Application of TETA grafted nanobiocomposite for the removal of EDTA-metal complexes from electroplating and municipal wastewater

Devlina Das[1] and Nilanjana Das[1]*

[1]Environmental Biotechnology Division, School of Biosciences and Technology
VIT University, Vellore, Tamil Nadu -632014, India

Abstract: The present investigation is focused on the use of TETA grafted nanobiocomposite (Aloe gum-mushroom nanopowder) for the removal of EDTA-metal complexes (EDTA-Zn, EDTA-Ni and EDTA-Ag) from aqueous environment. Batch studies were conducted in single, binary and ternary system. At an acidic pH of 3.0 and a molar ratio of 0.06:0.06, the COD removal and metal uptake followed the following order : EDTA-Zn (99.1%) > EDTA-Ni (98.4%) > EDTA-Ag (97.5%). The overall COD removal potential was reduced to 92.1% in ternary system. Equilibrium and kinetic studies suggested a homogeneous mode of intra-particle diffusion as the major mechanism. Further elucidation was done using FT-IR, SEM/EDX and XPS analysis. PVA-alginate immobilized nanobiocomposite was packed in a column for the remediation of electroplating and municipal wastewater. Among the three bead system in column, 1000 bead system exhibited maximum COD removal and found to be more suitable for the remediation of electroplating wastewater.
Key-words: COD ; EDTA-metal complex; nanobiocomposite ; triethylene–tetramine (TETA) ; wastewater.

Introduction

Ethylenediaminetetraacetic acid (EDTA), a powerful chelating agent form stable complexes with heavy metals in wastewater being responsible for making the conventional treatment methods ineffective for removal of heavy metals and increase the overall COD in wastewater. EDTA shows poor biodegradability and also affects plant growth severely[1]. Wastewater containing EDTA- metal complexes released into the environment cause persistent pollution to the aquatic environment causing increased mobility of toxic species to the groundwater and soil system[2]. Hence, EDTA- metal complex contamination has become a challenging issue during wastewater treatment. Among all the traditional treatment technologies, adsorption is considered to be the cost effective and potential method for removal of EDTA – metal complexes[3].

There are reports on the application of plant gum based adsorbents viz. poly(methacrylic acid) grafted functionalized guar gum, *Cassia grandis* seed gum-graft-poly(methylmethacrylate) and gum ghatti crosslinked with nanoparticles for decontamination of wastewater[4]. As metallic nanoparticles may lead to nanopollution owing to their nonbiodegradable nature, it is necessary to replace it using organic nanoparticles.

Triethylene–tetramine (TETA) grafting is reported to enhance the mechanical stability of the adsorbent for removal of heavy metal and to provide additional amine functional groups[5].

To the best of our knowledge, no report is available on the application TETA grafted nanobiocomposite for the removal of EDTA-metal complexes from aqueous environment. The present work is focused on the removal of EDTA-metal complexes using TETA grafted nanobiocomposite made up of mushroom nanopowder and Aloe gum. Batch studies were conducted in single, binary and ternary EDTA- metal systems. The isotherm study and adsorption kinetics could be well elucidated with Langmuir isotherm model and intraparticle diffusion model. TETA grafted nanobiocomposite was further immobilized in PVA- alginate beads for uniform

pore distribution and enhanced diffusivity. The beads were packed in fixed bed columns containing 200, 600 and 1000 bead systems for the assessment of COD removal from electroplating and municipal wastewater.

Experimental

Reagents and equipments

All the chemicals used in the present study were purchased from Sigma-Aldrich and were used without further purification.

Preparation of TETA grafted nanobiocomposite

Fruit bodies of oyster mushroom (*Pleurotus platypus*) were washed with deionized water and dried overnight in an oven at 50°C. The dried fruit bodies were pulverized in a grinder and sieved. Aloe gel was scooped out from the leaves, blended with deionized water (80: 20 v/v) and heated to form a viscous slurry (80% v/v). TETA grafting was done following the method of Kuang et al.[5] After noting the changes in colour of the biocomposite, the slurry was oven dried at 60°C for 48 h and mechanically sheared in a pulverizing mill (Pulverisette 7 monomill, Fristch) to obtain the particles in nano-form.

