SORPTION OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS IN THE PRESENCE OF COMPLEXING AGENTS ON POLYACRYLATE ANION EXCHANGERS

Dorota KOŁODYŃSKA, Halina HUBICKA, Zbigniew HUBICKI

Department of Inorganic Chemistry, Faculty of Chemistry,
Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq.2. 20-031
Lublin, Poland, tel.: +48 (81) 5375736; Fax: +48 (81) 533 33 48,
e-mail address: kolodyn@poczta.onet.pl

Aminopolycarboxylic acids such as ethylenediaminetetraacetic (EDTA), nitrilotriacetic (NTA), diethylenetriaminepentaacetic (DTPA), hydroxyethylethylenediaminetriacetic (HEDTA), iminodiacetic (IDA) and iminodisuccinic acid (IDS) (Fig.1) are widely used for industrial, pharmaceutical and agricultural purposes including, among others, metal, textile, leather, rubber, food, cosmetic, paper and textile production. [1,2].
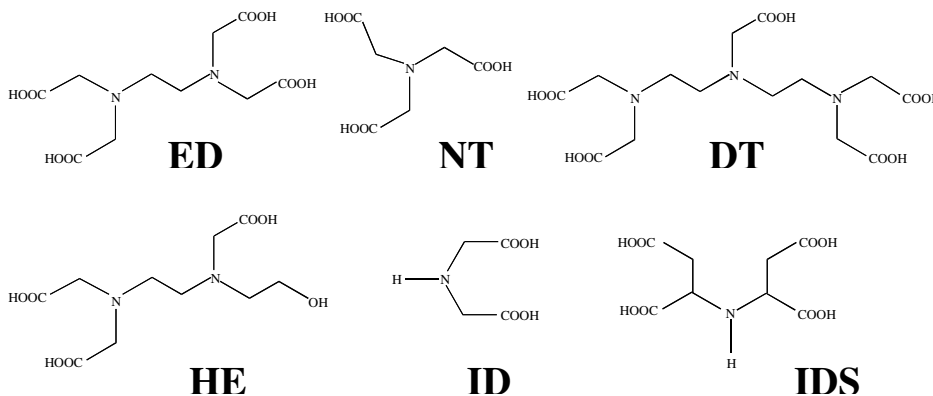

Fig.1. Structural formulae of the complexing agents – EDTA, NTA, DTPA, HEDTA, IDA and IDS

Synthetic chelating agents form strong and water soluble complexes with various cations, but (except for NTA) they are almost resistant to biodegradation. Therefore their concentrations have often increased in some aquatic systems to unacceptable levels. There is also much interest in changing them by a new generation of chelates of improved biodegradability such as EDDS or IDS (Fig.1). Additionally, in the environment chelating agents have some undesired features such as the remobilization of radionuclides and toxic heavy metal ions from sediments and soils [3,4].

Typical chemical precipitation methods (e.g. OH^- and S^{2-}), the most economical for the treatment of effluents containing heavy metal ions in the presence of strong chelating agents such as EDTA, NTA are ineffective. For treatment of these industrial wastewaters, when these metals are present as anionic complexes, the anion exchange plays a main role. In this case sorption, separation, removal and recovery of heavy metal ions are achieved by variation in parameters affecting the sorption process. The kind of applied anion exchanger is also a very important factor.

Polyacrylate anion exchangers are widely applied in water purification processes. They are characterised by favourable mechanical properties and high resistance to the osmotic shock. Polyacrylate anion exchangers possess unique physical and chemical properties, high ion exchange capacity, perfect physical resistance, quick kinetic exchange, very high resistance to organic impurities and greater basicity than polystyrene anion exchangers. They can be applied for deacidification, deionization and desalination of water where the removal of strong mineral acids and adsorption of organics are desired. Amberlite IRA 458 the strongly basic, gel polyacrylate anion exchanger has been applied to remove arsenate from drinking water as well as cyanide complexes of Ni(II), Fe(III), Cu(II), Co(II) from the effluent of metallurgical processing plants [5,6]. Amberlite IRA 68 the weakly basic, gel and Amberlite IRA 958 the strongly basic, macroporous anion exchangers are used for removal of heavy metal complexes particularly of Pb(II), Co(II), Cu(II), Ni(II) with EDTA from the effluent of metallurgical processing plants [7,8]. The structures of the strongly basic polyacrylate anion exchanger Amberlite IRA 458 and the weakly basic anion exchanger of this type Amberlite IRA 67 are presented in Fig.2.
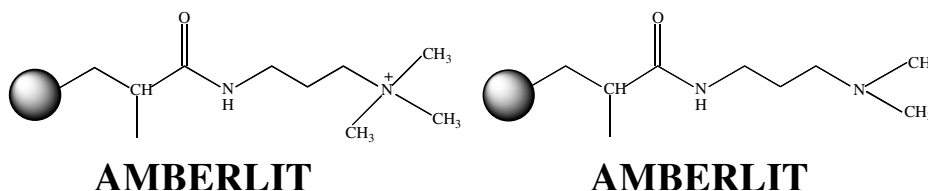

