

---

ANNALES  
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA  
LUBLIN – POLONIA

## Selected aspect in the separation of inorganic and organic species on ion exchangers and sorbents of various types

Z. Hubicki, M. Majdan, M. Gęca, A. Gładysz-Płaska, D. Kołodyńska,  
M. Makarska-Białokoz, M. Wawrzekiewicz, A. Wołowicz and G. Wójcik  
*Department of Inorganic Chemistry, Faculty of Chemistry,  
Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 2.  
20-031 Lublin, Poland, Tel.: +48 (81) 5375511; Fax: +48 (81) 533 33 48.*

In the paper the example papers from the Department of Inorganic Chemistry are presented. They are connected with the research of sorption and separation of inorganic and organic species on ion exchangers and sorbents of various types are presented. The main subjects include physicochemical studies of metal ions removal on anion exchangers, chelating and modified ion exchangers as well as zeolites, sorption and separation of rare earth elements, recovery of noble metal particularly from chloride solutions by ion exchange or extraction method, application of the anion exchangers of various types in dyes removal from aqueous solutions and wastewaters and chemistry of porphyrins in the aspect of environmental protection.

### 1. NOVEL COMPLEXING AGENT IN SORPTION OF HEAVY METAL IONS FROM WASTEWATERS ON ION EXCHANGERS OF VARIOUS TYPES

It is well known that heavy metal ions are a major environmental problem. Copper, zinc, cadmium, lead, arsenic and chromium ions occur particularly in many industrial effluents. One way for removing heavy metal ions is their treatment with complexing agents to form anionic species. In this group the most important is EDTA (ethylenediaminetetraacetic acid). EDTA is used as an additive to sequester undesirable cations in many areas. The sequestering capacity which is expressed as the number of the mmol bound per gram of

complexing agent is a measure of the complexing capacity. For example it was found that the sequestering capacity of EDTA for Cd(II) is equal to 4.1 [1]. Therefore, it is widely used in washing and cleansing products, cleaning, electroplating, water softening, polymerisation for industrial purposes, photographic industry, textiles, pulp and paper, pharmaceuticals, cosmetics, food and agriculture. Nearly all of these applications will eventually result in the release of EDTA to the environment, in many cases via the sewage system. Heavy metals bound to EDTA may well be transported in water. However, the major disadvantage of EDTA is its non-biodegradability [2, 3]. As a result, EDTA can accumulate in waste treatment installations and affect the effectiveness of water treatment. Another disadvantage of EDTA is the fact that a flocculating agent must be applied to precipitate the metal complexes with EDTA. It is also quite mobile in soils and can thereby be transported to the groundwater, together with the mobilized metals and finally, because this complexing agent is rich in nitrogen, its degradation products are to some extent notable promoters of eutrophication. In spite of that the short-term toxicity of all commonly used complexing agents either as a sodium salt or in a fully protonated form is low, the complexing agents are expected to have harmful long-term effects in concentration at mg/l level [4]. Therefore, there is legislation limiting the use of strong complexing agents and phosphate. In some states in the USA, for example, industrial use of EDTA is banned. Taking these into account there is a need of introducing new complexing agents. Also many compounds have been examined in the search for substitutes for sodium triphosphate (STPPs). Only a few compounds have been found to be both ecologically acceptable and commercially viable. In this group, with good eco-friendly profile, IDS (iminodisuccinic acid), DS (polyaspartic acid), EDDS (N,N'-ethylenediaminedisuccinic acid) have been proposed. GLDA (tetrasodium salt of N,N-bis(carboxymethyl)-L-glutamic acid), and MGDA (methylglycinediacetic acid) are other examples of environmentally friendly chelators.

The our previous research the possibilities of removal of heavy metal ions from aqueous solutions on chelation ion and anion exchangers using various ion exchangers commercially available and focusing on chloride, sulfate, ammonia and aminocarboxylic systems – most frequently found in wastes from various types of industry were carried out. There were determined the effects ions on the investigated ion exchangers: phase contact time, system, pH, acids concentration, external solution composition, functional group types as well as skeleton structure and porosity (macroporous and microporous). There was investigated the possibility of selective removal of copper(II), cobalt(II), nickel(II) and zinc(II) ions from chloride solutions differing in hydrochloric acid structure on selective ion exchangers of the thiol functional (Duolite GT-73) and polyamine groups (Diaion CR-20) indicating that the highest values of removal

coefficient are obtained for copper(II) on both ion exchangers of which Duolite GT-73 is better; possibilities of removal of these ions on chelating ion exchangers with aminophosphonic ammonia solutions stating that the best sorption results from sulfate solutions are obtained using the aminophosphonic ion exchanger (Duolite C-467 with almost 100% removal coefficients for all four ions. There were determined the conditions of sorption of the Cu(II), Co(II) and Ni(II) complexes with aminocarboxylic acids on chelating ion exchangers as well as strongly and weakly basic anion exchangers pointing out that the values of removal coefficients of the above mentioned complexing exchanger, kind of complexones, stability of complexes, system pH, phase contact time as well as solution composition. It was proved that all ion exchangers were characterized by largest affinity for Cu(II)-IMDA complexes.

Also applicability of novel complexing agents in sorption of heavy metal ions from wastewaters on ion exchangers of various types has been carried out [5-18]. The promising results were obtained using, among others, polyaspartic acid (DS).

It is well known that polyaspartic acid and polyaspartic acid sodium salts are anion-active, water-soluble polyaminocarboxylates with a multifunctional property profile. Polyaspartates have excellent toxicological properties, they are biologically neutral, hygroscopic and water soluble. Degradation of this acid leads to preparation of amino acids – the most friendly compounds for men. The above-mentioned properties provide vast application possibilities of polyaspartic acid and its salts as well as copolymers with other amino acids. Polyaspartates are biodegradable polyanions which can substitute the currently used polycarboxylates or polyacrylates as inhibitors of mineral formation and scaling, widely occurring problems in various industrial processes. Polyaspartates can be used in many applications such as detergents and cleaners, water treatment agents, or as agents in mining and oil recovery. Production in commercial scale is possible by polycondensation of enzymatically produced L-aspartic acid. However, complete substitution of polycarboxylates, which are mainly non-biodegradable, would only be possible by using chemical precursors of aspartic acid. Pharmaceutical and medical industries basing on non-toxicity and biological inertness uses them as substrate for artificial leather in burn treatment, artificial tissues, orthopaedic implants and others [19]. Polyasparginates constitute a base for drug administration, decrease their toxicity not causing side effects. Hydroscopic abilities of polyacid are made use of, among others, in cosmetic and sanitary industries. The structure of the DS and the speciation distribution of its form depending on pH is presented in Fig.1.

