

Adsorption of Heavy Metal Ions by Immobilized Phytic Acid

GEORGE T. TSAO, YIZHOU ZHENG, JEAN LU,
AND CHENG S. GONG*

*Laboratory of Renewable Resources Engineering,
Purdue University, West Lafayette, IN 47907*

ABSTRACT

Phytic acid (myoinositol hexaphosphate) or its calcium salt, phytate, is an important plant constituent. It accounts for up to 85% of total phosphorus in cereals and legumes. Phytic acid has 12 replaceable protons in the phytic molecule, rendering it the ability to complex with multivalent cations and positively charged proteins. Poly 4-vinyl pyridine (PVP) and other strong-based resins have the ability to adsorb phytic acid. PVP has the highest adsorption capacity of 0.51 phytic acid/resins. The PVP resin was used as the support material for the immobilization of phytic acid. The immobilized phytic acid can adsorb heavy metal ions, such as cadmium, copper, lead, nickel, and zinc ions, from aqueous solutions. Adsorption isotherms of the selected ions by immobilized phytic acid were conducted in packed-bed column at room temperature. Results from the adsorption tests showed 6.6 mg of Cd^{2+} , 7 mg of Cu^{2+} , 7.2 mg of Ni^{2+} , 7.4 mg of Pb^{2+} , and 7.7 mg of Zn^{2+} can be adsorbed by each gram of PVP-phytic acid complex. The use of immobilized phytic acid has the potential for removing metal ions from industrial or mining waste water.

Index Entries: Phytic acid; heavy metal ion removal; immobilization; poly 4-vinyl pyridine (PVP).

INTRODUCTION

In nature, phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$) exists as free acid, phytate, or phytin according to the physiological pH and metal salts. For instance, the sodium salt is known as sodium phytate, calcium salt as calcium phytate, and calcium/magnesium salt is known as phytin. In literature, the name

*Author to whom all correspondence and reprint requests should be addressed.

phytic acid has been used interchangeably with the term phytate, which is a salt. Phytic acid has six "phosphate covalent bond groups" that account for up to 85% of the total phosphorus in many cereals and legumes (1).

Phytic acid serves many physiological functions, and influences the functional and nutritional properties of cereals and legumes and their derived foods by forming the complex with essential minerals and proteins. It also provides the starting materials for germinating plants. During seed germination, phytate is hydrolyzed to inorganic orthophosphorus, and a series of lower phosphoric esters of myoinositol and free myoinositol by the seed enzyme, phytase (2). The young seedlings utilize the myoinositol as the substrate for the myoinositol oxidation pathway and for cell-wall polysaccharide formation (2). The presence of phytate in seeds and grains also gives additional benefits for the preservation of foods and protection against some diseases in plants (3).

Phytic acid has a complex structure that has been subjected to intense studies. With potentiometric titration study, Cosgrove (4) demonstrated that phytic acid has 12 replaceable protons in the phytic molecule. Six are strongly dissociated at a pK_a of about 1.84; two are weak acid with pK_a of 6.3; and six are weakly dissociated at a pK_a of 9.7. Using NMR and pH titration methods, Costello et al. (5) reported the similar results with six replaceable protons in the strong acid range with pK_a of 1.1–2.1. One in the weak range of $pK_a = 5.7$, two with pK_a of 6.8–7.6, and three at range of $pK_a = 10.0$ –12.0. Therefore, phytic acid exists as a strong negatively charged molecule over a wide pH range. With this property, it has tremendous potential for forming a complex with positively charged multivalent cations and positively charged proteins. With heavy metal ion binding capacity, phytic acid can have the potential for removing metal ions from industrial waste water. Furthermore, the adsorbed metals can be recovered for reuse.

As a strong acid, phytic acid forms a variety of salts with metal ions easily and exists as the phytate–metal ion complex. The stability and the solubility of the complex depend on the pH and the concentrations and type of metal ions. The solubility and stability of various phytate–metal complexes have been studied. Vohra et al. (6) indicated the order of stability of phytate–metal complex as $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+}$ at pH 7.4, whereas Maddaiah et al. (7) establish the stability order as $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+}$.

