



Removal of cyanide and zinc–cyanide complex with malachite green functionalized amberlite XAD-4 resin from electroplating wastewater

Hamid Hashemi-Moghaddam*, Zeinab Noshiri

*Department of Chemistry, Damghan Branch, Islamic Azad University, P.O. Box 36716-39998, Damghan, Iran
Tel. +98 232 5225029; Fax: +98 232 5225044; email: h.hashemimoghdam@damghaniau.ac.ir*

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ABSTRACT

A new chelating resin was prepared by coupling Amberlite XAD-4 with malachite green through an azo spacer, and it has been used for the removal of cyanide and zinc from electroplating wastewater. The resulting chelating resin was characterized by elemental analysis, thermogravimetric analysis and infrared spectra. The effect of pH, electrolytes, and foreign ions was evaluated on the efficiency of cyanide removal, and some eluents were considered for the regeneration of synthesized resin. For the initial 200 mg L^{-1} cyanide solution, the packed bed gave a cyanide effluent concentration of 0.2 mg L^{-1} at 110 bed volume and in the mixture of 200 mg L^{-1} cyanide and 100 mg L^{-1} zinc. The packed beds were exhausted at 185 bed volumes. In order to validate the methodology, the proposed method was applied to electroplating wastewater for the removal of cyanide and zinc. Wastewater was analyzed, before and after of passing from synthesized resin. The results clearly indicated the success in removing cyanide in wastewater using the chelating process.

Keywords: Solid-phase extraction; Chelating resin; Malachite green; Cyanide; Electroplating

1. Introduction

Cyanide is a carbon–nitrogen radical, which may be found in a wide variety of organic and inorganic compounds [1]. Cyanides are present in effluent waters of several industries. It is used in a number of chemical syntheses (nylon, fibers, resins, and herbicides) and metallurgical processes (plating and surface fishing), and therefore, it is present in effluent waters. Cyanides are highly toxic. From short-term exposure, it can cause the following health effects: rapid breathing, tremors, and other neurological effects. From long-term exposure, it can cause weight loss, thyroid effects, and nerve damage. Therefore, cyanide must be

destroyed or removed from wastewater prior to discharge. The strict environmental regulations to the discharge of cyanides make it necessary to develop processes for their removal from wastewater [2].

Cyanide-contaminated water is often treated by alkaline chlorination or biological oxidation process [3,4]. These techniques are only effective for free cyanide (HCN , CN^-) and cyanide that is weakly bonded to metals. Cyanide that is strongly bonded or complexed with metals cannot be treated with these methods. The presence of metals, such as zinc, copper, and iron, increases both the oxidant demand and the cost of the processes.

To reduce the cyanide level for the disposal of the effluent ($<0.2 \text{ mg L}^{-1}$), several cyanide treatment systems have been developed. All these methods are based on cyanide recovery by acidification and/or

*Corresponding author.

destruction by chemical oxidation [5,6]. In many cases, the process is burdened with high reagent costs and royalty payments. Biological treatment processes have also been suggested, but their practical use in cyanide detoxification is limited [7].

Granular-activated carbon and ion-exchange resins have been used for the treatment of cyanide in water. These have been shown to be effective in removing both free cyanide and metal–cyanide species. The ion-exchange resins processes have the unique advantage of recovering cyanide to offset the cost of reagent used. Ion-exchange resins can be used over a wide range of cyanide concentrations [8–14]. It is not used commonly for the treatment of cyanide-bearing wastewaters, but it has been evaluated and used for the removal of metal–cyanide complexes from solution [15].

In aqueous solution, cyanide forms relatively stable anionic coordination complexes with most transition metals of the form $[M(CN)_x]^{n-}$ (M = the transition metal, x = the number of cyanide groups, and n = the electronic charge of the complex). Due to the stable nature of these complexes, they can be separated using anion exchange [15].

Some of the anion-exchange resins, which were used for the removal of cyanide, are as follows: weakly basic anion-exchange resin Amberlite XE-275 for the removal of ferrocyanide complex [16], and zinc cyanide and cyanide [17], Dowex 1X8–50, a strong base anion-exchange resin beads were contacted with water-containing heavy metal (Cu, Cd, and Zn) and cyanide ions [18] and Amberlite IRA-402 Cl for the removal of cyanide and zinc–cyanide complex [19], cross-linked poly(4-vinyl pyridine), PVP, for the removal of ferrocyanide complex [20] and a new type of ion-exchange resin (PS-PIP) incorporating a piperazine group, linked to a styrene–divinylbenzene macroporous network, for the extraction of $Au(CN)_2^-$ and other metal cyanides [10].

