Removal zinc ions from contaminated soil using biodegradable polyaspartate via soil washing process

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Abstract. This work reports the potential use of polyaspartate (PASP) synthesized from L-aspartic acid via a newly modified thermal procedure as a soil washing chelating agent for Zn ions removal from contaminated-soil. Response surface methodology (RSM) via faced central composite design was employed for evaluating and optimizing the influence of operational parameters. RSM response models developed describe well the Zn removal efficiency with high R² (> 0.994-0.998; p-values < 0.001) and insignificant lack of fit. Zn washing efficiency was found to increase with increase in Zn initial concentration and decrease in PASP/soil ratio. The relative contribution of the operating conditions on Zn removal follows the order; PASP/soil ratio, initial heavy metal concentration, PASP concentration, initial pH and extraction time. Optimal conditions occurred at 500 mg/kg Zn concentration, 36 mM PASP concentration, 10 polymer-soil ratio, pH 4 and 6 hours retention time when Zn ions removal was 39% with most efficient PASP utilization. Although, 100% removal of Zn was achieved at low Zn concentration (100 mg/kg), yet, more amount of the PASP was needed. These results demonstrated the feasibility of effective utilization of PASP for decontamination of Zn ions polluted soils.

1. Introduction
Due to its simplicity, cost-effectiveness, possibility of complete decontamination and feasibility of recovery of heavy metals from variety of types of soils, soil washing has been considered as one of the best alternative technology for remediation of heavy metals contaminated soils. Several studies have demonstrated the effectiveness of employing ethylenediaminetetraacetic acid (EDTA) as a chelating agent for effective removal of heavy metals from contaminated soils. However, EDTA’s persistence in the environment- characteristics of low biodegradability -is of a great concern for deployment in soil remediation due to its potential long term environmental impact [1-3]. More recent studies have identified ethylenediamineisuccinic acid (EDDS)-a derivative of EDTA- as an effective alternative to EDTA [3-9]. This owes to the fact that EDDS has been proven to be highly biodegradable agent for...
enhancing the uptake of heavy metals in phytoremediation demonstrating improved uptake of metal ions by plants as well as limiting their leachability from soil [4,10]. Yet, cost prohibition still challenges the utilization of most of EDDS and other EDTA alternatives when related to large-scale applications [11]. Polyaspartate (PASP), a biopolymer synthesized from L-aspartic acid, a natural amino acid, has been recently found to be a good candidate as a chelating agent due to its low cost production as well as its environmentally attractive characteristics. These include high solubility, non-corrosiveness, complete biodegradability, recyclability. Thus, the aim of this work was to investigate the feasibility of using PASP as a soil washing chelating agent for the removal of Zn from heavy metals contaminated soil. The PASP employed in the present study was synthesized through a modified thermal process.

2. Materials and methods

2.1. Synthesis of water soluble PASP chelating agent

A slightly revised version of a procedure reported by Nakato et al [12] was adopted for the synthesis of the PASP as illustrated in figure 1. Detailed of the polymerization process has been reported elsewhere [13].

![Figure 1. PASP synthesis scheme using modified thermal procedure [13].](image)

2.2. Soil sampling and preparation and extraction batch experiments

Soil used in this work was a local sandy soil (93.8 % sand) collected (top 20 cm layer beneath the ground surface) in site located at Imam Abdulrahman Bin Faisal University, in Dammam Saudi Arabia. The sampled soil, air-dried, grounded and then passed through a sieve (< 2 mm). Stock solutions (1000 mg/L) of the PASP and mixture of heavy metals were prepared by dissolving appropriate amount of the polymer and nitrate salts of the heavy metals in 1L, respectively. The prepared soil was then spiked with appropriate concentrations of Zn and other metals (Ni, Cu, Cd, Hg and Pb) mixture in solution to get targeted metals ions concentrations as per table 1. The contaminated soils were left for up to three (3) weeks prior to using in the soil washing batch tests. Employing a Nicolet 6700 spectrometer at 4 cm⁻¹ resolution, Fourier transform-Infrared (FITR) analyses of the treated soil was undertaken before and after extraction experiments. The experimental program adopted was based on a 3² full faced centered central composite design (FC-CCD) according to table 1. Detailed experimental procedure has been reported earlier [13].
Table 1: Zn ions extraction operational conditions actual and coded values and their levels.

| Variable                      | Designation | Unit | Values (coding) |
|-------------------------------|-------------|------|-----------------|
| PASP conc.                    | A           | mM   | 36 (-1)         |
| PASP/soil ratio               | B           | -    | 5 (-1)          |
| Zn concentration in soil      | C           | mg/kg| 100 (-1)        |
| pH                            | D           | -    | 3 (-1)          |
| Extraction time               | E           | hours| 6 (-1)          |

3. Results and discussion

3.1. FC-CCD RSM modelling

Using multiple nonlinear regressions with the aid of Design Expert 8.0, the experimental data were fitted to equation 1 to develop polynomial models describing the main as well as the interactive effects of the investigated parameters (A, B, C, D and E as defined in table 1) on Y1, Y2 and Y3. Moreover, the Design Expert 8.0 also provided the analysis of variance (ANOVA) and estimated the regression models coefficient. The best fitted the experimental data were reduced cubic models as given in equations 2 to 4, respectively.

\[ y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_i x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \varepsilon \]  

(1)

Where \( y \) is the predicted response, \( \beta_0, \beta_i, \beta_{ij}, \beta_{ii} \) are constant, the linear, interaction and quadratic coefficients and \( x_i, x_j \) are experimental values of the independent variables (coded).