Although many studies indicated the wide existence of phytate–metal complex in nature, phytic acid has not been considered an adsorbent for the removal of heavy metal ions from contaminated water. In order for phytic acid to be considered the adsorbent, it is necessary to find a solid support material that can be used to immobilize phytic acid with good capacity. The immobilized phytic acid should be stable and should have a good adsorption capacity within a reasonable pH range. Furthermore, the adsorbed metal ions should be able to be separated from the adsorbent readily and recovered in concentrated form that can be easily disposed of or recovered for reuse.

Table 1
Some Properties of PVP-425^a

Property	PVP-425
Appearance	white spherical beads
Particle size	18-50 mesh
Surface area (m ² /g)	≅ 90
Bulk density (g/cm ³)	0.29
H ⁺ capacity, in water (meq/g)	5.5
pKa	3-4
Swelling (%) in water (free base to HCl form)	52%
Temperature stability (°C)	260
Solubility	insoluble in water, acid, base or organic solvent

^aData supplied by Reilley Ind., Indianapolis, IN.

Previously, we reported the use of poly 4-vinyl pyridine (PVP) to remove phytic acid from corn steep water (8). In this article, we study the immobilization of phytic acid onto PVP and use the immobilized phytic acid for heavy metal adsorption.

MATERIALS AND METHODS

Materials

The heavy metal ions used in this study were Cd²⁺, Cu²⁺, Pb²⁺, Ni²⁺, and Zn²⁺. The aqueous solutions of 1000 ppm each was prepared from cadmium chloride, cupric sulfate, lead nitrate, nickel chloride, and zinc chloride, respectively. Phytic acid (40% solution in water) was purchased from Aldrich Chemical Co., Milwaukee, WI. A polymeric resin, poly (4-vinyl pyridine) or PVP-Reillex 425, was generously supplied by Reilly Ind., Indianapolis, IN. Some properties of PVP resins are listed in Table 1.

Methods

Preparation of Resins

A column with PVP resins was washed with three bed volumes of 5% HCl, five bed volumes of deionized water, followed by three bed volumes of 4% NaOH and another five bed volumes of deionized water. The flow rate was adjusted to allow at least 30 min of contact time between the

resins and washing solution. The final water rinse was performed until the effluent pH was < 8.0.

Batch Adsorption

Composite adsorption isotherms were determined using a 1:10 (w/v) ratio of dry resins and a starting sodium phytate solution using equilibrium method. A sodium phytate solution with concentration ranging from 0.5–16 mg/mL at different pHs (adjusted with sodium hydroxide) was used as the starting solution. The flasks containing the adsorbents and phytate were mixed at 25°C in an incubator-shaker (New Brunswick Scientific, Edison, NJ) and allowed to equilibrate for at least 24 h. The pH of the bulk solution at equilibrium was recorded, and phytic acid concentrations were determined by HPLC.

Fixed-Bed Immobilization of Phytic Acid

The acid-alkaline-washed PVP resins were transferred into a jacked column (25 × 1.0 cm) equipped with adjustable plungers. Air trapped in the resin bed was removed, and the plunger was lowered to the top of the resin bed. The feed solution containing 100 mg of sodium phytate/mL at pH 6.5 was introduced into the column by a peristaltic pump. The flow rate was adjusted to allow at least 30 min of contact time between the resins and feed solution. Samples were collected from the column, and the phytate concentration was analyzed to monitor the breakthrough point. The resins were considered saturated when the phytic acid concentration in the effluent was at least 95% that in the feed. At this point, the column was washed by distilled water until no more phytate could be detected in the effluent. The adsorbed phytate is considered immobilized, since it cannot be removed from the resins by dilute acid or alkaline solution. The adsorption capacity was expressed as g phytic acid adsorbed/g of dry resin.

Adsorption of Metal Ions on Immobilized Phytic Acid

A PVP column (25 × 1.0 cm) with immobilized phytic acid was used to carry out the metal ion adsorption experiments at 25°C. The breakthrough point for column adsorption is defined as the time when the effluent metal ion concentration reached 0.1% of the feed metal ion concentration of 1000 ppm at pH 6.5. The feed rate was maintained at 1.0 mL/min. For comparison, adsorption experiments were also carried out using PVP column without phytic acid.