AMBERLIT   **AMBERLIT**

Fig.2. Structure of the polyacrylate anion exchangers Amberlite IRA 458 and Amberlite IRA 67

This paper investigates the use of the commercially available polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67 for the removal of heavy metal ions Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Fe(III) in the presence of the complexing agents EDTA and NTA.

The solutions of metal complexes with EDTA and NTA were prepared by dissolving equimolar amounts of each metal chloride/nitrate in the EDTA (at pH

4.6) or NTA (at pH 4.0) solutions. The initial concentration of metal ions was 10^{-3} M, which is located within the level of real effluents such as planting waste waters. The experiments were carried out at pH values without adjustment. For anionic complexes of these heavy metals the recovery factors (%R) were determined by means of the static method (0.5 g of appropriate dry anion exchanger was placed in a 100 cm^3 stoppered conical flask containing 50 cm^3 of complexed heavy metal ion solution and shaken at the constant temperature - 25°C in the three parallel series). After equilibrium, the pH was measured with a Radiometer pH meter (Model PHM 82). The concentrations of Cl$^-$/NO$_3^-$ ions were not determined. The contents of each metal in the raffinate and eluate were determined by the AAS method (Varian SpectrAA- 880).

As follows from the literature data [7,8] the capacity of polyacrylate anion exchangers like Amberlites for metal ions complexed with aminopolycarboxylic acids depends on the pH value. At pH about 2 where the dominant species are monovalent complexes, the removal of metal complexes is insignificant. It was also stated that the presence of calcium complexes with EDTA in the form of divalent species [Ca(edta)]$^{2-}$ does not influence the heavy metal removal.

Taking into consideration the above statements, the studies of sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Fe(III) complexes with EDTA on polyacrylate anion exchangers in the pH range from 2.0 to 6.0 using the static method, at the constant phase contact time which is 6 h were carried out. With the increasing pH of the solution, the values of recovery factors (%R) of metal ions on the anion exchangers Amberlite IRA 458, Amberlite IRA 67 and Amberlite IRA 958 increase and reach the plateau at pH above 5 (these data are not presented). Therefore in the next stage, the investigations of sorption by the static method depending on the phase contact time were carried out in the 0.001M M(II)/(III)-0.001M EDTA and 0.001M M(II)/(III)-0.001M NTA systems. The values of recovery factors (%R) of the complexes determined for the anion exchangers in question are presented in Fig.3.