As was shown in [6, 7] polyaspartic acid is suitable for removal of Cu(II) and Zn(II) on the strongly basic anion exchangers such as Lewatit MonoPlus M 500, Lewatit MonoPlus M 600 and Lewatit MonoPlus MP 500. For heavy metal ions

removal in the presence of DS chelating ion exchangers Lewatit TP 207, Lewatit TP 260, Purolite S-930, Purolite S-940, and Purolite S-950 can also be applied.

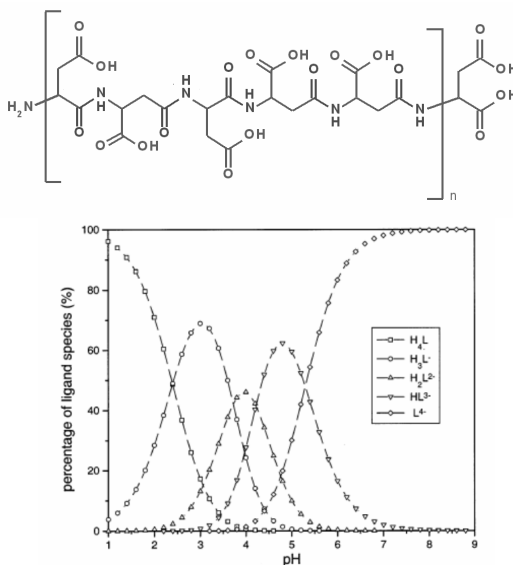


Fig.1. Structure of DS and the speciation distribution of its form depending on pH.

The exemplary results of the sorption of Cu(II) and Pb(II) complexes with DS on strongly basic anion exchangers Amberlite IRA 402, Amberjet 4400 and Amberjet 4600 manufactured by Rohm and Haas (France) were presented in Fig.2. The Langmuir and Freundlich isotherm models were applied to describe the equilibrium sorption data, whereas the kinetic data were analysed using the sorption kinetic Lagergren, Ho and McKay models. In batch adsorption experiments known weights of anion exchanger samples (0.2 g) were added to glass flasks containing 20 mL of heavy metal solution with DS of adjusted pH and shook using an Elpin type 357 temperature-controlled shaker at 180 rpm. The effect of initial concentration of heavy metal ions was examined by studying different initial concentrations. At the end of each mixing period the liquid phases were separated from the solution by filtration. All adsorption experiments were performed twice and the average values were used for all calculations. The metal content was measured by the AAS method using VarianAA-Z240 (Varian, Australia).

Adsorption isotherms are critical in optimizing the use of adsorbents. The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption

processes. The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multiplayer sorption.

As follows from the obtained results the regression correlation coefficients ( $R^2$ ) for Cu(II) and Pb(II) complexes with DS sorption are very high for the Langmuir and Freundlich models. According to the  $1/n$  values, the deviation from linear sorption is higher in the case of Cu(II) sorption on Amberlite IRA 402, Amberjet 4400 and Amberjet 4600 than Pb(II) one. The  $K_F$  values indicate that the anion exchangers used favour the sorption of Cu(II) complexes over that of Pb(II). However, Amberlite IRA 402 possesses higher sorption affinity for Pb(II) compared with Amberjet 4400 (not presented) and Amberjet 4600. The maximum sorption capacities ( $q_0$ ) appear to be also significantly higher for Pb(II) in comparison with that of Cu(II). Therefore the applicability series for Cu(II) complexes with DS can be as follows: Amberjet 4600 (25.21 mg/g) > Amberlite IRA 402 (22.81 mg/g) > Amberjet 4400 (20.34 mg/g) whereas for the complexes of Pb(II) it can be as follows: Amberlite IRA 402 (130.48 mg/g) > Amberjet 4600 (85.96 mg/g) > Amberjet 4400 (83.75 mg/g).

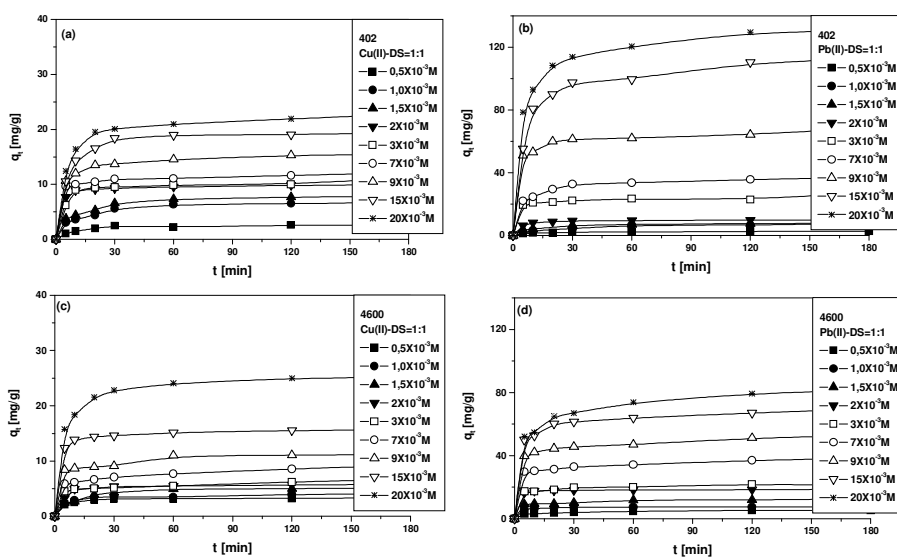


Fig.2. Effect of the phase contact time on the sorption capacities depending on the concentration of Cu(II) and Pb(II) complexes with DS ( $M(II):L=1:1$ ,  $c_0=0.5 \times 10^{-3} - 20 \times 10^{-3}$  M, anion exchanger dose 10 g/L, shaking speed 180 rpm, temperature 295 K).

Based on the Langmuir model, the calculated  $R_L$  values also reveal that at all initial heavy metal ion concentrations and used anion exchangers sorption of heavy metal complexes is favourable under various conditions.

As for the kinetic studies it was shown that the time to reach an equilibrium state was about 2 h. The pseudo second order model provides better description of the adsorption kinetics of Cu(II) and Pb(II) complexes with DS on Amberlite IRA 402, Amberjet 4400 and Amberjet 4600 and the rate constant ( $k_2$ ) is increased with temperature for each concentration and decreased with the increasing initial Cu(II) and Pb(II) complexes concentration. It was also stated that the highest sorption percentages were obtained for pH >7.