Characterization of nanobiocomposite

The nanobiocomposite was characterized using various techniques viz., BET, pore volume analysis and mass transfer resistance studies[6]. X-ray diffraction analysis (D8 Advance, BRUKER, Germany) and SEM-EDX analysis (Thermo Electron Corporation, Japan). The thermal stability of nanobiocomposite was analysed using a thermogravimeter (Diamond TG/DTA, Perkin Elmer, USA).

Batch studies

Various parameters viz., pH (2.0-8.0), time (5-30 minutes), biomass dosage (0.1 g/L-0.7 g/L) and initial molar ratio (0.02:0.02 - 0.1:0.1) were analysed under batch condition. The analysis was done in terms of the overall COD removal (%) and metal uptake capacities (mg/g). The mode and nature of the process was studied using equilibrium and kinetic models in single, binary and ternary systems. The overall COD and metal uptake capacities were calculated following the method of Lan et al.[7] The effect of anionic ligands (chlorides, sulphates, nitrates, phosphates, bicarbonates and carbonates) on the remediation process was studied following standard methodologies[8]. Elucidation of mechanism was done using FT-IR analysis (Shimadzu IR affinity-1), SEM- EDX analysis (Thermo Electron Corporation, Japan) and XPS analysis (Omicron nanotechnology, Germany).

Packed bed column studies

Real wastewater was collected from electroplating factory outlet in Chengalpet and a municipal area in Ranipet, Tamil-Nadu, India. Fixed bed column studies were conducted using nanobiocomposite immobilized in PVA-alginate beads which were prepared following the method of Lakshmi et al.[9] BDST and regeneration studies were also conducted.

Results and Discussion

Physical characterization of nanobiocomposite

In the present study, TETA grafted aloe gum-mushroom nanopowder (AG-MP) nanobiocomposite was found to validate its adsorption potential owing to its high BET surface area and a pore volume of 384.5 m^2 g^{-1} and 0.81 cm^3 g^{-1} as compared to that of non grafted nanobiocomposite (178.9 m^2 g^{-1}; 0.57 cm^3 g^{-1}). The mass transfer coefficient was found to be lower in case of TETA grafted nanobiocomposite (β_L : 3.71*10^{-5} m s^{-1}) as compared to non grafted nanobiocomposite (β_L: 2.07*10^{-4} m s^{-1}). The amorphous nature of the nanobiocomposite was confirmed by XRD analysis (Figure not shown) which showed the presence of a low intensity peak at 30.4° thereby supporting its adsorptive nature [5]. SEM images showed that the particles were roughly spherical in shape and possessed slight aggregation (Figure not shown). The size of the nanobiocomposite was found to lie in the range of 16-20 nm. According to the energy dispersive X-ray studies (EDX), the N/C ratio was found to be higher in case of TETA grafted nano-biocomposite (5.79) as compared to non grafted biocomposite (2.39). Thermogravimetric analysis of the grafted and non grafted nanobiocomposite

suggested that TETA grafted biocomposite exhibited a high mechanical strength (resistance upto 900°C) as compared to non grafted biocomposite (resistance upto 600°C). Hence, the study was further conducted using TETA grafted nanobiocomposite.

Removal of EDTA-metal complexes using nanobiocomposite in batch mode

The removal of EDTA-metal complexes viz., EDTA-Zn, EDTA-Ag and EDTA-Ni from aqueous environment using TETA grafted AG-MP nanobiocomposite was evaluated as a function of several factors namely, pH, contact time, biomass dosage, initial molar ratio. The removal efficiencies were calculated in terms of both COD removal (%) and metal uptake (mg/g) capacities.