Analytical Methods

Phytic acid was quantified by high-performance liquid chromatography (Hitachi Instrument, L-6200A) using a Bio-Rad Aminex HPX-87H ion-exclusion column (300 × 7.8 mm) with a refractive index Detector (Hitachi Instrument, L-3350 RI). The column was eluted with dilute sulfuric acid (0.005M) at a column temperature of 80°C and a flow rate of 0.8 mL/min

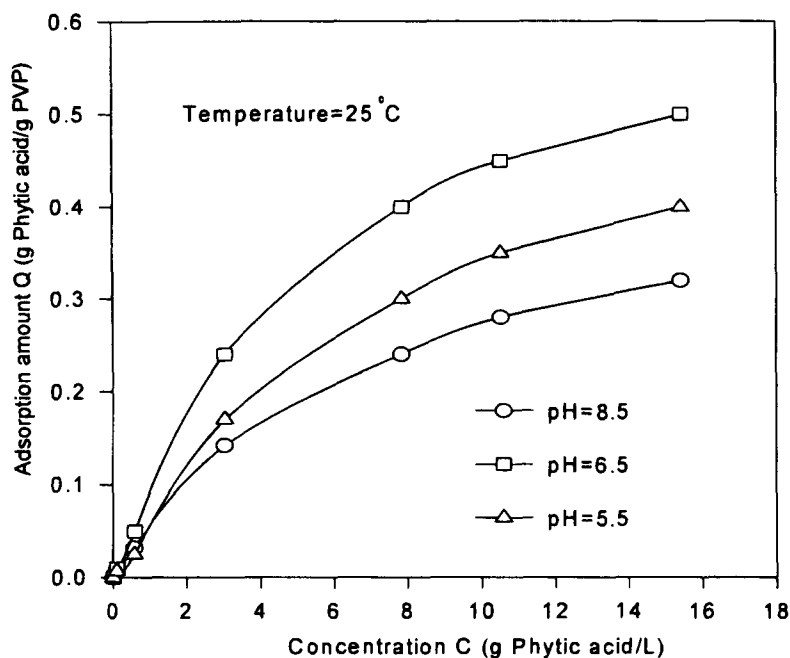


Fig. 1. Adsorption isotherms of phytate at different initial pHs by PVP resins.

over an 8-min period. The concentrations of metal ions were determined using a Perkin Elmer 2280 Atomic Absorption Spectrophotometer.

RESULTS

Similar to other organic acids, pH is one of the important factors determining the adsorption capacity of resins. The adsorption isotherms of phytic acid by PVP-425 at pHs of 5.5, 6.5, and 8.5 are shown in Fig. 1. Resins exhibited highest adsorption capacity for phytic acid at pH 6.5 with 0.51 g phytic acid adsorbed/dry g PVP resin. The capacity dropped to 0.4 g/g at pH 5.5 and 0.31 g/g at pH 8.5.

The feed solution containing 1000 ppm of different metal ions at pH 6.5 was introduced into the columns containing phytic acid by a peristaltic pump at different flow rates. When flow rate was raised to 3.7 mL/min, the shape of the breakthrough curve remained more or less unchanged. Figures 2–6 show the breakthrough data for five different metal ions with or without immobilized phytic acid. With PVP alone, the metal ion adsorption capacities are in the range of 3.1 mg/g PVP for lead ions to 3.7 mg/g PVP for nickel ions. With PVP–phytic acid, the ion adsorption capacity is considerably higher. Table 2 summarizes the capacities of PVP and PVP–phytic acid resins to adsorb different metal ions. The adsorption capacity of as much as 7.7 mg zinc ions/g of immobilized phytic acid was recorded. The order of metal ion's adsorption capacities at pH 6.5 by PVP–phytic acid is as follows: $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$.