In the sorption and separation of heavy metal ions the application of impregnated ion exchangers is very important. The impregnated sorbents like e.g. Amberlite XAD 7 HP impregnated with Hostarex A 324 enables to avoid inconveniences caused by emulsions formation during extraction in the liquid-liquid system. Impregnated sorbents may also exhibit sorption properties towards chromate(VI) ions. Possibility of preparation of a sorbent impregnated with Aliquat 336 based on Amberlite XAD 16 was also investigated [20]. It was found that such sorbent exhibits reducing properties towards chromate(VI) ions enabling quick reduction of Cr(VI) ions to Cr(III) ions which is of significant importance in the environment protection as Cr(VI) ions are harmful for living organisms. The studies of preparation of new anion exchangers making sorption of chromate(VI) ions from aqueous solutions possible were also carried out. The prepared anion exchanger including functional tertiary amine, quaternary ammonium and ketone groups exhibits large sorption capacity for chromate (VI) ions in the pH range 3-4 [21]. Possibility of reduction of chromate(VI) ions to chromium(III) in the pH range 1.5-7 was also pointed to. The reduced chromium(III) ions in the pH 3.5-7 remain in the sorbent phase and their presence was confirmed by the DRS method. The phenomenon of reduction of chromate(VI) ions to chromium(III) in acidic solutions on strongly basic anion exchangers including functional quaternary ammonium groups was used for working out a way of their removal and reduction. This way was reserved by the patent application [22].

## 2. RARE EARTH ELEMENTS SORPTION AND SEPARATION

Rare earth elements of high purity play a significant role in many areas of contemporary techniques. Mainly cation exchangers and elution by complexing agents are used for separation of these elements using ion exchange methods. In this process the order of elution of individual rare earth(III) elements depends on the values of stability constants of formed complexes. They generally increase from light(III) lanthanides to heavy(III) lanthanides. Ion exchange of rare earth elements with chelating organic ligands on anion exchangers is still a poorly studied field. However, the papers published during the last few years show particular applicability of anion exchangers to this end. The anion exchangers

have been used so far for separation of thorium(IV) and uranium(IV,VI) from lanthanides(III) from mineral acid solutions and studies of chromatographic separation of rare earth(III) elements using anion exchangers. Referred mainly to isotopes of these elements and were mainly of analytical or physicochemical character.

In separation of rare earth(III) elements complexes with chelating organic ligands strongly basic, gel polystyrene anion exchangers of quaternary ammonium groups proved to be the most effective. The research carried out covered mainly application in the lanthanides separation of such complexing agents as: ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IMDA), N-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (HEDTA) and *trans*-1,2-cyklohexanediaminetetraacetic acid (DCTA) [23-34]. These complexing agents allow to obtain the large separation effectiveness of the above mentioned elements by means of simple and economical methods. Applying the above-mentioned complexones there was carried out the process of separation of Y(III) from Ho(III), Dy(III) and Er(III) as well as Yb(III) from Ho(III) and Er(III) using IMDA, and also Sm(III) from Ho(III) and Y(III), Nd(III) from Y(III), Y(III) from Ho(III), Er(III) and Dy(III) as well as Yb(III) from Ho(III) and Er(III) using HEDTA. Additionally, from the known affinity series of rare earth(III) elements complexes with *trans*-1,2-cyklohexanediaminetetraacetic acid (DCTA) separation of the pairs Y(III)-Nd(III) and Y(III)-Sm(III) was studied. As for the results, it is important that in the studies there were used commercially available standard strongly and weakly basic anion exchangers of polystyrene or polyacrylic skeleton and the frontal analysis technique which is the most effective for separation of a macrocomponent from microcomponent. This subject was result of increasing demand for rare earth elements, particularly of large degree of purity in many modern fields of industry and technology.

Another problem taken into consideration in the studies of lanthanides(III) separation on anion exchangers was the fact that in most cases partition coefficients of metal ions complexes in mixed water-alcohol, water-acetone etc. solutions are greater than in water solutions. Therefore the effect of addition of a polar organic solvent (methanol, ethanol, acetone, 1-propanol, 2-propanol) on separation of rare earth(III) elements using various types of ion exchangers was investigates for Y(III)-Nd(III) and Y(III)-Sm(III) pairs. The exemplary research results obtained in separation of the Y(III)-Nd(III) pair are presented in Figure 3.

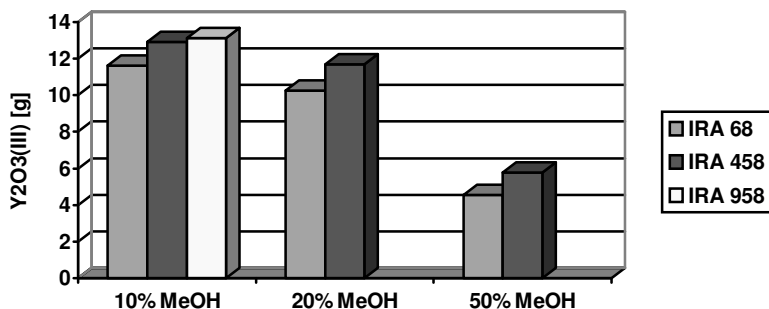


Fig. 3. Results of separation of the Y(III)-Nd(III) pair (0,35%) from % v/v MeOH on polyacrylic anion exchangers in the  $H_2edta^{2-}$  form.

Particularly attention has been paid to separation and removal of rare earth(III) elements nitrate complexes by means of frontal analysis from the polar organic solvent- $H_2O$ - $HNO_3$  on anion exchangers of various types [35-44]. The affinity series of rare earth(III) elements nitrate complexes were determined and the effects of kind of functional groups (basicity), kind of the skeleton, porosity of skeleton (microporous, macroporous, isoporous) cross linking degree of anion exchanger skeleton as well as kind and concentration of polar organic solvent (methanol, ethanol, isopropanol, acetone, dimethylformamide, dimethylsulfoxide), concentration of nitric acid, addition of another organic solvent and concentration of rare earth(III) (up to 100 g  $Ln_2O_3$ ) on effectiveness of rare earth(III) elements sorption and separation were studied. The differences in affinity of rare earth(III) elements nitrate complexes for anion exchangers in individual systems are probably due to a different structure of complexes (degree of their solvation) or different stability or kinetics of their formation in the anion exchanger phase. It was found that employing macroporous but not microporous anion exchangers gives better separation results in the system. In the case of latter the best results can be obtained using anion exchangers of the average degree of cross linking (4-6% DVB) and deterioration in separation of larger degree of cross linking of ion exchanger can be assigned to the 'sieve effect'. In the studied system yttrium(III) behaves like heavy lanthanides(III). As follows from the theory of yttrium(III) migration in the lanthanide(III) series it is a light pseudolanthanide(III) when the central ion-ligand bonding in the complex is covalently is covalently shortened and behaves like heavy lanthanides(III) when this bonding is of ionic character. As yttrium(III) in most presented systems is a heavy pseudolanthanide(III). One can believe that the central ion-nitrate ligand bonding is of ionic character. Atypical affinity series create new possibilities of



ion exchange separation of rare earth elements(III) which is very significant from a practical point of view. The results of rare earth elements nitrate complexes separation in the micro-macro component system can be successfully applied in production of rare earth elements(III) particularly yttrium(III) of a large purity degree. It is worth remembering that regeneration of anion exchanger bed in this system is very economical because distilled water is a regenerator.