Optimization of pH is an integral part of a process since it affects the degree of dissociation of functional groups on the biomass surface[10]. In the present study, a pH value of 3.0 was found to be optimum owing to the availability of more number of protonated amine groups. The removal process was found to reach a state of equilibrium within a time period of 20 minutes. The process was found to occur in four stages viz., rapid pore diffusion (upto 5 minutes), rapid non-uniform pore diffusion (upto 10 minutes), rapid uniform pore diffusion (upto 15 minutes) and slow uniform pore diffusion (upto 20 minutes). The process took less time and proved to be quite efficient as compared to the conventional technologies[7,11] as shown in Figure 1. A biosorbent dosage of 0.5 g/L was found to be optimum in the present case for the removal of all the three complexes. Maximum COD removal and metal uptake capacities were noted at a molar ratio of 0.06:0.06 (COD: 1579.97 mg/L). Under optimized conditions (pH: 3.0, contact time: 30 min, biosorbent dosage: 0.5 g/L and molar ratio: 0.06:0.06), a maximum decrease in the overall COD (99.1%) was noted in case of EDTA-Zn followed by EDTA-Ni (98.4 %) and EDTA-Ag(97.5%). Metal uptake was found to follow the order as : Zn (157.8 mg/g) > Ni(151.3 mg/g) > Ag(149.9 mg/g).
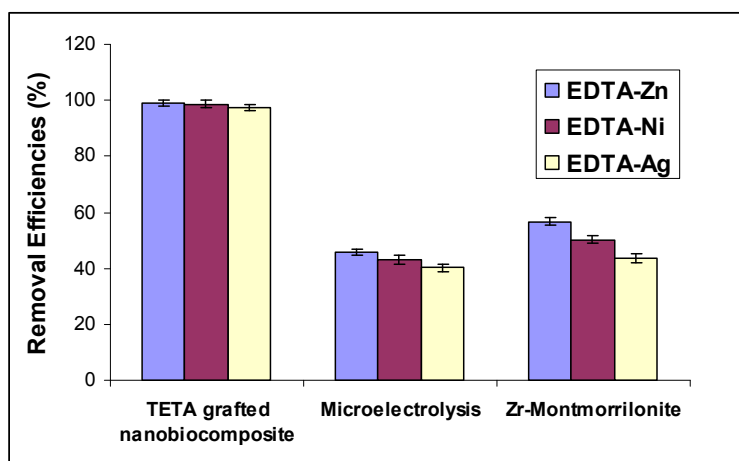

Figure 1: Comparative analysis of EDTA-metal removal after a time period of 20 minutes

Studies on single, binary and ternary systems

Equilibrium studies were conducted in single, binary and ternary systems and the values are presented in Table 1. Among the three equilibrium isotherms, Langmuir was found to exhibit the best fit in case of biosorption of all the three chelate anions in single system thereby suggesting a monolayer mode of adsorption in case of all the three EDTA-metal complexes. Maximum COD removal and metal uptake was noted in case of EDTA-Zn system (476.19 mg g^{-1}; 99.1%) followed by EDTA-Ni (416.67 mg g^{-1}; 98.4%) and EDTA-Ag (322.58 mg g^{-1}; 97.5%). In case of binary systems, the COD removal was found to be maximum in case of EDTA-Ni/ EDTA-Ag system (94.7%) as compared to the other two systems. In contrast to the single systems, the metal uptake of Zn, Ni and Ag was found to follow a heterogeneous mode of adsorption in case of EDTA-Zn/ EDTA-Ni and EDTA-Ni/EDTA-Ag systems which could be attributed to the competition between the chelate anions. Results indicated that maximum anion competition existed between EDTA-Ni and EDTA-Ag systems owing to their high R^2 values. In case of ternary systems, the maximum COD removal was noted to be 92.1% whereas the uptake of all the chelate anions was found to follow a heterogeneous mode of adsorption owing to the competition among them.

Kinetic studies were conducted in order to study the nature of biosorption. As shown in Table 2, intra-particle diffusion model was found to exhibit an accurate fit owing to the high correlation coefficient thereby suggesting pore diffusion of EDTA-metal complexes through the pores of the grafted nanobiocomposite.