Thus, ion exchange is a technology that has been demonstrated to be capable of removing cyanides, especially metal–cyanide compounds, from aqueous solution. The technology has not been widely adopted for this purpose; however, because of the relatively high cost of ion-exchange materials, the inability to regenerate the material after use with a high degree of efficiency, and concern about HCN gas formation during resin regeneration.

The formation of HCN is common in acid regeneration of ion exchangers with adsorbed metal–cyanide species. This is a potential problem in that HCN is volatile and highly toxic [15].

Malachite green (MG) is traditionally used as a dye. It is classified in the dyestuff industry as

a triarylmethane dye. Millions of kilograms of MG and related triarylmethane dyes are produced annually for this purpose [21]. In 1992, Canadian authorities determined that eating fish contaminated with MG posed a significant health risk. MG was classified a Class II Health Hazard. Due to its low manufacturing cost, MG is used in many countries [22].

In this study, for the selective removal of cyanide a new chelating resin was prepared, as a cationic dye (MG) coupled to Amberlite XAD-4, and formation of ion associate between $Zn(CN)_4^{2-}$, and it was investigated. Cyanide could form a complex with zinc, and this ionic complex formed an ion associated with MG.

2. Experimental

2.1. Reagents

Analytical reagent grade chemicals were employed for the preparation of all solutions.

Solutions were prepared using deionized water from a Nanopure water system, Millipore Corporation, (Bedford, MA, USA) with specific resistivity of $18.3 M\Omega\text{ cm}^{-1}$.

Cyanide stock solution was prepared by adding solid crystals of KCN Merck (Darmstadt, Germany) to a 0.05 M NaOH solution. A zinc nitrate $[Zn(NO_3)_2]$ salt Merck (Darmstadt, Germany) was added into de-ionized water to prepare a stock solution of zinc.

Amberlite XAD-4 (surface area: $725\text{ m}^2\text{ g}^{-1}$ and bead size 20–60 mesh) was obtained from Fluka (Buchs, Switzerland).

The MG hydrogen sulfate (MG) Merck (Darmstadt, Germany) was used. All other chemicals used were of analytical grade. The glass apparatus were soaked in 4 M nitric acid overnight and cleaned with double-distilled water before use.

The pH of the solution was adjusted by adding either $0.01\text{ mol L}^{-1}\text{ HNO}_3$ or $0.01\text{ mol L}^{-1}\text{ NaOH}$.

The eluent was 0.5 mol L^{-1} sodium acetate, $0.1\text{ mol L}^{-1}\text{ NaOH}$, and 0.5% (v/v) ethylenediamine at a flow rate of 1 mL min^{-1} . Zinc–cyanide solutions were prepared by mixing cyanide and zinc solutions. Extraction efficiency was calculated by the following equation:

$$\% \text{ Efficiency} = \frac{\text{concentration of analyt after of treatment}}{\text{concentration of analyt before of treatment}} \times 100 \quad (1)$$

2.2. Instrumentation

Absorbances were measured using computer-controlled UV–Vis spectrophotometer UV–2101 PC Shimadzu (Kyoto, Japan). A pH meter Metrohm 744A

model was used for pH measurements. IR spectra ($4,000\text{--}400\text{ cm}^{-1}$) were taken by KBr pellet method using a 6700 Thermo Nicolet FTIR spectrometer. Elemental analyses were carried out using a Perkin–Elmer Elemental analyzer (Rotkreuz, Switzerland). Thermogravimetric analysis (TGA) was carried out by using TGA-50H Shimadzu (Kyoto, Japan).

A column (glass made, with an inside diameter of 1.6 cm and a height of 10 cm) was used in this study. The resin (20.1 mL) was packed into the column. Distilled water was pumped from the bottom of the column at a flow rate of 12 mL min^{-1} for 10 min. The cyanide and zinc–cyanide complex solutions were introduced separately into the column upwardly at a flow rate of 12 mL min^{-1} . The effluent solution was periodically taken for analysis.

Batch (Static) method was used for the investigation of optimized pH. MG resin (0.1 g) was added to the solution containing cyanide and zinc cyanide, and the pH was adjusted with the NaOH solution and then stirred for 10 min. The resin was filtered, and the Zn (II) and cyanide were determined in the solution.

Cyanide concentrations were determined spectrophotometrically by picric acid. Zinc concentrations were determined using a Varian Atomic Absorption Spectrophotometer (Model AA 240).