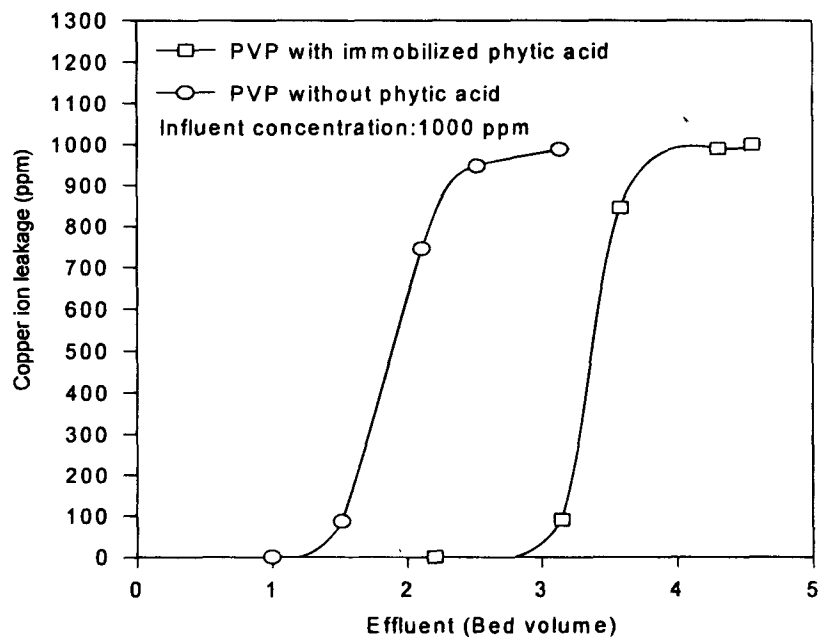


Fig. 2. Adsorption breakthrough curves of copper ions from aqueous solution using PVP with or without immobilized phytic acid.

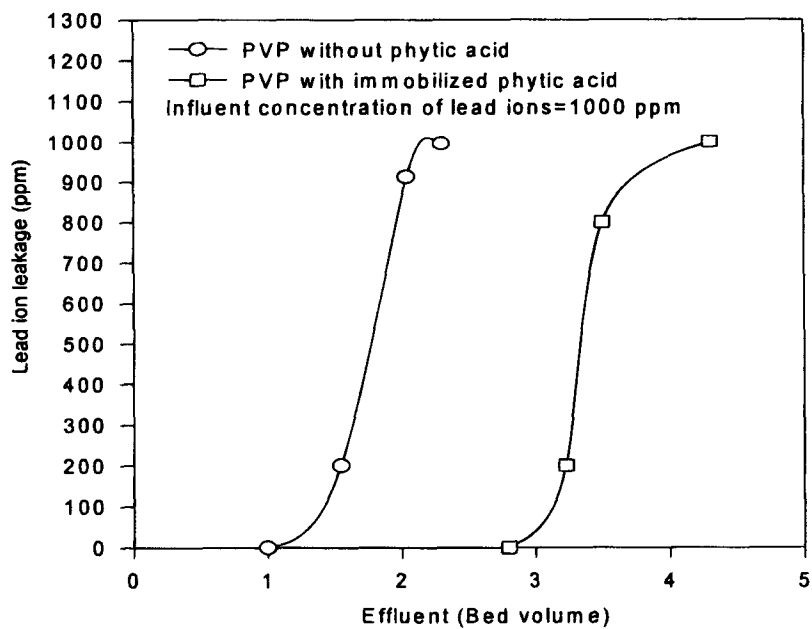


Fig. 3. Adsorption breakthrough curves of lead ions from aqueous solution using PVP with or without immobilized phytic acid.

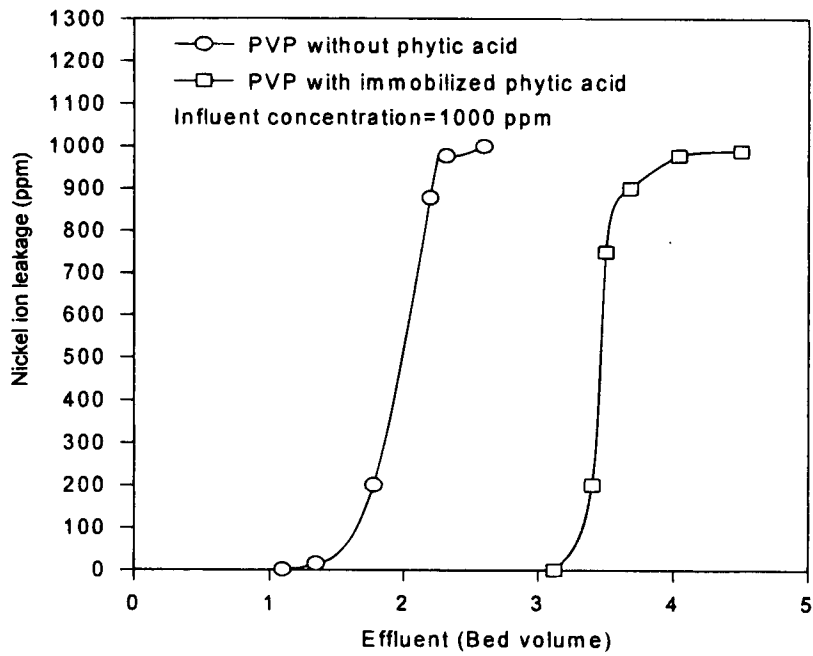


Fig. 4. Adsorption breakthrough curves of nickel ions from aqueous solution using PVP with or without immobilized phytic acid.