Table 1. Equilibrium isotherm parameters

	Langmuir	Freundlich	D-R
Single system			
EDTA-Zn COD removal 99.1 (%)	q_m(mgg^{-1}) 476.19 $K_{L(Lg}$$^{-1}$)0.0213 $R^2$0.9902	K_F $_{(Lg}$$^{-1})$91.6 n 2.62 R^2 0.8683	q_m (mgg^{-1}) 298.00 b 3X10^{-5} E(KJmole^{-1})0.13 R^2 0.8810
EDTA-Ag COD removal 97.5 (%)	q_m (mgg^{-1}) 322.58 K_L $_{(Lg}$$^{-1}$) 0.07 $R^2$0.9577	K_F $_{(Lg}$$^{-1})$ 45.45 n 2.21 R^2 0.7698	q_m (mgg^{-1}) 173.169 b 8X10^{-5} E(KJmole^{-1})0.05 $R^2$0.9586
EDTA-Ni COD removal 98.4 (%)	q_m(mgg^{-1}) 416.67 $K_{L(Lg}$$^{-1}$)0.0152 R^2 0.9892	K_F $_{(Lg}$$^{-1})$ 19.26 n 1.46 R^2 0.9714	q_m(mgg^{-1})174.16 b 6X10^{-5} R^2 0.9360
Binary system			
EDTA-Zn EDTA-Ni COD removal (92.6%)	q_{mZn} 357.7 q_{mNi} 312.5 K_{LZn} 0.054 K_{LNi} 0.037 R^2_{Zn} 0.9972 R^2_{Ni} 0.9866	K_{FZn} 44.25 K_{FNi} 40.76 n_{Zn} 2.26 n_{Ni} 2.58 R^2_{Zn} 0.9744 R^2_{Ni} 0.9123	$q_{m\,Zn}$ 256.36 $q_{m\,Ni}$ 229.97 b_{Zn} 9X10^{-6}; b_{Ni} 2X 10^{-5} E_{Zn} 0.330 E_{Ni}0.2240 R^2_{Zn} 0.9124 R^2_{Ni} 0.9755
EDTA-Zn EDTA-Ag COD removal (93.7%)	q_{mZn} 296.17 q_{mAg} 172.41 K_{LZn} 0.112 K_{Lag} 0.061 R^2_{Zn} 0.9816 R^2_{Ag} 0.9538	K_{FZn} 72.13 K_{Fag} 13.01 n_{Zn} 2.93 n_{Ag} 1.68 R^2_{Zn} 0.9980 R^2_{Ag} 0.9913	$q_{m\,Zn}$ 257.59 $q_{m\,Ag}$ 118.01 b_{Zn} 2X10^{-6} b_{Ag} 1X 10^{-5}; E_{Zn}0.707 E_{Ag}0.316 R^2_{Zn} 0.8583 R^2_{Ag} 0.8282
EDTA-Ni EDTA –Ag COD removal (94.7%)	q_{mNi} 294.12 q_{mAg} 185.19 K_{LNi} 0.166 K_{Lag} 0.041 R^2_{Ni} 0.9784 R^2_{Ag} 0.9760	K_{FNi} 65.61 K_{Fag} 16.82 n_{Ni} 3.03 n_{Ag} 1.80 R^2_{Ni} 0.9875 R^2_{Ag} 0.9724	$q_{m\,Ni}$ 251.31 $q_{m\,Ag}$ 122.57 b_{Ni} 5X 10^{-6}; E b_{Ag} 7X 10^{-6}; E_{Ag}0.378 R^2_{Ni} 0.8717 R^2_{Ag} 0.7883
Ternary system			
EDTA-Zn EDTA-Ag EDTA-Ni COD removal (90.1%)	q_{mZn} 400.00 q_{mNi} 166.17 q_{mAg} 208.33 K_{LZn} 0.022 K_{LNi} 0.183 K_{Lag} 0.0198 R^2_{Zn} 0.9981 R^2_{Ni} 0.7740 R^2_{Ag} 0.9754	K_{FZn} 21.07 K_{FNi} 9.25 K_{Fag} 6.60 n_{Zn} 1.74 n_{Ni} 1.88 n_{Ag} 1.39 R^2_{Zn} 0.9952 R^2_{Ni} 0.9431 R^2_{Ag} 0.9824	$q_{m\,Zn}$ 237.63 $q_{m\,Ni}$ 124.05 $q_{m\,Ag}$ 106.54 b_{Zn} 3X10^{-5}; E_{Zn}0.129 b_{Ni} 1X 10^{-4} E_{Ni}0.071 b_{Ag} 2X 10^{-5} E_{Ag}0.158 R^2_{Zn} 0.8971 R^2_{Ni} 0.6073 R^2_{Ag} 0.8189