2.3. Synthesis of MG functionalized Amberlite XAD-4 resin

Procedures described in the literature for similar reagents [23,24] were used for the synthesis of MG-XAD. Amberlite XAD-4 beads (5 g) were treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 . The mixture was stirred at 60°C for

one hour on an oil bath. The reaction mixture was and then poured into 150 mL ice-cold water. Subsequently, it was filtered and washed repeatedly with distilled water until it was free from of acid and then treated with a mixture of 40 g of SnCl_2 , 45 mL of concentrated HCl and 50 mL ethanol. The mixture was refluxed for 12 h at 90°C to reduce the nitrated form of the resin. Then, the solid precipitate was filtered off and washed with distilled water and 2 M NaOH in order to get the free amino polymer.

The amino polymer was treated with 100 mL of 2 M HCl for 30 min and washed with distilled water to remove the excess of HCl. It was then suspended in 150 mL ice-cold water and mixed a diazotizing mixture of 1 M HCl and 1 M NaNO_2 in aliquots of 1 mL each time with constant stirring until the reaction mixture showed a permanent dark blue color with starch-iodide paper. The diazotized resin was then filtered, washed with ice-cold water and treated with MG solution (0.03 mol in 500 mL water) and stored for 40 h at $0\text{--}3^\circ\text{C}$. The resulting resin that appeared as green-colored beads was finally washed and filtered (Fig. 1).

3. Results and discussion

3.1. Characterization studies

The synthesized resin was characterized by elemental analyses, TGA-DTA and IR spectra. Data obtained from elemental analysis (C, 89.10; H, 8.03; N, 2.87%) were comparable with the theoretically calculated values (C, 88.19; H, 8.79; N, 3.00%) by presuming the stoichiometry of the repeat unit to be $\text{C}_{25}\text{H}_{38}\text{N}_4$. It shows that on average, one MG molecule is present in each 14 repeat unit of the polymer.

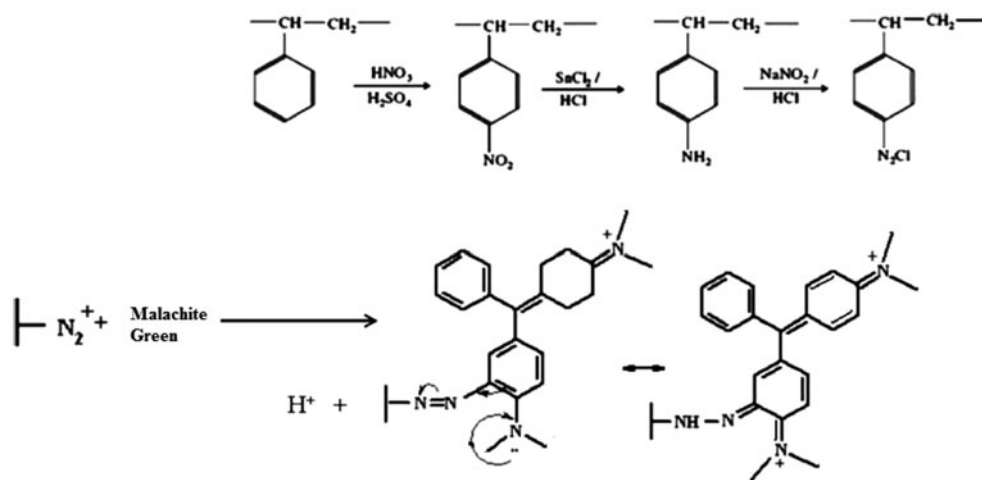


Fig. 1. Schematic representation of the synthesis reaction sequence.

The infrared spectrum of the MG contains normal aromatic absorptions, such as the C–H stretching in $2,926\text{ cm}^{-1}$, and the characteristic ring vibrations at approximately $1,620$ and $1,511\text{ cm}^{-1}$. It exhibits additional band at $1,278$, which may be contributed by C–N group. Also, an additional bond in $1,726$ refer to $\text{C} = \text{N}^+$ vibration in molecular structure of resin. According to the TGA-DTA a finding, the weak mass was lost up to a temperature of 130°C may be due to the sorbed water. In the second step, the mass loss up to 220°C is corresponding MG group. Thermal analysis indicated that the synthesized resin was stable up to 450°C , above which the degradation began.

FTIR spectra and TGA graphs are shown in Figs. 2 and 3, respectively.

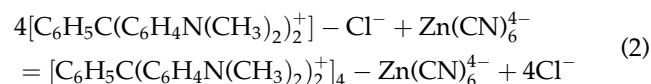
The chemical stability of the resin was tested by shaking a 0.5 g portion of the resin in turn with 100 mL of $1\text{--}12\text{ M HNO}_3$ or HCl for 24 h . The performance of the resin treated by acid was found to be similar to that of the untreated resin (variation: $<3\%$). This shows that the present resin can withstand acid concentration up to 6 M . It can also be reused for 50 cycles of sorption/desorption without any significant change in the sorption capacity ($<1.5\%$).