### 3. SORPTION OF HEAVY METALS AND PHENOL ON NATURAL INORGANIC SORBENTS

The natural red clay (illite 23-37%, kaolinite 6-12%, quartz 30-45%), bentonite and chabazite, modified by the cationic surfactants: hexadecyltrimethylammonium bromide (HDTMA-Br), octadecyltrimethylammonium bromide (ODTMA-Br), benzyldimethylhexadecylammonium chloride (BDMHDA-Cl), benzyldimethyloctadecylammonium – bromide (BDMODA-Br), phenyltrimethylammonium bromide (PTMA-Br), benzyltrimethylammonium chloride (BTMA-Cl) have been used in adsorption of toxic ions (phenol, Cr(VI), U(VI)).

The adsorption of U(VI) on ODTMA-bentonite and HDTMA-bentonite was investigated at the pH values of the aqueous phase ranging from 3 to 10 and concentrations of U(VI) : 0.1 -1 mmol/dm<sup>3</sup> [45, 46]. The concentrations of alkylammonium cation in bentonite were changed from 18 to 157% of CEC (cation exchange capacity). It was established, that the adsorption of U(VI) on modified bentonite decreases with the percent of mineral modification until it attains the minimum at 76% CEC and then increases. The decrease of U(VI) removal with its initial concentration as a result of gradual reduction of the active sorption sites number in the sorbent structure was observed. The effective adsorption of U(VI) was found to be in the pH range: 6-10 for modified bentonite (100-157% CEC) and was explained as the consequence of U(VI) anionic hydroxycomplexes adsorption. The increase of U(VI) sorption in the pH range 3-6 and decrease in 8-10 for the lower values of surfactant concentrations (<100% CEC) was observed. The experiments concerning the pH influence on the U(VI) adsorption on modified bentonite showed that the species:  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{OH})^+$ ,  $\text{UO}_2(\text{OH})_2$ ,  $(\text{UO}_2)_3(\text{OH})_5^+$ ,  $(\text{UO}_2)_3(\text{OH})_7^-$ ,  $(\text{UO}_2)(\text{OH})_3^-$ ,  $(\text{UO}_2)(\text{OH})_4^{2-}$  present in the aqueous phase, are responsible for uranium sorption. The luminescence spectra of bentonite suspensions, i.e. their character at pH 5 and 9, proved the existence of hydroxy-like planar polymeric U(VI) species in the bentonite phase at pH 9. The FTIR, XRD spectra of the modified bentonite were analyzed and provided the arguments for the existence of surfactant cations in the form of monolayer and bilayer in the interlamellar space of bentonite. In turn, the luminescence spectra of bentonite suspensions, i.e. their character at

pH 5 and 9, proved the existence of hydroxy-like planar polymeric U(VI) species in the bentonite phase at pH 9.

The adsorption of phenol on PTMA-bentonite, BTMA-bentonite, HDTMA-bentonite and BDMHDA-bentonite was compared. The BTMA-bentonite had an evidently higher sorption affinity for phenol than other forms of bentonite. The adsorption isotherm of phenol on BTMA - bentonite was of a convex character, characteristic of physical sorption. The dual model [47-49] for quantitative evaluation of the sorption data was used. The maximum value of phenol concentration in the bentonite phase  $a_{\max}=0.0003$  mol/g was found. For PTMA-bentonite, HDTMA-bentonite and BDMHDA-bentonite the sorption behaviour of phenol was drastically different. The adsorption isotherms had a straight line character, which resulted from simple partition of phenol between the aqueous and organic phases sorbed on the surface of bentonite. The distribution constants of phenol to the BTMA-bentonite phase decreased with the rise of equilibrium concentration of phenol whereas the slight change of phenol distribution constants with its concentration in the PTMA-, HDTMA- and BDMHDA-bentonite phases was observed. The adsorption of phenol on HDTMA- and BDMHDA-bentonite in the pH range: 2-8 was small as a consequence of predominantly nonspecific, i.e. van der Waals interaction of phenol molecules with hydrocarbon chains of surfactant cations. The best adsorption was observed for higher pH values and then the electrostatic interaction between the phenolate anions and the positively charged bilayers of surfactant cations was the driving force of phenol adsorption on the modified bentonite. In the case of adsorption of phenol on PTMA- and BTMA-bentonite the situation was different, the sudden fall of the adsorption was evident for the alkaline pH range.

FTIR results showed that sorption of phenol on BTMA-, PTMA-bentonite occurred via interaction between phenyl rings of phenol molecules and those of the organoclay complex, but for BTMA-bentonite this interaction was stronger and affected the strength of the hydrogen bond between phenol and water.

The HDTMA-bentonite and BDMODA-bentonite were used for the removal of Cr(VI) ions from aqueous solutions [50, 51]. The adsorption reaction of Cr(VI) anions on the modified bentonite was of the first order in relation to chromate anions concentration, with the first order rate constant  $k=0.037/\text{min}$ . The Langmuir-Freundlich isotherm equation was taken to describe the experimental data. The decrease of the concentration of Cr(VI) in the bentonite phase with the temperature increase was observed. Exothermicity of the adsorption resulted from the strong electrostatic interaction on the negatively charged Cr(VI) ions with the positively charged alkyloammonium ions of surfactants. Based on the studies of pH influence it was found that the maximum adsorption of Cr(VI) ions on modified bentonite was in the pH range from 2 to 7. For higher pH values a sudden decrease of chromates adsorption was found.

This fact was explained by the presence of different forms of Cr in aqueous solution. In the pH range 2-7 the dominant forms of Cr(VI) were  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$  ions and for higher pH values ions  $\text{CrO}_4^{2-}$  prevailed in the solution. The affinity of the  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{HCrO}_4^-$  ions for the modified bentonite was probably higher than that of  $\text{CrO}_4^{2-}$  ions. Similar relationships were obtained for adsorption of Cr(VI) ions on chabazite modified by HDTMA [52]. In this case the equilibrium was established within 120 min (fast kinetics with the first order rate constant  $k=0.025/\text{min}$ ) and the adsorption maximum was  $a=0.00005 \text{ mol/g}$ . It was established that HDTMA cations were incorporated into the chabazite structure via ion exchange and van der Waals forces.