Table 2. Kinetic parameters

Kinetic model	EDTA-Zn	EDTA-Ni	EDTA-Ag
Pseudo first order	$q_{eZn\,(mg\,g}{}^{-1})$ 178.57 $K_{1p\,(g\,mg}{}^{-1}$ $min^{-1})$0.745 R^2 0.4952	$q_{eNi(mg\,g}{}^{-1})$170.09$K_{1p\,(g\,mg}{}^{-1}$ min^- $0^{-1})$.827 R^2 0.7043	$q_{eAg\,(mg\,g}{}^{-1})$133.69 $K_{1p\,g\,mg}{}^{-1}$ $min^1)$ 0.713 R^2 0.7997
Pseudo second order	$q_{eZn\,(mg\,g}{}^{-1})$ 285.71 $K_{2p(\,g\,mg}{}^{-1}$ min^-1)0.011 R^2 0.9709	$q_{eNi(mg\,g}{}^{-1})$153.80 $K_{2p(g\,mg}{}^{-1}$ $min^1)$0.030 R^2 0.9784	$q_{eAg\,(mg\,g}{}^{-1})$147.06 K_{2p} $_{(g\,mg}{}^{-1}$ $min^1)$0.008 R^2 0. 9757
Intraparticle diffusion	v 53.03 C 36.97 R^2 0.9838	v 22.79 C 35.22 R^2 0.9881	V 34.41 C 26.22 R^2 0.9849

Presence of anionic ligands

The effects of various anionic ligands viz., nitrates, sulphates, chlorides, carbonates, bicarbonates and phosphates were tested in a ternary system (EDTA-Zn/EDTA-Ni/EDTA-Ag system). Results indicated that the COD removal was lowered to a maximum limit of 90.9%. Based on the effect of individual anion species, the order could be written as : sulphates>carbonates>bicarbonates>phosphates>chlorides>nitrates.

Instrumental analysis

Mechanism of biosorption was elucidated using various spectroscopic techniques viz., FTIR, SEM and XPS in case of EDTA-Zn complex since maximum removal was reported. Major involvement of amines (N-H stretches 3324.7cm^{-1} ;3476.5 cm^{-1} to 3320.1 cm^{-1}; 3425.7 cm^{-1}) and amide groups (C-N stretches 1039.7 cm^{-1} to 1034 cm^{-1}) was indicated by broad and strong peak shifts. An increase in transmittance was noted in case of amine stretches (60%) and amide stretches (32%) thereby suggesting a decrease in their IR absorbance due to their involvement in the biosorption process. SEM images were taken at regular time intervals (5, 10, 15, 20 minutes). Results suggested that the subsequent contact with the EDTA-metal anions resulted in an increase in the surface porosity thereby facilitating the removal of EDTA-metal complexes through intraparticle diffusion. X-ray photo-electron studies showed the appearance of a Zn2p3/2 peak at 1022.1 eV which confirmed the linkage of Zn with O atom of EDTA. Similar result on Zn-O linkage was reported by Amor et al[12].