3.2. Adsorption mechanism

Synthetic ion exchanger beads consist of a cross-linked polymer matrix to which charged functional groups are attached by covalent bonding. The usual matrix is polystyrene cross-linked with $3\text{--}8\%$ divinylbenzene for structural stability. Negatively charged

acid groups are attached for cation exchange; positively charged base groups are attached for anion exchange. A common type of functional group on anion exchangers, for example, is the strongly basic quaternary amine group $(\text{RN}(\text{CH}_3)_3^+)$, Where R represents a hydrocarbon group in the resin matrix.

Ion exchange involves the exchange of one bound ion for another at the charged sites on the exchanger surface. In this study, a new anion-exchange resin was synthesized, where all sites are initially occupied with chloride (Cl^-) ions. The exchange of zinc cyanide for chloride would occur as follows:



3.3. Optimization of sorption and elution of cyanide

Chemical variables that can influence on the sorption and desorption processes were optimized.

3.3.1. Investigation of optimum pH for the removal of cyanide and zinc cyanide

Cyanide and zinc cyanide retention on the resin were investigated as a function of pH, in the range of $8\text{--}12$ in a batch experiment. About 20 mL of 200 mg L^{-1} of cyanide and 200 mg L^{-1} of cyanide and 100 mg L^{-1} of zinc solutions were contacted with 0.5 gr MG Amberlite resin.

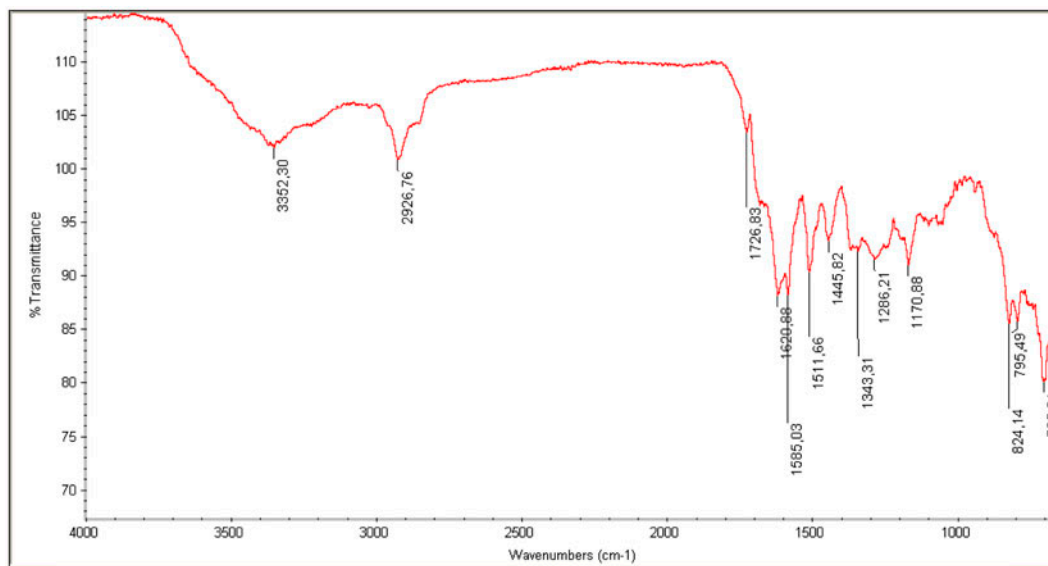


Fig. 2. FT IR Spectra of XAD resin functionalized by MG.