The adsorption of Cr(VI) ions on the natural red clay modified by HDTMA cations was also studied [53]. The adsorption isotherm of Cr(VI) was determined based on the Langmuir-Freundlich model and exhibited the adsorption capacity of  $0.0005 \text{ mol/g}$  in relation to Cr(VI). The study of the pH effect showed that the optimal pH range corresponding to the Cr(VI) adsorption maximum on this clay was 2-6.5. Beginning with pH 6.5 a sudden drop of the chromates concentrations in the adsorbent phase appeared, which resulted probably from the concurrent formation of alkylammonium hydroxide HDTMA(OH). The equilibrium was established within 120 min, the kinetics was fast and the specific rate constant of Cr(VI) anions adsorption was  $k=0.033/\text{min}$ . The studies have shown, that the natural red clay from Pałęga pit modified by HDTMA-Br can be potentially useful in removal of chromates or chromate and phenol, simultaneously [54], from aqueous solutions with respect to fast kinetics and high efficiency of adsorption.

The studies of removal of heavy metals ions: Zn(II), Cu(II), Ni(II) and Pb(II) as well as ammonium from sedimentary waters from municipal waste water treatment plants using natural sorbents were also carried out. As for the group of natural sorbents clinoptilolite, paligorskite and bentonite were studied. These studies enabled elaboration of technological scheme of treatment system of sedimentary waters formed in waste water filtration processes [55, 56].

#### 4. NOBLE METALS

The recovery of noble metal particularly from chloride solutions by ion exchange or extraction method is carried out using anion exchangers and selective ion exchangers [57]. Among numerous anion exchangers, those of different basicity of functional groups (strongly, medium and weakly basic) found application in ion exchange chromatography of noble metals. Strongly basic anion exchangers with well dissociated functional groups e.g. quaternary ammonium groups capable of exchange of anions of even weak acids are widely used in the whole pH range. In this group of anion exchangers, strongly basic

anion exchangers types 1 and 2 of functional trimethylammonium and dimethylhydroxyammonium groups respectively can be distinguished. Weakly basic anion exchangers possess poorly dissociated functional groups i.e. primary-, secondary- and tertiary amine ones. The research carried out on applicability of commercial microporous and macroporous anion exchangers for removal of noble metal ions, particularly Pd(II) and Pt(IV) from the chloride and chloride-nitrate(V) systems e.g. the weakly (Amberlyst A-21, Amberlyst A-23, Amberlyst A-24, Amberlite IRA-67, Duolite A-6, Duolite A-7, Duolite S-37, Dowex 66, Dowex WGR-2, Varion ADAM, Lewatit MP-62, Amberlite IRA-92, Amberlite IRA-93, Amberlite IRA-96), medium (Duolite A-30B, Lewatit MP-64, Amberlite IRA-478) and strongly (Amberlyst A-26, Amberlyst A-29, Amberlite IRA-458, Amberlite IRA-958, Dowex MSA-1, Dowex MSA-2, Lewatit MP-500, Lewatit MP-500A, Lewatit M-600, Purolite A-520, Purolite A-850, Varion AP, Varion ATM, Varion ADM, Wofatit EA-60, Amberlite IRA-910) basic anion exchangers was published in many papers [58-71]. The addition of Na(I), Cu(II), Ni(II), Zn(II), Fe(III) and Al(III) ions to the solution decreases drastically capacity of most anion exchangers towards Pd(II) and Pt(IV) ions. Efficiency of Pd(II) and Pt(IV) chloride complexes sorption depends not only on the kind of matrix and anion exchanger skeleton structure (different contribution of the sieve effect) but also on basicity of functional groups. The differences in affinity of Pd(II) and Pt(IV) ions may also due to the difference in solvation degree and stability of  $[\text{PdCl}_4]^{2-}$  and  $[\text{PdCl}_6]^{2-}$  complexes. In the case of weakly and medium basic anion exchangers of primary, secondary and/or tertiary amine groups, the sorption mechanism of the above mentioned complexes is connected with initial protonation of free amine groups of the ion exchanger due to the presence of  $\text{H}^+$  ions originating from HCl dissociation and formation of  $-\text{NH}_3^+$ ,  $=\text{NH}_2^+$  or  $\equiv\text{NH}^+$  groups respectively e.g.  $\text{R}-\text{NH}_2 + \text{HCl} \rightarrow \text{RNH}_3^+\text{Cl}^-$ . Change of surface charge of anion exchanger pores contributes to occurrence of electrostatic interaction between the positively charged  $\text{R}-\text{NH}_3^+$  groups and negatively charged Pd(II) chlorocomplex of  $[\text{PdCl}_4]^{2-}$  type and anion exchange between  $[\text{PdCl}_4]^{2-}$  and  $\text{Cl}^-$  ions:  $2\text{RNH}_3^+\text{Cl}^- + [\text{PdCl}_4]^{2-} \rightarrow [\text{RNH}_3^+]_2[\text{PdCl}_4^{2-}] + 2\text{Cl}^-$ . A small number of free amine groups of weakly basic anion exchangers can undergo protonation due to the reaction with water according to the equation:  $\text{RCH}_2\text{N}(\text{CH}_3)_2 + \text{H}_2\text{O} \leftrightarrow \text{RCH}_2\text{NH}(\text{CH}_3)_2^+ + \text{OH}^-$ . In the case of strongly basic anion exchangers in the chloride form which are quaternary ammonium salts, the sorption mechanism of Pd(II) chlorocomplexes proceeds forming an ionic pair according to the reaction:  $2\text{R}-\text{N}(\text{CH}_3)_3^+\text{Cl}^- + [\text{PdCl}_4]^{2-} \rightarrow [\text{RN}(\text{CH}_3)_3^+]_2[\text{PdCl}_4^{2-}] + 2\text{Cl}^-$ . Moreover, in the group of selective ion exchangers Lewatit TP 214 was found to be characterized by large ion exchange capacity compared to platinum (IV) ions. It possesses functional thiourea groups [72]. In the case of this type of ion exchanger the

