI) adsorption capacities. Both roots and stems are composed of woody material necessary to physically support the plant. Leaves are not composed of woody material and so may have other types of metal binding compounds which differ from those found in stems or roots. The main components of woody material in roots and stems are cellulose and hemicellulose. Both of these contain hydroxyl groups that are able to bind with metal ions, but to a lesser extent than carboxyl groups. Therefore, leaves may contain higher protein levels that will supply sulhydryl, amino and carboxyl groups. These groups may cause the reduction of Cr(VI) when using leaves of weed plants.

Cr(VI) Adsorption Capacities of Biomass

The results show that of the dicots, the leaves of *P. reticulatus* had the Cr(VI) adsorption capacity greater than those for *P. indica* and *A. viridis*. These were 53,000, 45,000 and 36,400 mg/kg, at a pH of 2 and a Cr(VI) concentration of 50 ppm. Of the monocots, the leaves of *E. colonum* had the Cr(VI) adsorption capacity which were higher than for *C. dactylon* and *V. nemoralis*. These were 36,600, 33,900 and 27,500 mg/kg, respectively. Among the three parts of the plant, leaves were found to adsorb most effectively, while stems and roots had lower Cr(VI) adsorption capacities. This research shows that leaves of *P. indica* were found to have maximum Cr(VI) adsorption capacity at a pH of 2 and an EBCT of 30 min at a Cr(VI) concentration of 50 ppm. This was higher Cr(VI) absorption than that observed for other biomass. This biomass had a breakthrough volume of 51.3 mg/g biomass at 102 hours. Moreover, this research found that the Cr(VI) adsorption capacity increased as pH decreased and that the flow rate decreased over time.

Therefore, the effect of pH and the effect of flow rate can be summarized as in Fig. 4. Figs. 4a to 4d show the breakthrough curves of *P. indica, E. colonum* and *P. reticulates* leaves at pH differences of 2, 4, 6 and 8 and at a flow rate of 1.3 ml/min. The results show that the *P. indica* leaves had the maximum Cr(VI) adsorption capacities of 51.3, 0.5, 0.3 and 0.1 mg/g biomass at breakthrough times of 102 hours, 60 min, 30 min and 15 min, respectively. However, leaves from *E. colonum* had the Cr(VI) adsorption capacities lower than those of *P. indica* at all the pH levels, at 12.1, 0.1, 0.1 and 0.1 mg/g biomass, and with breakthrough times of 24 hours, 15 min, 15 min and 15 min, respectively. Leaves from *P. reticulatus* had even lower Cr(VI) adsorption capacities at all pH levels of 6.1, 0.3, 0.1 and 0.1 mg/g biomass in breakthrough times of 12 hours, 30 min, 15 min and 10 min, respectively. Altogether, this experiment had procedure and sample correction until the equilibrium time was reached and no further change in Cr(VI) concentration occurred.

Effect of Flow Rate (EBCT)

Figs. 4a, 4e and 4f show the breakthrough curves of *P. indica*, *E. colonum* and *P. reticulatus* leaves at flow rate differences of 1.3, 2 and 4 ml/min, at a pH of 2. The results show that the *P. indica* leaves had the maximum Cr(VI) adsorption capacities for all flow rates at 51.3, 18.1 and 9.4 mg/g biomass with breakthrough times of 102, 24 and 6 hours, respectively. Leaves from *E. colonum* had Cr(VI) adsorption capacities which were lower than those of *P. indica* at all flow rates. The adsorption capacities were 12.1, 6.9 and 1.5 mg/g biomass with breakthrough times of 24, 9 and 1 hour, respectively. Leaves from *P. reticulates* had even lower adsorption capacities at these flow rates. This plant had adsorption capacities of 6.1, 4.6 and 1.5 mg/g biomass with breakthrough times of 12, 6 and 1 hour, respectively. Therefore, the effect of pH and the effect

of flow rate can be summarized as in Fig. 4a. Fig. 4a shows the breakthrough curve of *P. indica, E. colonum* and *P. reticulatus* leaves, at the maximum Cr(VI) adsorption capacities, pH of 2 and at a flow rate of 1.3 ml/min. However, the Cr(VI) adsorption capacity decreased as a pH increased from 2 to 8, and also decreased as flow rate increased from 1.3 to 4 ml/min.

