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ORIGINAL PAPER

Chitosan from Waste Marine Sources Immobilized Silica: Differential Pulse Voltammetric Determination of Heavy Metal Ions from Industrial Effluent

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Abstract

In availability of marine products India is one of the top most countries in the world. Approximately 40–50% of the total production consists of waste in the form of shell. Marine product shell is rich in chitin, chitosan, and cellulose. The important characteristic of these constituents is capability to adsorb heavy metals. Heavy metal pollution is one of the most serious environmental (effluent) problems. The objective of this study is to understand removal of heavy metal using chitosan immobilized on silica using electroanalytical technique. Adsorption conditions such as pH, amount of adsorbent, contact time, effect of eluent type, flow rate of sample solution, etc. are optimized using differential pulse voltammetric measurements. The best recovery results were observed at pH – 5 and 6, 200 mg adsorbent and 120 min contact time, 1.0 M HCl eluent, 0.2 ml/min flow rate. The devised procedure applied for determination of Zn (II), Cu (II), Cd(II), Pb(II), Fe(II), and Mn(II) in industrial effluent was reproducible with a relative standard deviation of 0.8%. This study highlighted that chitosan immobilized on silica from waste material is a promising adsorbent in removing heavy metals from wastewater and effectively estimated by differential pulse voltammetry.

Keywords Heavy metals · Industrial effluent · Laboratory waste · Chitosan-immobilized silica · Bioadsorption

Abbreviations

FAAS	Flame atomic absorption spectrophotometry
ICP-AES	Inductively coupled plasma-atomic emission spectrophotometry
HMDE	Hanging mercury drop electrode

Introduction

The heavy metal pollution is a current issue for environmental pollution control boards [1]. Industrial wastewater contaminated with heavy metals such as lead, mercury, cadmium, arsenic, etc. is commonly produced from many kinds of industrial processes [2]. In order to remove toxic heavy metals from water systems, several methods have been suggested and investigated. Ion exchange [3], solvent extraction [4], chemical precipitation [5], coagulation [6], filtration [7], evaporation [8], and membrane [9] methods have been applied for these investigations. However, their utilization is not common and confined to special treatment due to high installation and operating cost. Therefore, many researchers have applied regenerated natural wastes such as agricultural waste [10–14] and marine waste [15–17], to treat heavy metals from aqueous solutions. Approximately 40–50% out of the total marine products consists of waste in the form of shell. Marine product shell is rich in chitin, chitosan, and cellulose [16, 17]. The important characteristic of the waste marine products is adsorption of heavy metals [18–27]. The objective of this research is to study the removal of heavy metals [28–30] using chitosan as an adsorbent. A number of solid phase extraction methods have been developed for enrichment and determination of toxic metals using chitosan as a bioadsorbent. They involve physical interaction with a suitable solid support to prepare impregnated sorbents [18–27, 31]. The activated silica

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[28, 32] is an interesting support for immobilization of chitosan. The spectroscopic methods are available for quantitative determination of heavy metals which includes flame atomic absorption spectrophotometry (FAAS) [28] and inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) [33] that exhibit limitation due to the chemical and spectral interferences arising from matrix elements and also lack of adequate sensitivity for its detection at low levels. Hence, electroanalytical methods are benefited for low concentration of heavy metal ions determination [34–44].

Material and Method

Instrument

Differential pulse voltammetric analysis was performed with a Metrohm 797 VA computerized (Switzerland) equipment with at three electrode system consisting hanging mercury drop electrode (HMDE) as working electrode, platinum electrode as auxiliary electrode, and Ag/AgCl/KCl as reference electrode. A digital pH meter Equiptronics–605 (Equiptronics India Ltd.) with a combined glass electrode was used for pH measurement. Weighing Balance Contech–223 with 0.0001 g sensitivity was used. De-ionized double-distilled water was obtained from Borosil quartz double distillation plant.

