Journal of Hazardous Materials B119 (2005) 251–254

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Short communication

Crab shell-based biosorption technology for the treatment of nickel-bearing electroplating industrial effluents

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Received 9 September 2004; received in revised form 23 December 2004; accepted 24 December 2004
Available online 22 January 2005

Abstract

This paper discusses the possible application of a biosorption system with acid-washed crab shells in a packed bed up-flow column for the removal of nickel from electroplating industrial effluents. Between two nickel-bearing effluents, effluent-1 is characterized by considerable amount of light metals along with trace amounts of lead and copper. Effluent-2 is characterized by relatively low conductivity, total dissolved solids and total hardness compared to effluent-1. Crab shells exhibited uptakes of 15.08 and 20.04 mg Ni/g from effluent-1 and effluent-2, respectively. The crab shell bed was regenerated using 0.01 M EDTA (pH 9.8, aq. NH_3) and reused for seven sorption–desorption cycles. The EDTA elution provided elution efficiencies up to 99% in all the seven cycles. This, together with the data from regeneration efficiencies for seven cycles, provided evidence that the reusability of crab shell in the treatment of nickel-bearing electroplating industrial effluents is viable.

Keywords: Heavy metal; Packed column; Pollution; Regeneration; Waste treatment

1. Introduction

Effluent treatment is nowadays one of the most important issues that have to be addressed by industries. In recent years, several techniques for treating effluent have been reported in the literature, including chemical precipitation [1], ion-exchange [2] and electrochemical method [3]. But the selection of an effluent treatment method is largely based on the concentration of waste and the cost of treatment.

Biosorption is a proven technology for the removal of heavy metals from aqueous solutions. Several investigators have reported the potential of different biomaterials to adsorb heavy metal ions from solutions, including bacteria [4], fungi [5] and marine algae [6]. All these biomaterials have shown sufficient heavy metal-binding capacity to be considered for the use in full-scale biosorption process. However, Tsezos [7] clearly pointed out that a successful biosorption technology not only depends on the metal-sorbing potential of the biomass, but also on continuous supply of the biomass for the process. For this purpose the biomass should either be an industrial waste or available in plenty in nature. Crab shell, a well-known biosorbent, can be obtained in large quantities from seafood industries. Preliminary experimental results have established the potential of crab shells for continuous removal of nickel from synthetic solutions [8]. However, Kratochvil and Volesky [9] have explained the necessity of examining the performance of biosorbent on industrial effluents. Industrial effluents often contain several toxic metals, this usually results in competitive ion-exchange and therefore an extended testing of biosorption process is required. Taking this into consideration, nickel-bearing electroplating industrial effluents from two sources were used in the present

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doi:10.1016/j.jhazmat.2004.12.017

study to evaluate the biosorption performance of crab shell in an up-flow packed column.

2. Materials and methods

2.1. Crab shells

Waste shells of *Portunus sanguinolentus* were collected from the Marina beach (Chennai, India) and were sun dried and crushed to a particle size of 0.767 mm using ball mill. The shell particles were then treated with 0.1 M HCl for 4 h followed by washing with distilled water and then dried naturally. The resulted shell particles were used in sorption experiments.

2.2. Effluents

Two effluents were used, and these were obtained from two different electroplating industries located in Chennai (India). Both effluents were taken from the second rinse tank and they mainly contain nickel with significant amounts of other heavy and light metal ions. The pH of the solutions was not adjusted, unless otherwise stated. The characteristics of two effluents are listed in Table 1.

2.3. Column studies

Continuous flow sorption experiments were carried out in a glass column (2 cm internal diameter and 35 cm height) by loading 51.48 g of crab shells to yield 25 cm bed height. Raw effluent was pumped upward through the column at 5 ml/min. Metal concentration at the exit of the column was analyzed using atomic absorption spectrophotometer (AAS 6VARIO; Analytik Jena, Germany). Operation of the column was stopped when nickel concentration exceeded the desired value.

Total quantity of metal mass sorbed (m_{ad}) was calculated from the area above the breakthrough curve (C versus t) multiplied by the flow rate. Now, dividing this metal mass (m_{ad}) by the sorbent mass (M) leads to the uptake capacity (Q) of the crab shell.