Relationship of Phytoremediation and Biosorption Cr(VI) Contamination Medias

The results of the phytoremediation study show that *C. dactylon* had the highest TCr uptake capacities at a Cr(VI) concentration of 400 ppm and acted as a TCr hyperaccumulator. Phytoremediation using weed plant species can clean up large areas of Cr(VI) contamination as an *in situ* procedure. Another salient point is that high Cr(VI) concentrations may inhibit plant growth and thus Cr(VI) uptake capacity. The success of phytoremediation may be seasonal depending on geographical location. Other climatic factors will also influence the effectiveness with which plants can remove Cr(VI) by direct uptake. In contrast, biosorption with biomass can operate in areas of higher Cr(VI) concentrations and as an *ex situ* procedure. Whilst, biosorption cannot process large areas of Cr(VI) contamination, this method does prevent contaminants moving in soils or groundwater. Biomass can remove Cr(VI) by direct adsorption.

Possibility of Business Management

In phytoremediation, plant species must be used for a long time in order to clean up a site. Their maintenance and successful growth relies on effective operational measures such as irrigation and fertilizer application. This is costly and time consuming, because plant species used for phytoremediation may take several growing seasons to clean a site. Moreover, Cr(VI) accumulation in plants may pose a risk to animals that

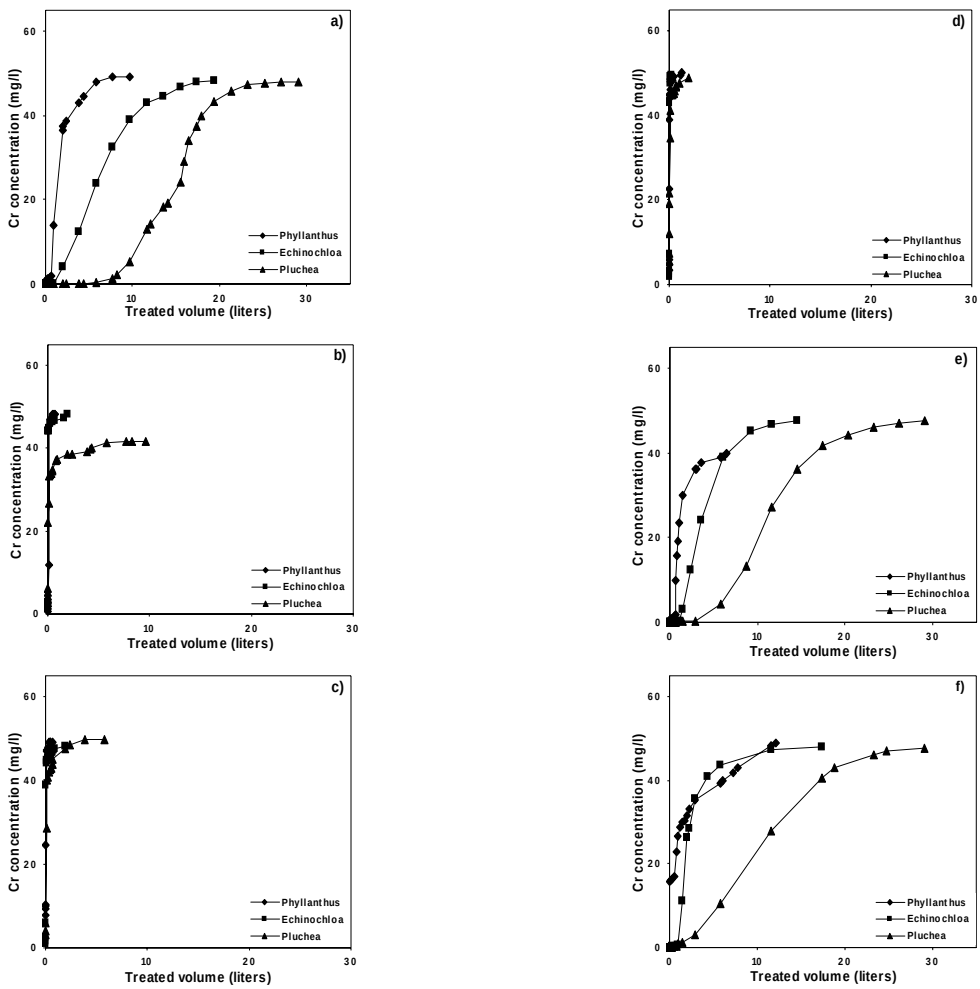

Fig 4. Breakthrough curve of *P. indica, E. colonum* and *P. reticulatus*: a) pH of 2, b) pH of 4, c) pH of 6 and d) pH of 8, all at EBCT of 30 min and e) pH of 2 at EBCT of 20 min, and f) pH of 2 at EBCT of 10 min.

eat these plants. Phytoremediation was also slower than biosorption treatment. However, phytoremediation has higher public acceptance than biosorption technology.[16] The biosorption process requires significant amounts of biomass material and there is difficulty in finding and collecting this material. This research shows that biosorption with biomass has shown short times in the consumption of toxins to clean wastewater and has no negative effect on animals.