As follows from the comparison of the obtained results (Fig.3) in the case of sorption of Cu(II), Zn(II), Co(II), Ni(II), Pb(II) and Cd(II) complexes with EDTA the recovery factors assume the values in the range 80-100% and are slightly differentiated for all the anion exchangers in the investigations. The equilibrium state of sorption for these anion complexes occurs at the ion exchanger–solution phase contact time about 30 min. However, the recovery factors of Fe(III) complexes are lower (values below 70 %) which confirms that the complexes of [M(edta)]$^-$ type exhibit lower affinity for polyacrylate anion exchangers in comparison to that of [M(edta)]$^{2-}$ type.
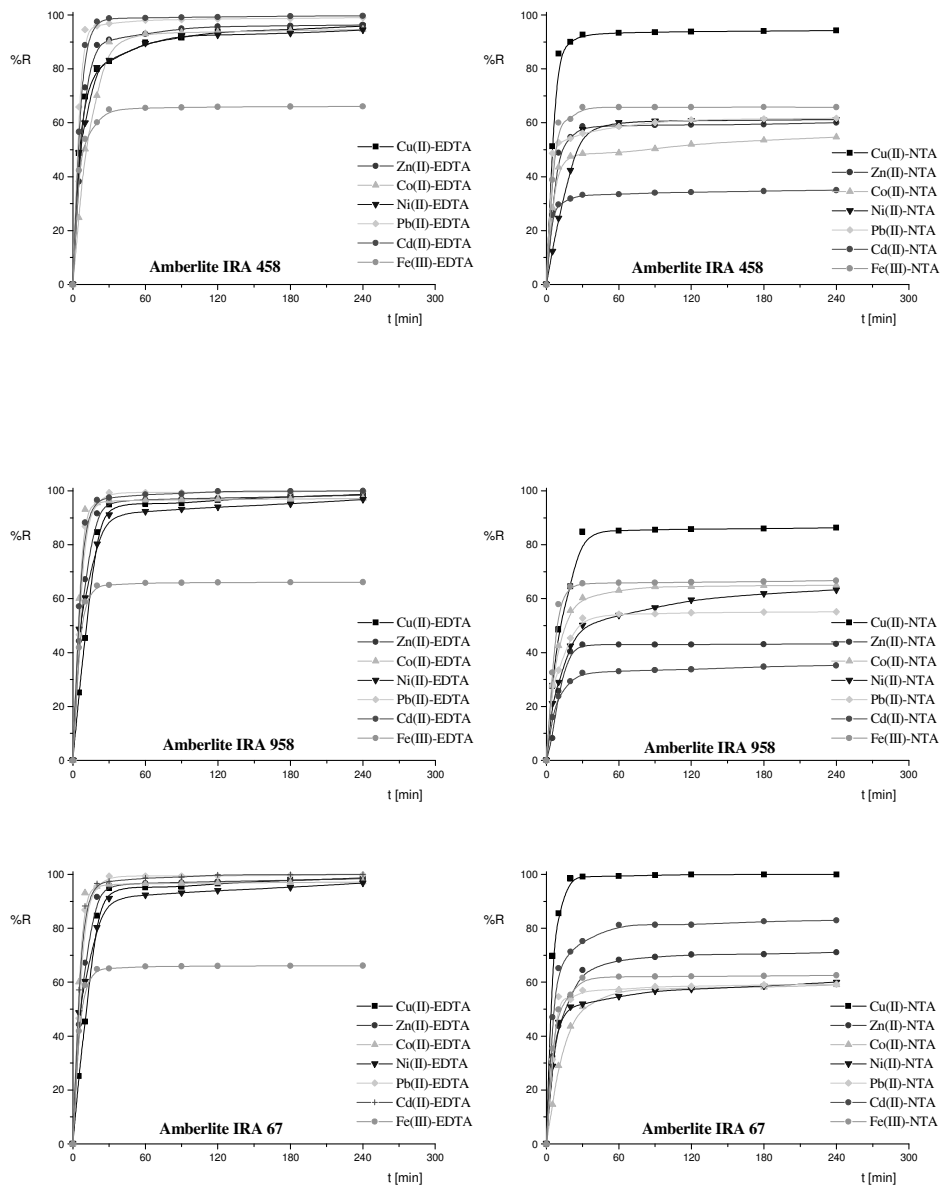
Fig.3. Comparison of the recovery factor (% R) values for Cu(II), Zn(II), Co(II), Ni(II), Pb(II), Cd(II) and Fe(III) complexes with EDTA and NTA on the polyacrylate anion exchangers Amberlite IRA 458, Amberlite IRA 958 and Amberlite IRA 67

In the case of heavy metal complexes with NTA the values of the recovery factors are lower but more differentiated. The affinity series of these complexes can be arranged as follows: for the strongly basic anion exchangers Amberlite IRA 458: *Cu(II) > Fe(III) > Ni(II) = Pb(II) = Zn(II) > Co(II) > Cd(II)*; Amberlite IRA 958 *Cu(II) > Fe(III) > Co(II)> Ni(II) > Pb(II) > Zn(II) > Cd(II)* and the weakly basic one: Amberlite IRA 67 C*u(II) > Cd(II) > Zn(II) > Fe(III) > Co(II) > Ni(II) > Pb(II).* It is worth mentioning that the weakly basic anion exchanger Amberlit IRA 67, contrary to the strongly basic anion exchangers Amberlite IRA 458 and Amberlite IRA 958 has the highest affinity for Cd(II) complexes with NTA. The data obtained indicate that the sorption of heavy metal complexes with aminopolicarboxylic acids is effective and provide the advantage of simultaneous removal of these metals and organic ligands.

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