Analysis of wastewater

In the present study, TETA grafted nanobiocomposite was immobilized in PVA-alginate hybrid bead for attaining uniform pore distribution and enhanced wastewater diffusion[9]. The immobilized nanobiocomposite was packed in a fixed bed column for the remediation of wastewater collected from electroplating and municipal sources. Immobilized PVA-alginate bead was found to contribute to 10.56 % of the overall COD removal process. Three different bead systems were used (200 beads; 600 beads; 1000 beads) for the overall treatment process. A bead diameter of 0.27 cm and a flow rate of 3 ml/min were maintained. As shown in Table 3, maximum reduction in wastewater components was noted in case of 1000 bead system. Moreover, the nanobiocomposite was found to be more effective in case electroplating wastewater remediation (COD reduction: 99.4%) as compared to the wastewater collected from municipal area (COD reduction: 96.7%). BDST studies were conducted with respect to COD removal. Longest breakthrough was noted in case of 1000 bead system (Electroplating wastewater: 11 h; Municipal wastewater: 10.5 h). A linear relationship between the bed depth and breakthrough time was obtained. In case of 1000 bead system, maximum column capacity was calculated to be more in case of municipal wastewater remediation (N_0: 45.82 gL^{-1}) as compared to electroplating wastewater remediation (N_0: 35.5 g L^{-1}) whereas a low value of rate constant was obtained in the former case (Ka: 0.0029 L mg^{-1} h^{-1} as compared to the latter (0.0019 L mg^{-1} h^{-1}) thereby suggesting the need of a longer bed for municipal wastewater treatment. The process could be successfully performed upto 14 cycles in case of both the wastewaters.

Table 3   Wastewater treatment in packed bed column using immobilized Nanobiocomposite

	200 bead system		600 bead system		1000 bead system	
	EW	**MW**	**EW**	**MW**	**EW**	**MW**
COD Electroplating Wastewater (EW) **1576.65 mg L^{-1}** Municipal Wastewater (MW) **1786. 35 mg L^{-1}**	COD reduction(%) 64.3	60.1	COD reduction(%) 87.9	83.8	COD reduction(%) 99.4	96.7
TDS Electroplating Wastewater (EW) **764.79 mg L^{-1}** Municipal Wastewater (MW) **879.97 mg L^{-1}**	TDS reduction(%) 56.9	51.7	TDS reduction(%) 63.2	60.1	TDS reduction(%) 81.1	70.3
Total anionic ligands (Tal) (chlorides, nitrates, sulphates,phosphates Carbonates, bicarbonates) Electroplating Wastewater (EW)**1792.59 mg L^{-1}** Municipal Wastewater (MW) **1257.99 mg L^{-1}** **Heavy metals** (Pb , Cd , Ag, Zn, Cr, Ni, Cu) ElectroplatingWastewater (EW) **1076.31 mg L^{-1}** Municipal Wastewater (MW) **876.2 mg L^{-1}**	Tal reduction (%) 45.2	40.1	Tal reduction (%) 57.1	53.2	Tal reduction (%) 71.1	69.9
	Heavy metals reduction (%) 52.1	50.1	Heavy metals reduction (%) 63.1	62.7	Heavy metals reduction (%) 92.1	90.1

Conclusion

TETA grafted nanobiocomposite could be successfully used for the removal of EDTA-metal complexes from single, binary and ternary systems. Under optimum conditions (pH: 3.0, biomass dosage: 0.5 g/L, molar ratio: 0.06 : 0.06 and time: 20 minutes) , maximum COD removal was noted in case of EDTA-Zn (99.1%) followed by EDTA-Ni (98.4%) and EDTA-Ag (97.5%).PVA-alginate immobilized nanobiocomposite could be effectively used for the remediation of electroplating and municipal wastewater. This is a cost effective, time saving and eco-friendly approach which can particularly be used to reduce the overall COD of wastewaters containing EDTA and EDTA-metal complexes.

Acknowledgement

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