\[ Y_1 (extracted \ Zn \ ions \ in \ PASP) = 8.934 -0.007A -5.850B +4.030C -0.662D -0.260E -0.205+AB -0.156AC-0.079AD +0.142AE-3.459BC +0.286BD -0.250CE+0.097DE +0.269A^2 +3.964B^2 -0.936C^2 -1.631D^2 +1.354A^2B +1.742A^2C +0.71AD^2 \]  

(2)

\[ Y_2 (Zn \ residual \ concentration \ in \ soil) = 167.34 +10.15A -38.23B +147.03C +6.76D +12.26E +2.75AB +2.36AC -1.98AE -6.34BC +2.59CE -7.72A^2 -4.29B^2 +10.40C^2 +20.85D^2 -10.65A^2E -8.60AB^2 \]  

(3)

\[ Y_3 (Zn \ removal \ efficiency, \%) = 44.21 -3.38A +14.82B -13.79C -3.27D +4.09E -1.01AB -0.80AC +0.54AE -11.33BC -0.98BD +1.62CD -0.91CE +2.59A^2 +5.68B^2 -6.93C^2 +5.35D^2 +4.16A^2E +3.40AB^2 \]  

(4)

3.2. Effects of operating conditions on extractible Zn ions into PASP solution (Y1)

The effects of operating conditions on Zn ions removal are depicted in figure 2a. When the PASP/soil ratio was increased, the amount of Zn extracted into the polymer solution decreases. At lower level of factor, A, the proportion of the contaminated soil was higher which implies more availability of Zn ions that was extractible into the polymer solution. This resulted in the higher concentration of the ions into the solution. Conversely, as the ratio was increased, availability of ions in the soil decreased proportionally and under fixed conditions of the remaining factors, this is expected to result in reduction in the amount of extractible Zn ions into the solution. Moreover, higher levels of factor A implies more tendencies for Zn ions in the soil to bind to the polymer from which complexation reaction was expected to improve [1,2,14]. However, its lower value implies limited availability of the polymer which creates more competitive complexation environment for the multi-component metal ions in the soil [1,3,15]. As a result, extraction efficiency of Zn decreases. Similarly, higher initial Zn concentration in the soil
(factor C) was found to significantly increase the concentration of the Zn in the polymer solution. The exhibited strong influences of these factors on the process dwarfed the role played by factor A.

3.3. Effect of operating conditions on removal efficiency of Zn ions from treated soil (Y3)
When factor A and B were increased, the removal efficacy of Zn from the treated soil increased while it decreased when factors C and D were increased (figure 2c). The influence of extraction time was more manifested on Y3 (than on Y1 and Y2 (figure 2b). Moreover, the extraction time had good interactive effect with the initial concentration of Zn ions as in the cases of Y1 and Y2.

Mainly, the influence of PASP concentration on Y3 deviated from Y1 and Y2 considering that an increase in factor A had a positive effect on it. This implies that under conditions of lower levels of PASP ratio, Zn ions concentration, pH and extraction time and higher levels of PASP concentration, it is expected that removal of Zn ions removal from the soil would be higher. Thus, higher Zn removal efficiencies (Y3 > 80%) were obtained under 100 mg/L and PASP ratio of 25 with the removal improving when the polymer concentration was increased from 36 to 145 mM. Conversely, the total removable Zn ions drastically reduced as the initial concentration was reduced from 500 to 100 mg/kg. Based on the forgone results analyses, it could be deduced that the relative contributions of the main effects on Y1, Y2 and Y3 during the extraction process could be ranked according to the order; B > C > A > D > E.

3.4. Optimization of Zn ions extraction
The optimal conditions for achieving target goal occurred at 500 mg/kg, 36 mM PASP concentration, polymer-soil ratio of 10, pH 4 and 6 hours retention time. Under these operating conditions, the extractible Zn ions in the PASP solution reached up to 26.44 mg/L, yielding up to 39% Zn removal or (195 mg/kg Zn removed) extraction efficacy Zn ions with minimal and efficient utilization of the amount of the PASP. This indicates that within the investigated range of parameters in this study, optimal utilization of the PASP would only possible when the initial Zn concentration was high and that little amount of the polymer (low polymer-soil ratio) is sufficient to remove considerable amount of the Zn ions. Despite considerable increased in the polymer concentration and polymer-soil ratio, higher considerable increased in the polymer concentration and polymer-soil ratio, higher extraction of the Zn ions from the soil into the polymer wasn’t realizable within the investigated range of parameters. However, at low concentration of the Zn (100 mg/kg), complete decontamination of the soil was achievable, though at the expense of using greater quantity of the PASP for smaller volume of the treated soil (high polymer-soil ratio needed i.e., only achievable at highest PASP/soil ratio of 25 and concentration of 145 mM).

4. Conclusion
In this work, feasibility of using PASP synthesized using L-aspartic acid via a newly modified thermal procedure as soil washing chelating agent for removal of Zn from heavy metals contaminated soil was investigated. Higher Zn extraction efficiency was found to increase with increase in Zn initial concentration and decrease in PASP/soil ratio with relative contributions of the operating conditions ranked according to the order; PASP/soil ratio > initial heavy metal concentration > PASP concentration > initial pH > extraction time. Within the investigated range of parameters in this study, optimal utilization PASP was only possible when the initial Zn concentration was high and that little amount of the polymer (low polymer-soil ratio) is sufficient to remove considerable amount of the Zn ions. However, at low concentration of the Zn (100 mg/kg), complete decontamination of the soil was achievable, though at the expense of using greater quantity of the PASP for smaller volume of the soil to be treated.
Figure 2. 3D plots showing effects of PASP concentration and PASP/soil ratio, pH and extraction time on \( Y_1 \), \( Y_2 \) and \( Y_3 \).

(a) 
(b) 
(c)
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