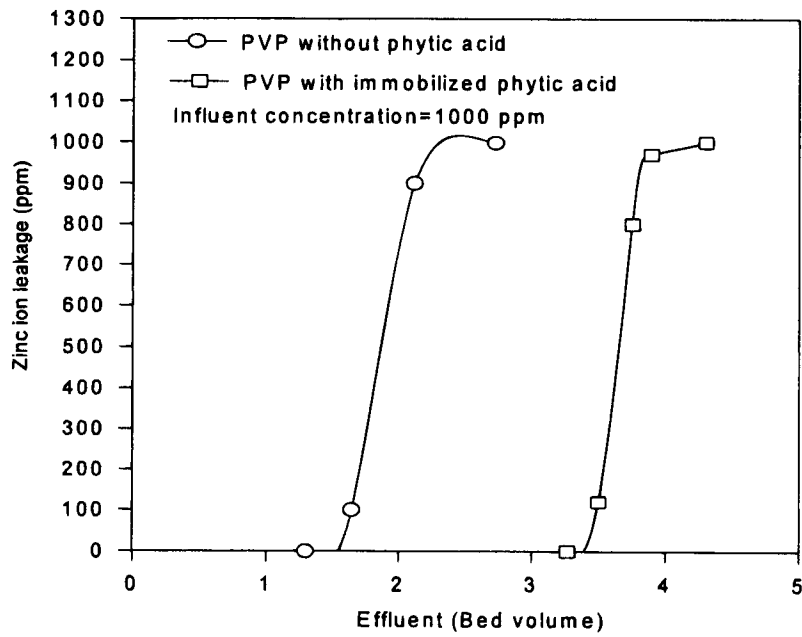


Fig. 5. Adsorption breakthrough curves of zinc ions from aqueous solution using PVP with or without immobilized phytic acid.

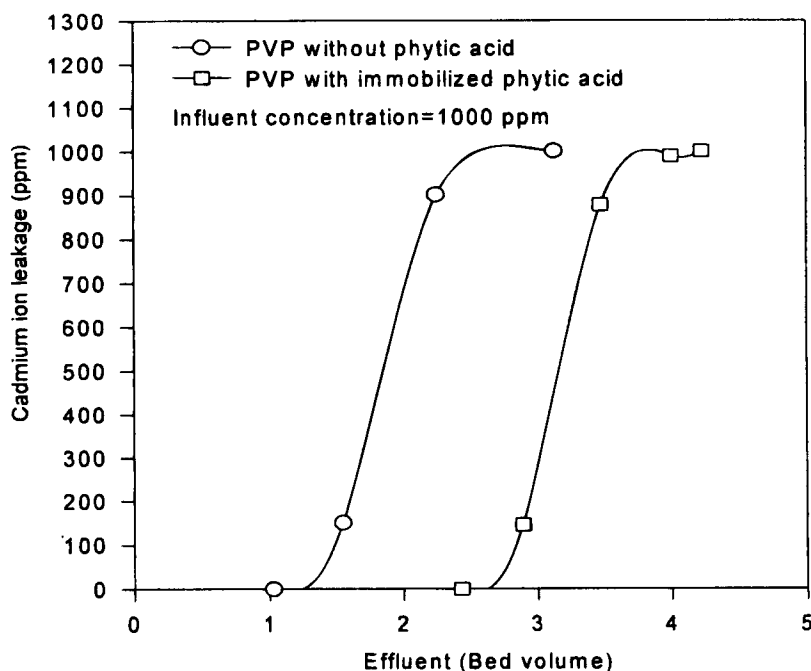


Fig. 6. Adsorption breakthrough curves of cadmium ions from aqueous solution using PVP with or without immobilized phytic acid.