Chemicals

All chemicals used were of analytical reagent grade. The stock solution containing 1000 $\mathrm{mgL^{-1}}$of Zn (II), Cu(II), Cd(II), Pb(II), Fe(II), and Mn(II) heavy metals were prepared by dissolving appropriate amount of $ZnCl_2$, $CuCl_2.2H_2O$, $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, $FeCl_3$, and $Mn(NO_3)_2$ metal ions in slightly acidic double-distilled water [45]. The solution was standardized volumetrically, and working standard solution containing 50 $\mathrm{mgL^{-1}}$ by appropriate dilutions was prepared. Silica gel 60–120 mesh was of Molychem India Pvt. Ltd. make. The activated silica was prepared on treatment with Con. HCl. A glass column (150 mm × 10 mm, Borosil, India) was used for packing chitosan immobilized on silica. All acids, bases, and salts were of Molychem Chemicals Pvt. Ltd. make analytical reagent grade. All volumetric glassware used were of A-grade Borosil India Ltd.

Preparation of Crude Adsorbent

Waste fish scale was collected from the local fish market of Ratnagiri (Maharashtra), India. Mature fish scale was washed repeatedly with water and allowed to dry in sunlight for 2 days. The scale was kept in an oven at 70 °C till the fish scales became crispy. The dried scale was converted into fine mesh (0.1–0.2 mm) by grinding in a mechanical grinder and stored in air tight polythene containers [17].

Preparation of Chitosan from Crude Adsorbent

About 50 g of powdered chitosan was taken, and 10% HCl was added in that sample in the 1:5 proportions (strong effervescence of CO_2 evolved). After 24 h, it was washed 4–5 times by distilled water. In that solution, 10% NaOH (1:5 proportions) solution was added for deprotonation reaction. After 24 h, it was washed 4–5 times by distilled water. Again, 50% NaOH (1:5 proportions) solution was added for deacetylation reaction. After 24 h, it was washed by distilled water till it becomes neutral. The solution was filtered by using regular filter paper. The residue was kept in oven at 60 °C temperature for 8 h. The dried yellowish-white powdered chitosan was stored in polythene bottle for further analysis of metal ion [46–50].

Preparation of Chitosan-Immobilized Silica

The physical method adopted to prepare the sorbent by immobilization of chitosan on silica. About 300 mg of prepared chitosan was mixed with 2.0 g of activated silica and wetted with double-distilled water to make a paste. The mixture was dried in an oven at 80 °C. This procedure was repeated to ensure complete immobilization of chitosan on silica [32, 51–53].

Preparation of Adsorbent Column and Optimization

A glass column (150 mm × 10 mm) having a stop cock and with glass wool as a support at the bottom was packed with 350 mg of the chitosan-immobilized silica [54]. The column bed was washed with distilled water prior to use. Using this column and 50 mg/L working standard solution, various parameters, i.e., pH, amount of adsorbent, contact time, effect of eluent type, flow rate of sample solution, were systematically investigated for heavy metals adsorption and desorption.

Preparation of Wastewater

The wastewater from different industries was collected. These samples were filtered through a nylon membrane filter of 0.45 μm pore size [54].

Heavy Metal Recovery

A 50 mL solution containing 50 mg/L heavy metal was passed through the column. The retained heavy metals were eluted from the packed column with 10 mL of 1.0 mol/L HCl.

Preparation of Supporting Electrolyte for Voltammetric Measurements

A 0.1 mol/L AR Grade acetic acid was mixed in equal proportion with 0.1 mol /L of sodium acetate that gives buffer solution pH −4.6. A 0.1 mol/L of KCl was prepared from AR grade potassium chloride and pure distilled water.

Preparation of Standard Solution for Voltammetric Measurements

A 1 mg/L standard and mixed standard solution of zinc, copper cadmium, lead iron, and manganese was prepared for the voltammetric analysis from stock solution of 1000 mg/L.

Differential Pulse Voltammetric Measurements

A 10 ml of ultrapure water, 5 ml of 0.1 M of KCl, and 1 ml of acetate buffer (pH 4.6) were taken in polarographic vessel, and then the measurement was started for blank under the given parameters in Table 1. About 1 ml of water sample was added to polarographic vessel, and then voltammogram of the sample solution was recorded under the same conditions. A 0.1 ml of 1 mg/L standards of Zn, Cu, Cd, Pb, Fe, and Mn solution was added twice, and then voltammogram of the standard was recorded. All the measurements are done by standard addition technique in which first the sample was taken into the polarographic vessel and the current was measured. After the addition of 0.1 mL of standard solution, the procedure was repeated three times, and the current was measured. After all measurement extrapolation curve was plotted between current vs concentration, the extrapolation curve will show the amount of metals present in the sample solution.