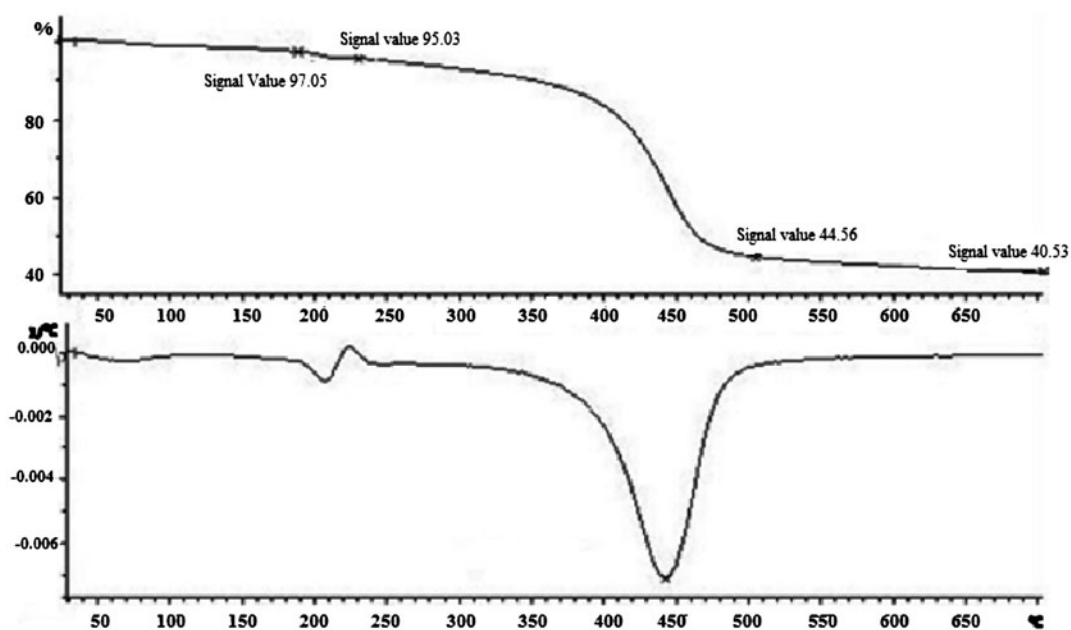


Fig. 3. TGA graph of XAD resin functionalized by MG.

To prevent the formation of HCN, only basic pH was considered. Alkaline pH in this study ensures that cyanide solutions remain in its ionic form (CN^-) ($\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$; $\text{pK} = 9.3$; [25]). A toxic HCN gas is predominately present at a neutral pH region.

Obtained results show (Fig. 4) that extraction efficiency decreased by increasing of the pH, which could be because of interference of hydroxide ion in alkaline pHs. An important parameter governing the selectivity of resins for metal cyanides is pH. Moore, for example, demonstrated that the removal of cyanide and zinc cyanide from electroplating wastewater by anion exchange decreased significantly at $\text{pH} > 10$ [17]. Thus, pH 8 was selected as optimum pH for future experiments.

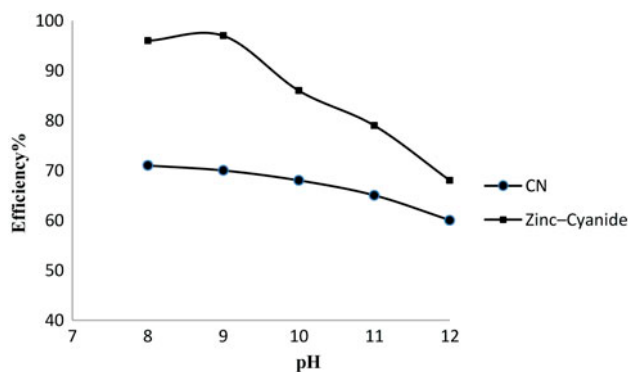


Fig. 4. Cyanide and zinc cyanide retention on the resin as a function of pH.

Fig. 5 shows the speciation of zinc in a zinc(II)/cyanide/ OH^- system as a function of the pH. In

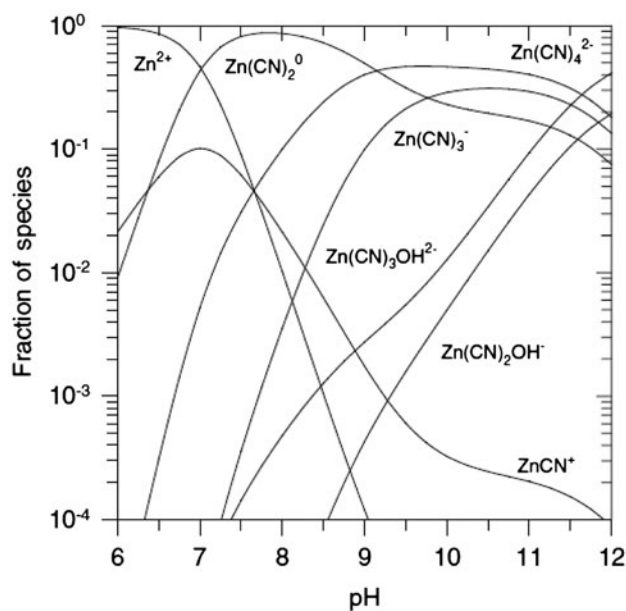


Fig. 5. Speciation of Zn(II) in the Zn(II)/ CN^- / OH^- system as a function of pH for $[\text{Cyanide}] = 2 \times 10^{-4}$ M using the formation constants as $\log \beta_1(\text{ZnCN}^+) = 5.34$; $\log \beta_2(\text{Zn}(\text{CN})_2^0) = 11.97$; $\log \beta_3(\text{Zn}(\text{CN})_3^-) = 16.05$; $\log \beta_4(\text{Zn}(\text{CN})_4^{2-}) = 19.62$; $\log \beta_{21}(\text{Zn}(\text{CN})_2\text{OH}^-) = 0.71$; $\log \beta_{31}(\text{Zn}(\text{CN})_3\text{OH}^-) = 4.08$ [19].

the studied pH range (pH 8–12), the predominant species in the zinc(II)/cyanide/ OH^- system are $\text{Zn}(\text{CN})_4^{2-}$, $\text{Zn}(\text{CN})_3^-$, $\text{Zn}(\text{CN})_2\text{OH}^-$, and $\text{Zn}(\text{CN})_3\text{OH}^-$. The individual zinc–cyanide species interacts differently with the resin, and a fraction of each species also varies with pH.