Type of Plant

The research using phytoremediation of weed plant species for the clean up of Cr contaminants from soil found that *P. indica* and *C. dactylon* had TCr uptake capacities which were more than those for *E. colonum, V. nemoralis, P. reticulatus* and *A. viridis*. The biosorption of biomass experiment found that of the leaves, *P. indica, E. colonum* and *P. reticulatus* showed the maximum Cr(VI) adsorption capacities. Both of these experiments tested different plant material for Cr removal from soil and water. Thus, both of them showed that the leaves of *P. indica* had greater accumulation than that for other weed plants. This plant had greater Cr(VI) adsorption capacities over other species and other parts of plants. In addition, plants can absorb both Cr(VI) and Cr(III), although the more toxic Cr(VI) could be more easily transported through an active mechanism inside the plant than the less toxic Cr(III) which was transported through a passive mechanism.[17] This indicates that the two forms do not share common uptake mechanisms.

Efficiency of Cr Accumulation in Plants and Cr Adsorption in Biomass

Results from the phytoremediation research show that the plant species *C. dactylon*, *P. indica, P. reticulatus, E. colonum, V. nemoralis* and *A. viridis* had TCr accumulation values of 0.152, 0.151, 0.101, 0.077, 0.069 and 0 mg/g of plant on a dry weight basis on day 30 at a Cr(VI) concentration of 100 ppm, respectively. Altogether, roots, stems and leaves of *C. dactylon* had Cr(VI) uptake results of 0.038, 0.018 and 0 mg/g, respectively. For *P. indica*, the Cr(VI) uptake results for roots, stems and leaves were 0.029, 0.035 and 0.073 mg/g, respectively. In contrast, the results from the biosorption experiment found that of the leaves of *P. reticulatus, P. indica, E. colonum, A. viridis*, *C. dactylon* and *V. nemoralis* had Cr(VI) adsorption capacities of 53, 45, 36.6, 36.4, 33.9 and 27.5 mg/g, respectively, at a pH of 2 and at a Cr(VI) concentration of 50 ppm. Altogether, this research found that *P. indica*, *E. colonum* and *P. reticulatus* had Cr(VI) adsorption capacities of 51.3, 12.1 and 6.1 mg/g, respectively, at a flow rate of 1.3 ml/min and pH of 2. In the phytoremediation and biosorption study, *P. indica* leaves, had the highest Cr(VI) accumulation and adsorption capacities of 73 mg/kg of plant on dry weight basis and 51.3 mg/g of biomass on dry weight basis, respectively. While, of monocot species, the root of *C. dactylon* in the phytoremediation study and the leaf of *E. colonum* in the biosorption study had the highest Cr(VI) accumulation and/or adsorption capacities of 38 mg/kg of plant and 12.1 mg/g of biomass, at a biomass dosage of 0.1 gram, pH of 2 and equilibrium time of 24 hours, respectively. Thus, leaves of both the plant and the biomass of *P. indica* had the highest uptake capacities and thus were selected to solve the problem of Cr contamination in both soil and water. The Duncan multiple range test on the data confirmed that these capacities are statistically in the same group and are significantly different to the other accumulation capacities. Moreover, the important point is that, leaves of *P. indica* in both the phytoremediation and biosorption sections of the experiment, had effected the highest Cr(VI) removal capacities. The dominance of this species shows the relationship between phytoremediation and biosorption. Thus, this relationship needs further research with regards to chemical relationships and interaction behavior between living plants and non-living plants.

Cr(VI) Removal after Plants Treatments

The management of plants after they have accumulated Cr(VI) in phytoremediation needs further research. Biosorption biomasses after Cr(VI) adsorption can be used in solidification and stabilization processes and can then be securely stored in landfill. However, the harvested plants used in phytoremediation and biomass on biosorption may require disposal as hazardous waste.