Table 2
Metal Ions Adsorption Capacity of PVP and PVP-Phytic Acid

Metal Ions	Adsorption Capacity		
	PVP mg/g	PVP-Phytic Acid	
		mg/g	mole/mole
Cd ²⁺	3.3	6.6	0.38
Cu ²⁺	3.6	7.0	0.72
Ni ²⁺	3.7	7.2	0.84
Pb ²⁺	3.1	7.4	0.24
Zn ²⁺	3.6	7.7	0.78

Comparing the breakthrough curves of different metal ions in the same mixture (Fig. 7), the concentration of ions in eluent promptly reached the concentration of feed solution after the breakthrough point. It also shows that the breakthrough curves cross each other. The order of adsorption capacity of different metal ions established is the same as those conducted

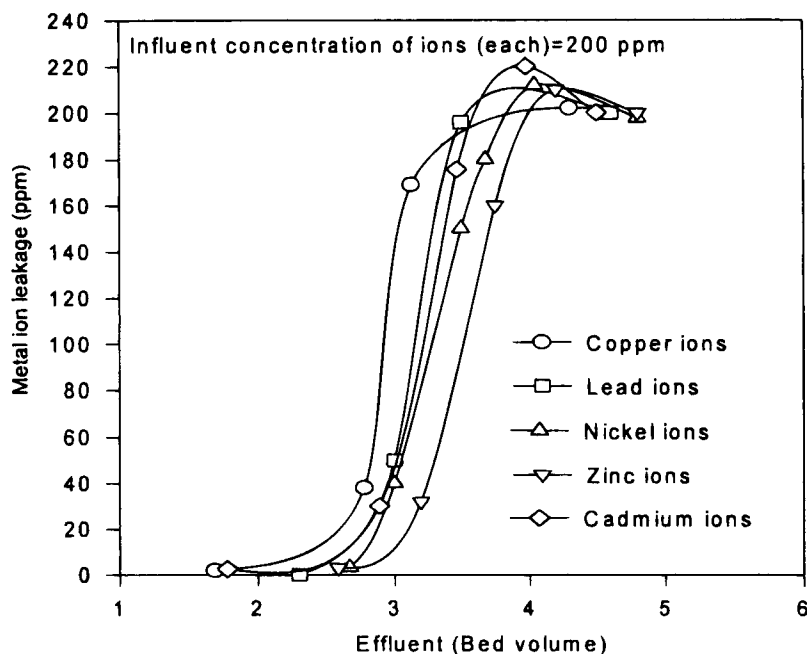


Fig. 7. Comparison of adsorption breakthrough curves of five different metal ions from mixed-ion aqueous solution using PVP with the immobilized phytic acid. Metal ion concentration: 200 PPM; pH = 6.5.

with single metal ions. Although the data are not shown, the PVP-phytate resins can be reused without loss of metal ion's adsorption activity.

DISCUSSION

Growing concern has been given to the potential health hazard presented by heavy metal contamination in drinking water, watershed, and the environment in general. Available processes for heavy metal decontamination/removal include chemical precipitation, evaporation, cementation, flotation, reverse osmosis, and ion adsorption or absorption. Most of these methods suffer from some drawbacks, such as high capital and operational costs and the disposal of residual metal sludge. Ion-exchange resins, which are used in treatment of several pollutants, are usually expensive to use and to regenerate. Therefore, there is a need for research and development of low-cost and readily available materials that can provide an alternative source for removing heavy metals economically. Recently, there has been research conducted, utilizing unconventional and renewable materials for heavy metal removal. The materials studied for heavy metal adsorption and removal include: sawdust (9), modified bark (10), egg shell (11), cyanobacteria (12), and marine algae (13). More recently, there have been efforts to remove heavy metals from contaminated soils using plants. This method is known as "phytoremediation" (14).

Phytic acid is a natural, biodegradable material that can be found in the seeds of cereals and legumes. One of the most readily available source of phytic acid is corn steep liquor, a byproduct from corn wet milling. For example, in a typical concentrated corn steep liquor from corn wet milling process, there is about 4% of phytic acid on a dry basis. Phytic acid in the corn steep liquor is derived from corn germ during steeping process. Considering that over 8 billion bushels of corn are expected to be produced each year in the US and approx 10% of the corn crop will be subjected to a wet milling process (15), the potential amount of phytic acid available is large. It is estimated that 3.6 pounds of corn steep liquor can be generated from each bushel of corn. The total amount of phytic acid that can be recovered is approaching 115 million pounds or 52 million kilograms, a portion can be used for heavy metal removal. Therefore, phytic acid can be a low-cost and readily available material suitable for decontamination of polluted water sources.