desorption process is rendered difficult and thiourea solutions in hydrochloric acid must be used. Besides selective ion exchangers, anion exchangers of various basicity were studied. In the weakly basic group containing the tertiary amine groups one can distinguish Amberlite IRA-67, Amberlite IRA-93 and Diaion CR 20 of functional polyamine groups. There was found an ion exchange mechanism of platinum (IV) ions sorption and it was proved the acrylic skeleton of the anion exchanger Amberlite IRA-67 affects significantly sorption capacity decrease with the increasing concentration of hydrochloric acid [73]. Weakly basic anion exchangers such as Amberlite IRA-67, Amberlit IRA-93 and Diaion CR 20 were used for selective sorption of microquantities of platinum(IV) ions from the systems containing such macrocomponents as: aluminium(III) chloride, copper(II) chloride, iron(III) chloride, nickel(II) chloride and zinc(II) chloride [74]. Macrocomponents have differentiated effects on platinum(IV) ions sorption. Zinc(II) and aluminum(III) ions decrease significantly sorption capacity of weakly basic anion exchangers compared to platinum(IV) ions. Strongly basic anion exchangers of functional quaternary ammonium groups such as Amberlyst A 26, Purolite A 850 and Lewatit MP 500A were also used for platinum(IV) ions sorption. They sorb platinum(IV) ions in accordance with the ion exchange mechanism and their capacity depends on hydrochloric acid concentration. Sorption capacity towards platinum(IV) ions decreases with the increasing concentration of hydrochloric acid and this is the most evident in the case of Purolite A 850 which possesses an acrylate skeleton. Most ion exchangers possess styrene-divinylbenzene skeletons, therefore possibility of using the anion exchanger Duolite S 37 of a phenol-formaldehyde skeleton as well as functional secondary and tertiary ammonium groups was studied [75]. It was found that this anion exchanger is characterized by smaller sorption capacity towards platinum(IV) ions compared to the above mentioned ones and it decreases with the increasing concentration of hydrochloric acid. There were also studied the systems containing the macrocomponents: aluminium(III) chloride, copper(II) chloride, iron(III) chloride, nickel(II) chloride and zinc(II) chloride. It was found that zinc(II) chloride decreases to the largest extent the sorption capacity of Duolite S 37 towards platinum(IV) ions as in the case of anion exchangers of various basicity. The studies of preparation of impregnated sorbents SIR selective for noble metal ions are also carried out [76].

## 5. APPLICATION OF THE ANION EXCHANGERS OF VARIOUS TYPES IN DYES REMOVAL FROM AQUEOUS SOLUTIONS AND WASTEWATERS

Coloured waste waters are one of the most dangerous sources of natural water environment contamination. Water protection has become a necessity. Therefore the most urgent tasks are drastic constraints of contaminated waste waters

release into receivers and their complex purification. The presence of dyes in water constitutes a serious problem in many branches of industry, particularly in dye production, textile and stationery industries. Even small amounts of dye (of a few ppm order) are undesirable as they tint water, make it look unaesthetic and disturb living process in water. Most dyes are not biodegradable, attenuate light penetration into water, inhibit photosynthesis, increases chemical and biological demand for oxygen. Some dyes are toxic and even carcinogenic for living organisms and therefore they should be removed thoroughly. Purification of waste waters containing dyes is becoming more and more important aiming at avoiding potential hazard for the environment and due to more serious legal consequences coloured waste waters purification by adsorbing methods proves to be economically the most effective making it possible to design modern, simple, little energy consuming, technological plants [77].

Great selectivity and capacity towards dyes of various types are characteristic of ion exchangers so called ion exchanger resins or reactive polymers. Weakly or strongly basic anion exchanger of polymerization type and functional groups (type 1) and (type 2) prove to be most effective in dye removal from waste waters. Type of functional groups in ion exchangers is a factor deciding about exchange reaction character and its applicability. Affinity of these anion exchangers depends first of all on structure, size and charge of a coloured anion.

Commercially available weakly and strongly basic anion exchangers of macroporous and gel types 1 and 2 structures i.e. Amberlite IRA-67, Amberlite FPA-51, Amberlyst A-21 and A-23, Amberlite IRA-402, Amberlite IRA-458, Amberlite IRA-900, Amberlite IRA-910, Amberlite IRA-958, Lewatit MonoPlus M-500 and M-600, Purolite A-850, A-520E and AC-20G were used for decolourization of aqueous solutions containing acidic and reactive dyes e.g. Acid Orange 7 [78, 79], Acid Orange 10 [77], Acid Red 88 [77], Acid Blue 29 [80, 81], Tartrazine [82-84], Sunset Yellow [85], Allura Red [86], Indigo Carmine [87, 88], Reactive Black [89], Reactive Red 2 and 120 [77] with respect to their application in coloured dyes purification. The influence of many parameters on effectiveness of dyes removal from waste waters, among others, phase contact time, initial concentration of a dye, pH and temperature of a solution, addition of electrolytes and surfactants of various types (nonionic, anionic and cationic). As follows from the obtained results of research, the presence of salts and surfactants does not affect significantly sorption capacity of anion exchangers which is important for their practical application in real waste waters decolourization.

Mechanism of dye sorption on anion exchangers is complex occurring, among others, with formation of an ion pair between functional groups of anion exchangers and sulfone groups of dyes. However, physical interactions between the ion exchangers skeleton and the dye aromatic ring can not be excluded as

indicated by the sorption results. Almost quantitative desorption can be performed in the system of methanol with the addition of 1 M NaOH (or 1 M HCl/1-2 M NaCl/1 M KSCN). Aqueous solutions of NaOH, HCl or NaCl are desorbing factors of low effectiveness.

## 8. CHEMISTRY OF PORPHYRINS IN THE ASPECT OF ENVIRONMENTAL PROTECTION

The specific physicochemical and optical properties as well as the ability to undergoing the redox, protonation and aggregation reactions, and formation of complex compounds with almost all known metal ions of porphyrins and their derivatives – phthalocyanines can be examined using different spectroscopic methods. The knowledge about proper molecular form and behaviour of porphyrins in different environments plays the key role in application of this class of compounds.

Characteristic changes in absorption (Soret and Q bands) and emission spectra of porphyrins occurring during the transformation of their molecules allow to determine their molecular form and complexing state, as well as the number and kind of substituent groups of particular porphyrin systems, depending on the reaction environment (pH, buffers, different types of solvents) [90, 91].

Utilization of spectroscopic methods permits also monitoring of specific interactions between porphyrin compounds and biologically important substances, such as nucleic agents, terpenes, or toxic compounds - phenol and xanthine derivatives. One of the examples can be caffeine (1,3,7-trimethylxanthine), one of the most popular stimulants and the ingredient of many medicines. In all of these products caffeine occurs in the form of solution or water mixture. The gigantic consumption of caffeine means simultaneously the similar order of caffeine sewage production. The environment contamination caused by caffeine influences also the condition of water plant and animal organisms. The porphyrins interactions with xanthine derivatives can help in better understanding of toxic substances influence on living organisms, which can be applied in the environmental protection for the elimination of caffeine sewage and be a base for the elaboration of a new porphyrin receptor for caffeine.