3.4. Breakthrough curves

3.4.1. Cyanide and zinc–cyanide removal

Initially, a cyanide solution without zinc at 200 mg L^{-1} concentration was passed through the column. The breakthrough curves obtained for cyanide at pH 8 is shown in Fig. 4. The effluent concentration profiles had the typical “S” shapes of breakthrough curves.

At a bed volume of 110, cyanide effluent concentration exceeded the 0.2 mg L^{-1} at pH of 8 levels. A cyanide concentration of 0.2 mg L^{-1} in drinking water is the highest level allowed by the US Environmental Protection Agency.

In the case of zinc–cyanide, a zinc and cyanide solution consisting of 100 mg L^{-1} of zinc and 200 mg L^{-1} of cyanide was prepared and then flowed into the column. The mixed solutions at pH 8 did not give any precipitation. The breakthrough curves for packed bed system are shown in Fig. 6. Cyanide concentration in the effluent reached 0.2 mg L^{-1} at bed volumes of 185 for pH 8.

3.5. Regeneration of loaded resin

A great deal of research and fieldwork has been conducted on the regeneration of anion-exchange materials after their use for the removal of metal cyanides from solution. Regeneration and reuse of ion-exchange material is critical to economic implementation of the process. Studies on regeneration and

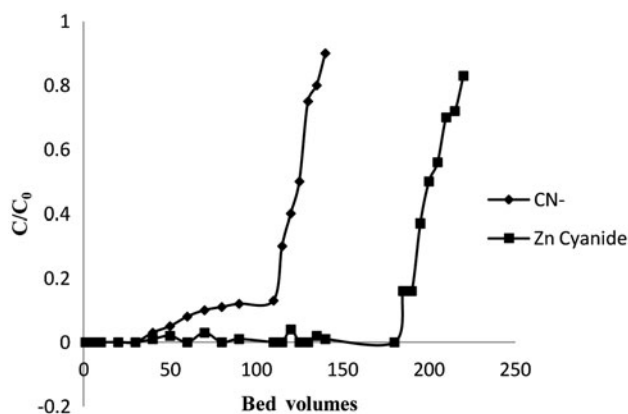


Fig. 6. Breakthrough curves of 200 mg L^{-1} of cyanide and 200 mg L^{-1} of cyanide– 100 mg L^{-1} of zinc solution by MG Amberlite resin packed bed column for pH 8.0.

reuse have included the investigation of eluents, efficiency of recovery, and loss of ion-exchange capacity with multiple cycles of regeneration. Commonly used eluents are concentrated solutions of sodium chloride, zinc cyanide, ammonium, and potassium thiocyanate, sodium hydroxide, and thiourea. The effectiveness of these eluents in removing cyanide compounds adsorbed on anion exchangers depends greatly on the solution conditions and exchanger properties. Recoveries are never complete, however, and sometimes can be very poor. In regeneration of an anion exchanger used to remove iron cyanide from various gold mill effluents, for example, Vachon achieved recoveries as low as 40% in regeneration with a 15% NaCl solution. In repeated exchange-regeneration tests with a particular effluent, Vachon further showed that the resin lost 25% of its exchange capacity in the first cycle, and the additional loss in exchange capacity for subsequent cycles was approximately 1% per cycle [26]. The loss of exchange capacity upon regeneration is reported to be a common problem, which limits the use of strong base anion exchangers. Another factor limiting use of ion exchange for the removal of cyanide species from water, in which there is concerns about formation of highly toxic HCN gas upon resin regeneration [15].

In this work, the effects of some eluents (NaCl, NaOH, thiourea, and alkaline solution of EDTA) on desorption of the zinc–cyanide was investigated in several concentrations and flow rates. The most optimal results was obtained with solution of 0.2 mol L^{-1} of NaOH and 0.1% (v/v) EDTA at a flow rate of 1 mL min^{-1} .