Cost Estimate of Phytoremediation and Biosorption

The application of phytoremediation with living plant species for soil clean up was estimated to cost lower than biosorption treatments with non-living biomass for wastewater clean up. The higher estimated cost of biosorption was a result of the installation of this operation. For the calculation, the associated costs between phytoremediation and biosorption included: 1) Capital costs, 2) Operation and maintenance costs and 3) Disposal costs.

Table 1 shows the cost estimates associated with phytoremediation and biosorption activity. Phytoremediation is emerging as a cost-effective alternative. The cost of soil remediation is highly variable and depends on the treatment strategy, the contaminants of concern, soil properties and site conditions.[18] However, this research shows the cost for phytoremediation operation was US$900 per 1 cubic meter ($m^3$) of soil at a soil depth of 50 cm for Cr(VI) removal at 50 mg/kg. In contrast, the cost for biosorption operation was estimated at US$1500 per

1 cubic meter (m^3) of wastewater for Cr(VI) removal at 50 mg/L.

The cost estimates also included the use of several technologies for the clean-up of metal contaminated soil. The data were sufficient to begin identifying patterns in costs of several technologies. However, additional cost data for remediation technologies, collected through the use of standard procedures, will help to further improve our understanding of the factors affecting the costs of technology application. The primary variables in the cost of phytoremediation are the total acreage of the contaminated site, depth of contamination, effectiveness of plants in removing the contamination, and the total amount of contaminant to be removed. Every remediation technology has certain limitations and disadvantages. Therefore, site specific evaluations must be made to assure that appropriate technologies are applied. If multiple contaminants are involved, it may be necessary to use a combination of techniques to reduce the concentration of pollutants to acceptable levels.

Conclusions

The alternative between Cr removal capacities of phytoremediation with weed plant species and biosorption with biomass were discussed. Plant species used in phytoremediation can also be used as biomass for biosorption. The weed plant species used for phytoremediation in this research were *C. dactylon*, *V. nemoralis, E. colonum, P. reticulatus*, *P. indica* and *A. viridis*. These plants can also be used as biomass for biosorption and both methods can be effectively utilized for remediating Cr(VI) contaminated soil and wastewater. The results of phytoremediation found that *P. indica* and *C. dactylon* had the highest TCr uptake capacities. The biosorption of biomass research found that the leaves of *P. indica, P. reticulatus* and *E. colonum* had maximum Cr(VI) adsorption. The Cr removal mechanisms experiment showed that the leaves of *P. indica* had the highest Cr(VI) accumulation capacities, which were higher than those for *C. dactylon*. The biosorption on column experiment found that the leaves of *P. indica* had the maximum adsorption capacities. Both the phytoremediation and biosorption experiments incorporated different media for Cr remediation of both soil and water. However, both of these showed that the leaves of *P. indica* had higher Cr accumulation and adsorption than the other weed species. More importantly, this research has shown the estimated cost for phytoremediation operation to be US$900 per 1 cubic meter ($m^3$) of soil at a soil depths of 50 cm for Cr(VI) removal at 50 mg/kg. In comparison, the cost of a biosorption operation was estimated at US$1500 per 1 cubic meter ($m^3$) of wastewater for Cr(VI) removal at 50 mg/L.

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Table 1. The estimated cost of phytoremediation and biosorption.*

Phytoremediation		Biosorption	
Activity	**Cost (US$)**	**Activity**	**Cost (US$)**
1. Capital cost		***1. Capital cost***	
-Car rent and gas	50	-Car rent and gas	50
-Soil and plant sampling for analysis	150	-Water sampling for analysis	50
-Labors	10	-Labors	10
-Design and Installation	250	-Design and Installation	750
2. Operation and maintenance cost		***2. Operation and maintenance cost***	
-Planting	10	-Biomass	10
-Labor and maintenance	250	-Labor and maintenance	250
-Water, pesticide and fertilizer	50	-Electricity	250
-Harvest plants	10	-Harvest biomass	10
-Monitoring	20	-Monitoring	20
3. Disposal cost		***3. Disposal cost***	
-Transportation to secure landfill	100	-Transportation to secure landfill	100

* For this research project the cost for phytoremediation was estimated on area of 1 cubic meter (m^3) of soil at the depth of 50 cm at Cr(VI) concentration of 50 mg/kg, and the cost for biosorption was estimated for a volume of 1 cubic meter (m^3) of wastewater at Cr(VI) concentration of 50 mg/L.

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