The porphyrin properties, particularly their catalytic activity in the process of redox reactions, can be examined not only in solutions, but also in solid silica matrices, obtained for example in the sol-gel process [92-96]. Such studies are the next stage of porphyrins applications in the environmental protection. Unquestionable advantage of silica gel monoliths doped with porphyrins is the fact that the encapsulated substances remain in contact with the outer medium

and undergo its influences, and moreover, these reactions are reversible. Sol-gel material can stabilize to a certain degree the porphyrin properties, simultaneously permitting repeated utilization of porphyrins immobilized in a matrix. The results obtained during the research are the base for practical use of silica matrices doped with adequate porphyrin systems – such hybrid materials could be applied in sensors designing, photodynamic therapy of cancer (PDT) and data storage, as well as powder luminescence materials and biomimetic catalysts of redox, cyclization and epoxidation reactions of different organic compounds (for example hydrocarbons).

There is no doubt that the versatility of porphyrin systems, both in solutions and in silica matrices confirms that the porphyrin chemistry is one of the most important, innovative and indispensable field of modern science.

## 9. REFERENCES

- [1] M. E. Bolkenbaas, H. C. Kuzee, H. Raaijmaker, EU Patent EP 1025050B1, 2003.
- [2] J. Conrad, Environmental policy regulation by voluntary agreements: technical innovations for reducing use and emission of EDTA, Environmental Policy Research Centre Report No. 00-04, 2000.
- [3] B. Nörtemann, *App. Microbiol. Biotechnol.*, 51, 751 (1999).
- [4] C.K. Schmidt, H.J. Brauch, *Environ Toxicol.*, 19, 620 (2004).
- [5] D. Kołodzyńska, H. Hubicka, Z. Hubicki, *Desalination*, 227, 150 (2008).
- [6] D. Kołodzyńska, Z. Hubicki, M. Gęca, *Ind. Eng. Chem. Res.*, 47, 3192 (2008).
- [7] D. Kołodzyńska, Z. Hubicki, M. Gęca, *Ind. Eng. Chem. Res.*, 47, 6221 (2008).
- [8] D. Kołodzyńska, H. Hubicka, Z. Hubicki, *Desalination*, 239, 216 (2009).
- [9] D. Kołodzyńska, *Przem. Chem.*, 88, 182 (2009).
- [10] D. Kołodzyńska, H. Hubicka, *Chem. Eng. J.*, 150, 308 (2009).
- [11] D. Kołodzyńska, *Chem. Eng. J.*, 150, 280 (2009).
- [12] D. Kołodzyńska, *Chem. Eng. J.*, 152, 277 (2009).
- [13] D. Kołodzyńska, *Desalination and Water Treatment*, 16, 146 (2010).
- [14] D. Kołodzyńska, *Chem. Eng. J.*, 159, 27 (2019).
- [15] D. Kołodzyńska, *Desalination*, 263, 159 (2010).
- [16] J. Jachuła, D. Kołodzyńska, Z. Hubicki, *Central Eur. J. Chem.*, 9, 52 (2011).
- [17] D. Kołodzyńska, *Desalination*, 267, 175 (2011).
- [18] J. Jachuła, D. Kołodzyńska, Z. Hubicki, *Solv. Extr. Ion Exch.*, doi:
- [19] T. Klein, R.J. Moritz, R. Graupner, Polyaspartates and Polysuccinimide, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Online ISBN: 9783527306732, DOI: 10.1002/14356007.
- [20] G. Wójcik, Z. Hubicki, J. Ryzkowski A. *Phys. Pol.*, 116, 432 (2009).
- [21] G. Wójcik, V. Neagu, I. Bunia, J. Haz. *Mat.*, 190, 544 (2011).
- [22] G. Wójcik, Z. Hubicki, P. Rusek, Sposób redukcji jonów chromu(VI) do jonów chromu(III) w roztworach wodnych, P391980.
- [23] H. Hubicka, D. Drobek, *Hung. J. Ind. Chem.*, 25, 99 (1997).
- [24] H. Hubicka, D. Drobek, *Hydrometallurgy*, 47, 147 (1997).
- [25] H. Hubicka, D. Drobek, *Hydrometallurgy*, 50, 51 (1998).
- [26] H. Hubicka, D. Drobek, *Chem. Environ. Res.*, 7, 229 (1998).
- [27] H. Hubicka, D. Drobek, *Hydrometallurgy*, 53, 89 (1999).