The efficiency of the regeneration process was determined by dividing the total amount of released ions (computed by numerical integration) to the total amount of ions already fixed in the resin. The regeneration found was 98% for zinc and 71% for cyanide. It demonstrates capability of synthesized resin for reusable removal of cyanide from real samples.

3.6. Effect of foreign ions

The effect of foreign ions was studied in treatment with aliquots of 200 mL of solutions containing 10 mg of zinc and 20 mg of cyanide ions and each of the coexisting ions with the concentration more than the zinc and cyanide ions. Cyanide concentration in the effluent was measured after each addition of foreign ions. Each of these foreign ions was considered as an interfering agent when the cyanide concentration in the effluent exhibited a + 5% growth (Table 1). It was observed that most of the other anions could not interfere in the removal of cyanide from examined

Table 1

Tolerance ratio of foreign ions on the determination of cyanide in aliquots of 200 mL of the solution at the conditions were: $C_{Zn(II)} = 50 \text{ mg L}^{-1}$, $\text{pH} = 8$ and $C_{\text{Cyanide}} = 100 \text{ mg L}^{-1}$

	Ions
Mole ratio of interfering ion to Cyanide	
5	Cl^- , SO_4^{2-} , PO_4^{3-} , F^- , NO_3^- , CO_3^{2-}
2	Br^- , SCN^-
Mole ratio of interfering ion to Zn(II)	
10	Na^+ , K^+ , NH_4^+ , Li^+ , Ca^{2+} , Mg^{2+}
2	Cd^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ , Hg^{2+} , Co^{2+}

samples. It is because of high formation constant of zinc with cyanide thus, other anions could not interfere in complex formation of cyanide and zinc. In the presence of other cations, the formation of anionic complex was reduced because of complex formation between cyanide and other soft metals thus these interfere somewhat in the removal of cyanide.

3.7. Applications

Cyanide in electroplating waste waters typically presents as free cyanide or weak metal–cyanide complexes. In order to validate the methodology, the proposed method was applied to Electroplating waste water. Electroplating waste water was collected from the electroplating factory in Semnan province, Iran. Column method was used for the removal of cyanide and zinc from real sample.

The pH of waste water samples was adjusted to 8, filtered through 0.45 mm Millipore membrane filters and fed into the resin column as 150 mL of wastewater was pumped from the bottom of the column at a flow rate of 12 mL min^{-1} .

Wastewater was analyzed, before and after of passing from synthesized resin, the composition is of influent and effluents were shown in Table 2.

Table 2

Removal efficiencies of cyanide and Zn, Cr, and Fe, at flow rate of 12 mL min^{-1} and $\text{pH} = 8$

Parameter	Influent	Effluent	Removal efficiency
pH	7.45	7.32	–
Conductivity	365	89	–
Zn	5.43	0.41	92
CN^-	8.86	0.09	98
Cr	11	10.1	0.08
Fe	2	0.07	96.5

4. Conclusion

The continuing generation of large volume of cyanide-bearing wastes from various industries, which resulted in contamination of soils and water, suggests that novel processes are required to alleviate the serious environmental consequences of cyanide pollution. Anion exchange has been demonstrated to be capable of removing cyanides, especially metal–cyanide complexes, from aqueous solution but has seen limited use because of the relatively high cost of ion-exchange materials, limitations in regeneration efficiency, and concern about HCN gas formation during resin regeneration. In this study, in order to separate cyanide, a low-cost cationic resin was prepared by coupling of MG to Amberlite XAD-4. The cyanide played a key role in the formation of selective complex with zinc, and this complex formed an ion associate with MG that immobilized on XAD-4. The results clearly indicated the success of removing cyanide in wastewater using chelating process.

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References

- [1] R.R. Dash, A. Gaur, C. Balomajumder, Cyanide in industrial wastewaters and its removal: A review on biotreatment, *J. Hazard. Mater.* 163 (2009) 1–11.
- [2] N. Adhoum, L. Monser, Removal of cyanide from aqueous solution using impregnated activated carbon, *Chem. Eng. Process* 41 (2002) 17–21.
- [3] D. Aggarwal, M. Goyal, R. Bansal, Adsorption of chromium by activated carbon from aqueous solution, *Carbon* 37 (1999) 1989–1997.
- [4] J. Pattanayak, K. Mondal, S. Mathew, S. Lalvani, A parametric evaluation of the removal of As (V) and As (III) by carbon-based adsorbents, *Carbon* 38 (2000) 589–596.
- [5] J.P. Chen, X. Wang, Removing copper, zinc, and lead ion by granular activated carbon in pretreated fixed-bed columns, *Sep. Purif. Technol.* 19 (2000) 157–167.
- [6] M. Zarrouki, G. Thomas, Etude de l'adsorption de complexes cyanures sur charbon actif [Study of the adsorption of cyanides complexes on activated carbon], *J. Chim. Phys.* PCB 88 (1990) 1715–1762.
- [7] A. Smith, T. Mudder, Chemistry and Treatment of Cyanidation Wastes, Mining Journal Books Ltd., London, 1991.
- [8] H. Kurama, T. Çatalsarik, Removal of zinc cyanide from a leach solution by an anionic ion-exchange resin, *Desalination* 129 (2000) 1–6.