Table 1 Operating parameters for cyclic voltammetry instrument

Parameters	Description
Working electrode	Hanging mercury dropping electrode (HMDE)
Calibration	Standard addition method
Number of replications	3
Drop size	4
Stirrer speed	2000 rpm
Mode	Differential pulse
Initial purge time	300 s
Addition purge time	10 s
Deposition potential	−1.15 V
Deposition time	90 s
Equilibration time	10 s
Pulse amplitude	0.05 V
Start potential	−1.3 V
End potential	0.05 V
Voltage step	0.006 V
Voltage step time	0.1 s
Sweep rate 0.06 V/s	0.06 V/s
Peak potential (Zn)	−9.80 V
Peak potential (Cu)	−0.10 V
Peak potential (Cd)	−0.56 V
Peak potential (Pb)	−0.38 V
Peak potential (Fe)	−0.46 V
Peak potential (Mn)	−1.2 V

Result and Discussion

Effect of Silica Surface on Adsorption

A 50 mL solution of each metal containing 50 mg/L concentration was adjusted to pH 5.0 and passed through the activated silica column. The retained metals were eluted from the packed column with 10 mL of 1.0 mol/L HCl. The differential pulse voltammetry technique was used to measure the amount of heavy metals by standard addition curve method. The result shows that 31–38% metals were removed by activated silica as an adsorbent. The graphical representation is given in Fig. 1.

Effect of pH on Wastewater Treatment

The pH of the sample solution is one of the key factors affecting the sorption in solid phase extraction techniques. In biomass, the pH regulates the charge of the functional group and hence the metal-binding ability [54]. Heavy metal adsorption was studied from pH 2.0 to 7.0 using chitosan-immobilized silica column. The solution of NaOH and HCl was used for pH adjustment. As the aqueous phase pH increases, adsorption increased, and it was quantitative (95.0 ± 2.0%). For Zn

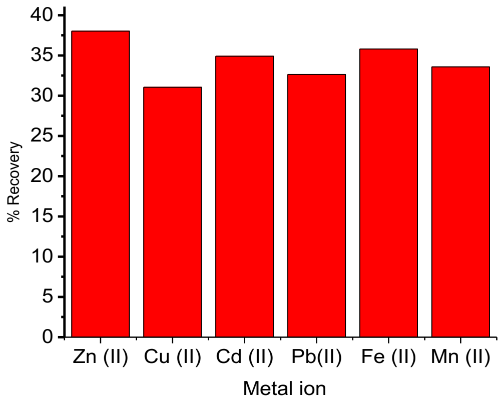

Fig. 1 % recovery of heavy metals with silica as adsorbent. (Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration solution, pH = 5.0, 350 mg of activated silica, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

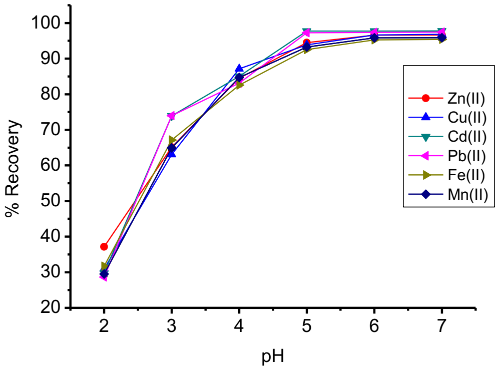

Fig. 2 % recovery of heavy metals at different pH with chitosan-immobilized silica column. (Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration at different pH, 350 mg of chitosan immobilized on silica, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

(II), Cu (II), Fe (II), and Mn (II) % recovery maximum at pH − 6 and for Cd (II) and Pb (II), it was pH − 5. [54]. The graphical representation is given in Fig. 2.

Effect of Amount of Chitosan-Immobilized Silica on Wastewater Treatment

The amount of chitosan-immobilized silica has considerable influence in solid phase extraction, as adsorption depends on active sites of chitosan-immobilized silica. As amount of chitosan-immobilized silica increases from 200 to 400 mg, efficiency of adsorption also increases. The different columns were prepared based on amount of adsorbent. The results at optimized pH show that % recovery was maximum for 350 mg of chitosan-immobilized silica. The graphical representation is given in Fig. 3.