Table 1
Characteristics of electroplating industrial effluents

Parameter	Effluent-1	Effluent-2
pH	7.48	7.91
Conductivity (mS/cm)	2.13	1.65
Total dissolved solids (mg/l)	1489	1137
Total hardness (as $CaCO_3$, mg/l)	580	360
Sodium (mg/l)	101	76
Potassium (mg/l)	84	58
Nickel (mg/l)	109	52
Lead (mg/l)	4.5	<0.1
Copper (mg/l)	1.3	<0.1
Iron, Fe^{2+} (mg/l)	1.6	<1
Chloride (mg/l)	289	230
Sulfate (mg/l)	558	300

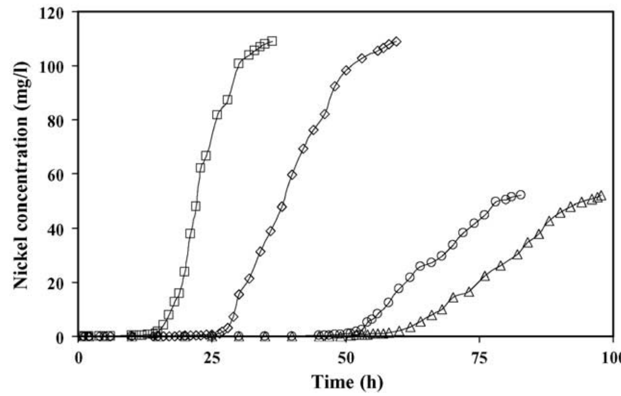

Fig. 1. Breakthrough curves for the removal of nickel from electroplating industrial effluents and synthetic solutions (bed height = 25 cm; flow rate = 5 ml/min). Type of solution: (□) effluent-1; (◊) 109 mg/l synthetic solution; (◯) effluent-2; (△) 52 mg/l synthetic solution.

The metal-loaded crab shell was regenerated using 0.01 M EDTA (disodium) solution adjusted to pH 9.8 with concentrated aqueous NH_3 [8]. The flow rate was adjusted to 10 ml/min. After elution, distilled water was used to wash the bed until the pH of the wash effluent stabilized near 7.0. The desorbed and regenerated crab shell column bed was reused for the next cycle.

3. Results and discussion

Breakthrough curves for the removal of nickel from effluent-1 and effluent-2 are shown in Fig. 1. Nickel-bearing synthetic solutions, prepared from $NiSO_4{\cdot}6H_2O$, were used to compare the sorption behavior of crab shell on real and synthetic nickel effluents. Relatively smooth breakthrough curves were observed for 52 and 109 mg/l synthetic nickel solutions. However, crab shell showed slightly lower sorption capacity when real effluents were considered. In the case of effluent-1, crab shell recorded a Ni uptake of 15.08 mg/g, whereas for synthetic solution (109 mg Ni/l of distilled water) crab shell recorded 25.62 mg Ni/g. In terms of percentage nickel removal, crab shell exhibited 65.4 and 67.9% for effluent-1 and synthetic solution, respectively. Even though an earlier breakthrough and exhaustion time was observed for effluent-2, crab shell sorbed nickel relatively close to that of synthetic solution (52 mg Ni/l of distilled water). Nickel uptakes were 20.04 and 23.71 mg/g for effluent-2 and synthetic solution, respectively. Also, crab shell maintained good nickel removal percentages of 79.9 and 80.1% for effluent-2 and synthetic solution, respectively.