- [9] K. Shams, M. Beigy, A. Gholamipour Shirazi, Platinum recovery from a spent industrial dehydrogenation catalyst using cyanide leaching followed by ion exchange, *Appl. Catal. A*. 258 (2004) 227–234.
- [10] A. Warshawsky, N. Kahana, V. Kampel, I. Rogachev, E. Meinhardt, R. Kautzmann, J.L. Cortina, C. Sampaio, Ion exchange resins for gold cyanide extraction containing a piperazine functionality, 1. Synthesis and physico-chemical properties, *Macromol. Mater. Eng.* 283 (2000) 103–114.
- [11] G. Lukey, J. Van Deventer, D. Shallcross, Selective elution of copper and iron cyanide complexes from ion exchange resins using saline solutions, *Hydrometallurgy* 56 (2000) 217–236.
- [12] D. Bachiller, M. Torre, M. Rendueles, M. Diaz, Cyanide recovery by ion exchange from gold ore waste effluents containing copper, *Min. Eng.* 17 (2004) 767–774.
- [13] S.J. Kim, K.H. Lim, Y.G. Park, J.H. Kim, S.Y. Cho, Simultaneous removal and recovery of cadmium and cyanide ions in synthetic wastewater by ion exchange, *Korean J. Chem. Eng.* 18 (2001) 686–691.
- [14] G. Lukey, J. Van Deventer, D. Shallcross, The effect of functional group structure on the elution of metal cyanide complexes from ion-exchange resins, *Sep. Sci. Technol.* 35 (2000) 2393–2413.
- [15] D.A. Dzombak, R.S. Ghosh, G.M. Wong-Chong, *Cyanide in Water and Soil: Chemistry, Risk, and Management*, Taylor & Francis/CRC Press, Boca Raton, FL, 2010.
- [16] N.L. Avery, W. Fries, Selective removal of cyanide from industrial waste effluents with ion-exchange resins, *Ind. Eng. Chem. Prod. Res. Dev.* 14 (1975) 102–104.
- [17] F. Moore, An improved ion exchange resin method for removal and recovery of zinc cyanide and cyanide from electroplating wastes, *J. Environ. Sci. Heal. A*. 11 (1976) 459–467.
- [18] S.-J. Kim, K.-H. Lim, K.-H. Joo, M.-J. Lee, S.-G. Kil, S.-Y. Cho, Removal of heavy metal-cyanide complexes by ion exchange, *Korean J. Chem. Eng.* 19 (2002) 1078–1084.
- [19] K. Osathaphan, T. Boonpitak, T. Laopirojana, V. Sharma, Removal of cyanide and zinc-cyanide complex by an ion-exchange process, *Water Air Soil Pollut.* 194 (2008) 179–183.
- [20] M. Chanda, K. O'Driscoll, G. Rempel, Cyanide detoxification by selective ion exchange with protonated poly (4-vinyl pyridine), *J. Chem. Technol. Biotechnol.* 33 (1983) 97–108.
- [21] S.J. Culp, F.A. Beland, Malachite green: A toxicological review, *Int. J. Toxicol.* 15 (1996) 219–238.
- [22] T. Gessner, U. Mayer, Triarylmethane and diarylmethane dyes, in: *Ullmann's encyclopedia of industrial chemistry*, Taylor & Francis/CRC Press, Boca Raton, FL, 2000.
- [23] D. Wu, A. Wang, L. Guo, Synthesis and application of amberlite XAD-2 functionalized with dithizone for field preconcentration and separation of trace cadmium in seawater, *Anal. Sci.* 22 (2006) 1245–1248.
- [24] H. Hashemi-Moghaddam, H.A. Panahi, M.N. Nezhati, Synthesis and application of new resin functionalized by brilliant green for spectrophotometric determination of mercury in environmental samples, *Anal. Lett.* 42 (2009) 1911–1922.
- [25] V.K. Sharma, W. Rivera, J.O. Smith, B. O'Brien, Ferrate (VI) oxidation of aqueous cyanide, *Environ. Sci. Technol.* 32 (1998) 2608–2613.
- [26] D.T. Vachon, Removal of iron cyanide from gold mill effluents by ion exchange, *Water Sci. Technol.* 17 (1985) 313–324.