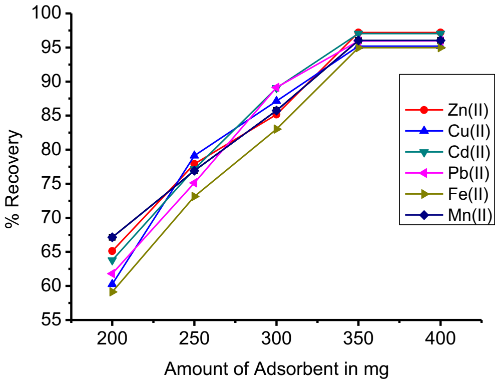

Fig. 3 % recovery of heavy metals at different amount of chitosan-immobilized silica. (Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration at different adsorbent amount, pH = 5 Cd(II) and Pb(II), pH = 6 for Zn(II), Cu(II), Fe(II), and Mn(II), eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

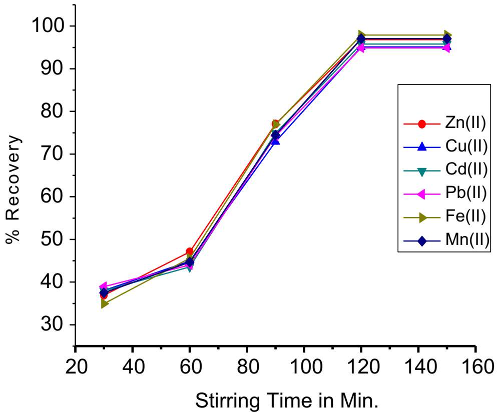

Fig. 4 % recovery of heavy metals at different contact time between metal ion and chitosan-immobilized silica. (Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration at different contact time, pH = 5 Cd(II) and Pb(II), pH = 6 for Zn(II), Cu(II), Fe(II), and Mn(II), 120 mg adsorbent amount, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

Effect of Contact Time of Adsorbent on Wastewater Treatment

The optimized adsorption condition, i.e., pH and amount of adsorbent for metal ions, was set externally before column preparation. The stirring time was varied from 30 to 150 min. The mixture was passed into the column for separation. The adsorbed metals were recovered by 1.0 M HCl. The results show that 120 min were sufficient contact time for adsorption. The graphical representation is given in Fig. 4.

Flow Rate of Sample Solution

The solid phase extraction depends on flow rate of heavy metal ion through solution. At high flow rates, it diminishes the contact between the analyte and adsorbent. Heavy metal adsorption was studied at flow rate of 1.0–4.0 mL min^{-1}, and

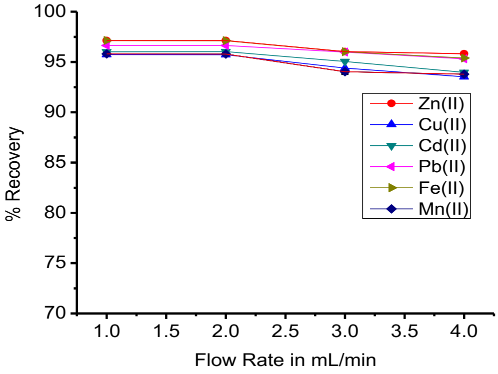

Fig. 5 % recovery of heavy metals at different flow rates (Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration at different flow rates, pH = 5 Cd(II) and Pb(II), pH = 6 for Zn(II), Cu(II), Fe(II), and Mn(II), 200 mg adsorbent amount, 120 min contact time, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

Table 2 Effect of type and concentration of eluent on the recovery of heavy metals

Metal ion	% Recovery of metal ions at different eluent type and concentration					
	Con. of HNO_3 in moles/L			Con. of HCl in moles/L		
	0.1	0.5	1.0	0.1	0.5	1.0
Zinc (II)	31.758	77.122	97.920	21.712	71.512	97.910
Copper (II)	32.018	79.124	97.780	22.904	72.508	98.002
Cadmium (II)	31.794	75.976	97.940	21.970	71.570	97.970
Lead (II)	31.790	76.912	97.900	22.046	72.910	97.578
Iron (II)	32.002	76.890	97.180	21.690	72.240	97.792
Manganese (II)	34.025	75.798	97.584	21.052	69.058	97.258

(Aqueous phase: − 50 ml of 50 mg/L of metal ion concentration at different concentrations of eluents, pH = 5 (Cd(II) and Pb(II), pH = 6 for Zn(II), Cu(II), Fe(II), and Mn(II), 200 mg adsorbent amount, 120 min contact time, 2.0 ml/min flow rate)

it was quantitatively adsorbed from 1.0 to 2.0 mL min^{-1} (Fig. 5). A sample flow rate of 2.0 mL min^{-1} was used in all studies. At higher flow rate, 3.0 mL min^{-1} and more resulted in decreased in metal adsorption. The graphical representation is given in Fig. 5.