On comparing two effluents on the basis of nickel removal, it was observed that crab shell performed relatively better on effluent-2. As it is well known, metal sorption strongly depends on solution chemistry of the metals and competing ions [10]. The presence of considerable amounts of lead and copper in effluent-1 may have a negative effect on nickel uptake, as they compete in occupying the binding sites. For the duration of sorption experiments up to the column exhaustion (in terms of nickel concentration), the exit concentrations of lead and copper were always below 100 μg/l. It has been known in the past that crab shells possesses unique ability to bind lead [11] and copper [12]. The excess amount of light metal ions (Na^+ and K^+) and total hardness (in terms of $CaCO_3$) in effluent-1 may have influenced the nickel binding. However, Volesky and Schiewer [13] inferred that light metals generally bind less strongly than heavy metal ions and therefore they do not strongly interfere with heavy metals binding. The presence of anions can lead to the following: (1) Formation of complexes that have higher affinity to the sorbent than the free metal ions (i.e. an enhancement of sorption). (2) Formation of complexes that have lower affinity to the sorbent than free metal ions (i.e. a reduction of sorption) [13]. However, in most cases of biosorption the metal binding tends to be reduced in the presence of anions [6,14]. Other parameters such as conductivity and the total dissolved solids can also be blamed for the significant deviation in nickel uptake from two effluents.

Reusability of a sorbent is of crucial importance in industrial practice for metal removal from the wastewater [15]. In the present study, crab shells were reused for seven sorption-desorption cycles. In practical applications, loading of a biosorption column has to be stopped as soon as the metal ion concentration in the effluent exceeds the regulatory limit [9]. Therefore, in regeneration cycles the column operation was stopped when nickel concentration in the effluent exceeded 1 mg/l. Table 2 summarizes the breakthrough time, nickel uptake and percentage nickel removal obtained for two effluents during seven cycles.

Both breakthrough time and nickel uptake decreased as the cycles proceeded, indicating gradual deterioration of crab shell due to repeated usage. Crab shells maintained a relatively good nickel biosorption capacity for effluent-2 in seven cycles examined. A decline of 27.1% in nickel uptake for effluent-2 compared to 76.7% decline for effluent-1 was observed at the end of the seventh cycle. Also, total volume of effluent-2 treated during seven cycles was nearly 4.5 times that of effluent-1. However, no major decrease in bed height was observed at the end of the seventh cycle. This supports the fact that the loss of sorption performance was not primarily due to sorbent damage, but due to sorbing sites whose accessibility becomes difficult as the cycles progressed [16]. The uptake also strongly depended on the previous elution step, since prolonged elution may destroy the binding sites or inadequate elution may allow metal ions to remain in the sites. The acid-washed crab shells are mainly comprised of chitin along with some proteins. Chitin has been postulated as the main constituent responsible for metal coordination [5,11]. The amino and the hydroxyl groups of chitin are the major effective binding sites for metal ions, forming stable complexes by coordination [17]. The elutant used, 0.01 M EDTA (pH 9.8, aq. NH_3), provided elution efficiencies greater than 99% (Table 2). The elution process resulted in very high concentrated metal solutions in early part, followed by gradual decrease in metal concentration. Similar trends were observed in all cycles for both effluents (graph not presented). The time for elution decreased as the cycles proceeded indicate that less metal ions were available for elution and also they were loosely bounded to the sorbent in the successive cycles. The overall achievement of the biosorption process is to concentrate the metal solution. This is accessed by expressing a simple overall process parameter, the concentration factor [13]. The concentration factor is defined as the ratio of the total volume of effluent treated (in sorption process) to the total volume of desorbent used (in elution process). The overall concentration factors for the entire seven cycles were 5.2 and 7.4 in the case of effluent-1 and effluent-2, respectively. This result was as expected, because the concentration factor strongly depends on the initial metal concentration. The higher the initial metal

Table 2
Column data and parameters obtained for two effluents during seven regeneration cycles

Effluent	Cycle number	t_b [a] (h)	Uptake (mg/g)	Bed height (cm)	Effluent volume (l)	Nickel removal (%)	Elution time (h)	Elution efficiency (%)
Effluent-1	1	14.6	9.26	25.0	4.38	99.85	1.2	99.6
	2	14.1	8.94	25.0	4.23	99.87	1.1	99.8
	3	12.8	8.12	24.9	3.84	99.91	1.1	99.5
	4	9.9	6.28	24.8	2.97	99.90	0.9	99.4
	5	8.2	5.20	24.8	2.46	99.91	0.9	98.9
	6	5.5	3.49	24.7	1.65	99.91	0.7	99.3
	7	3.4	2.16	24.6	1.02	99.81	0.7	99.1
Effluent-2	1	50.5	15.27	25.0	15.15	99.80	3.2	99.9
	2	49.8	15.05	25.0	14.94	99.75	3.2	99.4
	3	48.3	14.58	24.9	14.49	99.64	3.1	99.7
	4	45.2	13.67	24.9	13.56	99.83	3.0	99.6
	5	41.6	12.58	24.9	12.48	99.78	2.9	99.6
	6	38.3	11.59	24.8	11.49	99.84	2.9	99.7
	7	36.8	11.13	24.8	11.04	99.84	2.8	99.9