PVP is chosen as the adsorbent for the immobilization of phytic acid, because PVP adsorbs phytic acid, a strong acid. Phytic acid is difficult to remove from resins even by alkaline elution (8). This is not surprising, since PVP is known to adsorb acid that is not involved entirely in the ion-exchange mode. The exact mode of phytic acid adsorption by PVP is not yet clear. The adsorption could be in part owing to the interaction between pyridyl group of PVP that obtained a proton from phytic acid and formed the complex.

At stationary condition, the adsorption capacity of phytic acid for metal ions is the function of equilibrium concentration. The information regarding adsorption capacity as a function of product equilibrium concentration in kinetic condition is necessary for process design. This allows the estimation of the solid holdup required to remove as much metal ion from the aqueous solution as possible.

Phytic acid is very stable, particularly under the immobilized form by PVP. Likewise, PVP is very stable and will not deteriorate easily over time under normal application condition (unpublished observation). The adsorbed metal ions can be recovered in concentrated forms, but we have yet to conduct a systematic investigation for the recovery of adsorbed metal ions. A system based on the recovery of organic acid was tried; however a substantial amount of ions remained adhered to the column. Further investigation regarding the adsorption of metal ions in polluted water and the methods for the recovery of metal ions is required.

ACKNOWLEDGMENT

This study was supported in part by The Consortium for Plant Biotechnology Research, Inc. by DOE cooperative agreement no. DE-FC05-92OR22072. This support does not constitute an endorsement by DOE or by The Consortium for Plant Biotechnology Research, Inc. of the view expressed in this article.

REFERENCES

1. Reddy, N. R., Pierson, M. D., Sathe, S. K., and Salunkhe, D. K. (1989), in *Phytates in Cereals and Legumes*, CRC, Boca Raton, FL, 152 pp.
2. Loewus, F. A. and Loewus, M. W. (1983), *Annu. Rev. Plant Physiol.* **34**, 137–161.
3. Hall, J. R. and Hodges, T. K. (1966), *Plant Physiol.* **41**, 1459–1464.
4. Cosgrove, D. J. (1966), *Rev. Pure Appl. Chem.* **16**, 209–252.
5. Costello, A. J. R., Glonek, T., and Mayers, T. C. (1976), *Carbohydr. Res.* **46**, 159–171.
6. Vohra, P., Gray, G. A., and Kratzer, F. H. (1965), *Proc. Soc. Exp. Biol. Med.* **120**, 447.
7. Maddaiah, V. T., Kurnick, A. A., and Reid, B. L. (1964), *Proc. Soc. Exp. Biol. Med.* **115**, 391.
8. Moravec, S., Gong, C. S., Lu, J., Yang, C. W., and Tsao, G. T. (1995), Recovery of lactic acid and phytic acid from corn steep liquor using adsorption. IFT, 1995 Annual Meeting, Anaheim, CA.
9. Bryant, P. S., Petersen, J. M., Lee, J. M., and Brounds, T. M. (1992), *Appl. Biochem. Biotechnol.* **34/35**, 777–788.
10. Gaballah, I. and Kilbertus, G. (1994), in *Separation Process Heavy Metals, Ions and Minerals*, Mistra, M. ed., The Minerals, Metals & Materials Society, pp. 15–26.
11. Suyama, K., Fukazawa, Y., and Umetsu, Y. (1994), *Appl. Biochem. Biotechnol.* **45/46**, 871–879.
12. Corder, S. L. and Reeves, M. (1994), *Appl. Biochem. Biotechnol.* **45/46**, 847–859.
13. Holan, Z. R., and Volesky, B. (1994), *Biotechnol. Bioeng.* **43**, 1001–1009.
14. Salt, D. E., Blaylock, M., Kumar, N. P. B. A., Dushenkov, V., Ensley, B. D., Chet, I., and Raskin, I. (1995), *Bio/Technology* **137**, 468–474.
15. Johnson, L. A. (1991), in *Handbook of Cereal Science and Technology*, Lorenz, K. J. and Kulp, K., eds., Marcel Dekker, New York, pp. 55–131.