Effect of Eluent Type and Concentration

To recover the heavy metals and to reuse the adsorbent for next cycle, an appropriate choice of eluent and its concentration is necessary. Different concentrations of HCl and HNO_3 were studied (Table 2). The results shows that 10.0 ml of 1.0 M concentrated HCl and HNO_3 with flow rate 2.0 mL/min recovers metal ions quantitatively up to 98.0 ± 1.0%. Preliminary studies indicated that 1.0 M HNO_3 caused leakage of biomass from the column, thereby reducing its efficiency, and therefore, 1.0 M HCl was chosen as an eluent.

Table 3 Application to industrial effluent samples

Metal ion	Recovery of metal ions in mg/L		% Recovery
	By present method	By ICP-AES	
Zinc (II)	325.06	332.45	97.77
Copper (II)	448.19	459.10	97.62
Cadmium (II)	102.15	105.12	97.17
Lead (II)	135.39	139.10	97.33
Iron (II)	435.25	448.10	97.13
Manganese (II)	365.65	376.15	97.20

(Aqueous phase: − 50 ml of 50 mg/L of metal ions, pH = 5 Cd(II) and Pb(II), pH = 6 for Zn(II), Cu(II), Fe(II), and Mn(II), 200 mg adsorbent amount, 120 min contact time, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

Reusability of Column

The number of cycles for which a chitosan-immobilized silica can be used is important for its cost-effectiveness. The above described removal procedure was repeated for several cycles using the same column to evaluate the column reusability for quantitative sorption and desorption of heavy metals. For reusability study of a column, copper metal ion solution was used. The recovery of heavy metal from sample solution using the devised removal procedure was quantitative (98 ± 0.5%) up to 12 cycles after that recovery decreases. The graphical representation is given in Fig. 6.

Application to Industrial Effluent Samples

The sample solutions of industrial effluent were used for determination of heavy metals using the devised procedure (Table 3). The method was thus useful for analysis of complex materials with good sensitivity and reproducibility.

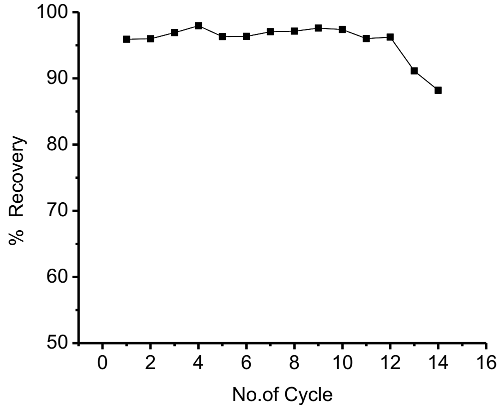

Fig. 6 % recovery of copper metals at different cycles**.** (Aqueous phase: − 50 ml of 50 mg/L of copper metal ion at different cycles of samples, pH = 6, 200 mg adsorbent amount, 120 min contact time, eluent − 10 mL of 1.0 mol/L HCl, 2.0 ml/min flow rate)

Conclusion

Chitosan immobilized on silica as solid phase offers a simple, efficient, and cost-effective method for removal of Zn (II), Cu (II), Cd (II), Pb (II), Fe (II), and Mn (II). Under the optimized conditions, these metals were quantitatively adsorbed at pH 5.0 for Cd (II) and Pb (II) and pH 6 for Zn (II), Cu (II), Fe (II), and Mn (II). About 200 mg of adsorbent and 120 min stirring time were sufficient for efficient adsorption of these heavy metals. The recovery of these metals was easy using 1.0 M HCl at 0.2 mL min^{-1} flow rate, enabling the reuse of the sorbent. Chitosan immobilized on silica was efficient adsorbent up to 12th cycle of adsorption. The real sample analysis data shows that devised procedure is suitable for treatment of industrial wastewater.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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