Conditions: sorption (flow rate = 5 ml/min), elution (flow rate = 10 ml/min, elutant = 0.01 M EDTA, pH 9.8).

[a] Breakthrough time.

concentration, the lower the concentration factor and vice versa.

4. Conclusions

This study showed that crab shell can efficiently remove nickel from electroplating industrial effluents. Crab shell could be regenerated and reused for at least seven cycles for nickel removal with a little decrease in sorption performance. This study has also underlined the importance to carry out extended testing for the compatibility of biosorption with a specific industrial effluent. Although a significant deviation in nickel uptake was observed between two effluents, crab shell still exhibited a good nickel removal capacity under unfavorable conditions. Regarding the cost of crab shell, it can be usually obtained free of charge or at low cost from the respective industries since it already presents disposal problems to them. Thus, crab shell has all the intrinsic characteristics for the treatment of nickel polluted electroplating industrial effluents.

References

[1] M.M. Matlock, B.S. Howerton, D.A. Atwood, Chemical precipitation of heavy metals from acid mine drainage, Water Res. 36 (2002) 4757–4764.

[2] J.A.S. Tenorio, D.C.R. Espinosa, Treatment of chromium plating process effluents with ion exchange resins, Waste Manag. 21 (2001) 637–642.

[3] L. Koene, L.J.J. Janssen, Removal of nickel from industrial process liquids, Electrochim. Acta 47 (2001) 695–703.

[4] C.L. Brierley, Bioremediation of metal contaminated surfaces and ground waters, Geomicrobiol. J. 8 (1990) 201–223.

[5] M. Tsezos, B. Volesky, Biosorption of uranium and thorium, Biotechnol. Bioeng. 23 (1981) 583–604.

[6] N. Kuyucak, B. Volesky, Accumulation of cobalt by marine alga, Biotechnol. Bioeng. 33 (1989) 809–814.

[7] M. Tsezos, Biosorption of metals. The experience accumulated and the outlook for technology development, Hydrometallurgy 59 (2001) 241–243.

[8] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column, J. Hazard. Mater. B113 (2004) 223–230.

[9] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, TIBTECH 16 (1998) 291–300.

[10] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, F. Veglio, Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations, Hydrometallurgy 60 (2001) 129–141.

[11] M.Y. Lee, J.M. Park, J.W. Yang, Micro precipitation of lead on the surface of crab shell particles, Proc. Biochem. 32 (1997) 671–677.

[12] H.K. An, B.Y. Park, D.S. Kim, Crab shell for the removal of heavy metals from aqueous solution, Water Res. 35 (2001) 3551–3556.

[13] B. Volesky, S. Schiewer, Biosorption of metals, in: M. Flickinger, S.W. Drew (Eds.), Encyclopedia of Bioprocess Technology, Wiley, New York, 1999, pp. 433–453.

[14] S. Ishikawa, K. Suyama, K. Arihara, M. Itoh, Uptake and recovery of gold ions from electroplating wastes using eggshell membrane, Biores. Technol. 81 (2002) 201–206.

[15] M. Zhao, J.R. Duncan, R.P. Van Hille, Removal and recovery of zinc from solution and electroplating effluent using *Azolla filiculoides*, Water Res. 33 (1999) 1516–1522.

[16] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *Sargassum* column, Water Res. 37 (2003) 297–306.

[17] L. Zhang, L. Zhao, Y. Yu, C. Chen, Removal of lead from aqueous solution by non-living *Rhizopus nigricans*, Water Res. 32 (1998) 1437–1444.