- [28] H. Hubicka, D. Drobek, *J. Rare Earths*, 18, 90 (2000).
- [29] H. Hubicka, D. Kołodyńska, *Adsorp. Sci. Technol.*, 18, 719 (2000).
- [30] H. Hubicka, D. Kołodyńska, *Hydrometallurgy*, 62, 107 (2001).
- [31] H. Hubicka, D. Kołodyńska, *J. Rare Earths*, 20, 611 (2002).
- [32] H. Hubicka, D. Kołodyńska, *Hydrometallurgy*, 71, 343 (2004).
- [33] Z. Hubicki, H. Hubicka, D. Kołodyńska, M. Olszak, *Chem. Environ. Res.*, 13, 153 (2004).
- [34] H. Hubicka, D. Kołodyńska, *J. Rare Earths*, 23, 124 (2005).
- [35] Z. Hubicki, H. Hubicka, M. Olszak, *Hydrometallurgy*, 34, 307 (1994).
- [36] Z. Hubicki, H. Hubicka, M. Olszak, *Hydrometallurgy*, 40, 181 (1996).
- [37] Z. Hubicki, M. Olszak, *Hung. J. Ind. Chem.*, 24, 51 (1996).
- [38] Z. Hubicki, M. Olszak, *Hung. J. Ind. Chem.*, 24, 255 (1996).
- [39] Z. Hubicki, M. Olszak, *Adsorp. Sci. Technol.*, 16, 521 (1998).
- [40] Z. Hubicki, M. Olszak, *Hydrometallurgy*, 50, 261 (1998).
- [41] Z. Hubicki, M. Olszak, *Adsorp. Sci. Technol.*, 16, 487 (1998).
- [42] Z. Hubicki, M. Olszak, *Adsorp. Sci. Technol.*, 16, 817 (1998).
- [43] Z. Hubicki, M. Olszak, *Sep. Sci. Technol.*, 35, 535 (2000).
- [44] Z. Hubicki, M. Olszak, *Adsorp. Sci. Technol.*, 18, 701 (2000).
- [45] M. Majdan, S. Pikus, A. Gajowiak, A. Gładysz-Płaska, H. Krzyżanowska, J. Żuk, M. Bujacka, *Appl. Surface Sci.*, 256, 5416, (2010).
- [46] M. Majdan, S. Pikus, A. Gajowiak, D. Sternik, E. Zięba, *J. Hazard. Mater.*, 184, 662 (2010).
- [47] M. Majdan, M. Bujacka, E. Sabah, A. Gładysz-Płaska, S. Pikus, D. Sternik, Z. Komosa, A. Padewski, *J. Environ. Manage.*, 9, 195 (2009).
- [48] M. Majdan, E. Sabah, M. Bujacka, S. Pikus, A. Gładysz-Płaska, *J. Mol. Struct.*, 938, 29 (2009).
- [49] Y. Gonen, G. Rytwo, *J. Colloid Interface Sci.*, 299, 95 (2006).
- [50] M. Majdan, O. Maryuk, S. Pikus, E. Olszewska, R. Kwiatkowski, H. Skrzypek, *J. Mol. Struct.*, 740, 203 (2005).
- [51] M. Majdan, O. Maryuk, A. Gładysz-Płaska, S. Pikus, R. Kwiatkowski, *J. Mol. Struct.*, 874, 101 (2008).
- [52] M. Majdan, S. Pikus, Z. Rzączyńska, M. Iwan, O. Maryuk, R. Kwiatkowski, H. Skrzypek, *J. Mol. Struct.*, 791, 53 (2006).
- [53] A. Gładysz-Płaska, M. Majdan, D. Sternik, S. Pikus, E. Zięba, *J. Therm. Anal. Calorim.*, 101, 775 (2010).
- [54] A. Gładysz-Płaska, M. Majdan, S. Pikus, D. Sternik, *Chem. Eng. J.*, doi:
- [55] P. Rusek, Z. Hubicki, G. Wójcik, *Przem. Chem.*, 89, 529 (2010).
- [56] P. Rusek, Z. Hubicki, Sposób oczyszczania wód osadowych z komunalnych oczyszczalni ścieków, P 390 089.
- [57] G. Wójcik, Rozprawa doktorska, UMCS, Lublin 2007.
- [58] M. Leszczyńska, Rozprawa doktorska, UMCS, Lublin 2005.
- [59] J. Korkisch, Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry, CRC Pres. Inc. Boca Raton, Florida 1989.
- [60] Z. Hubicki, M. Wawrzekiewicz, A. Wołowicz, *Chem. Anal.*, 53, 759 (2008).
- [61] A. Wołowicz, Rozprawa doktorska, UMCS, Lublin 2010.
- [62] Z. Hubicki, M. Leszczyńska, B. Łodyga, A. Łodyga, *Miner. Eng.*, 19, 1341 (2006).
- [63] Z. Hubicki, M. Leszczyńska, *Desalination*, 175, 289 (2005).
- [64] Z. Hubicki, M. Leszczyńska, *Desalination*, 175, 227 (2005).
- [65] Z. Hubicki, M. Leszczyńska, *Adsorp. Sci. Technol.*, 22, 603 (2004).
- [66] Z. Hubicki, A. Wołowicz, M. Leszczyńska, *J. Hazard. Mater.*, 159, 280 (2008).
- [67] Z. Hubicki, A. Wołowicz, M. Wawrzekiewicz, *Chem. Eng. J.*, 150, 96 (2009).
- [68] A. Wołowicz, Z. Hubicki, *Hydrometallurgy*, 98, 206 (2009).

- [69] A. Wołowicz, Z. Hubicki, *Chem. Eng. J.*, 152, 72 (2009).
- [70] A. Wołowicz, Z. Hubicki, *Chem. Eng. J.*, 160, 660 (2010).
- [71] A. Wołowicz, Z. Hubicki, *Chem. Eng. J.*, 171, 206 (2011).
- [72] Z. Hubicki, G. Wójcik, *Chem. Environ. Res.*, 12, 307 (2003).
- [73] Z. Hubicki, G. Wójcik, *Adsorp. Sci. Technol.*, 22, 627 (2004).
- [74] Z. Hubicki, G. Wójcik, *Adsorp. Sci. Technol.*, 24, 559 (2006).
- [75] G. Wójcik, Z. Hubicki, *J. Haz. Mat.*, 136, 770 (2006).
- [76] G. Wójcik, S. Pasieczna-Patkowska, Z. Hubicki, J. Ryczkowski, *Eur. Phys. J.* 154, 373 (2008).
- [77] M. Greluk, Rozprawa doktorska, UMCS, Lublin 2011
- [78] M. Greluk, Z. Hubicki, *Chem. Eng. J.*, 170, 184 (2011).
- [79] M. Greluk, Z. Hubicki, *Desalination*, (2011), doi:10.1016/j.desal.2011.05.024
- [80] M. Wawrzekiewicz, Z. Hubicki, *J. Hazard. Mater.*, 172, 868, (2009).
- [81] M. Wawrzekiewicz, Z. Hubicki, *Chem. Eng. J.*, 159, 29 (2010).
- [82] M. Wawrzekiewicz, Z. Hubicki, *Chem. Eng. J.* 150, 509 (2009).
- [83] M. Wawrzekiewicz, Z. Hubicki, *J. Hazard. Mater.*, 164, 502 (2009).
- [84] M. Wawrzekiewicz, *Solvent Extr. Ion Exch.* 28, 845 (2010).
- [85] M. Wawrzekiewicz, *Environ. Technol.*, 32, 455 (2011).
- [86] M. Wawrzekiewicz, Z. Hubicki, *Environ. Technol.*, 30, 1059 (2009).
- [87] M. Wawrzekiewicz, Z. Hubicki, *Sep. Sci. Technol.*, 45 1076 (2010).
- [88] Z. Hubicki, M. Wawrzekiewicz, *Przem. Chem.*, 87, 711 (2008).
- [89] M. Greluk, Z. Hubicki, *Chem. Eng. J.*, 162, 919 (2010).
- [90] M. Makarska, S. Radzki, J. Legendziewicz, *J. Alloys Comp.*, 341, 233 (2002).
- [91] M. Makarska-Białokoz, G. Pratiel, S. Radzki, *J. Mol. Struct.*, 875, 468 (2008).
- [92] M. Makarska, G. Pratiel, *J. Biol. Inorg. Chem.*, 13, 973 (2008).
- [93] M. Makarska, S. Radzki, V. Sol, R. Granet, P. Krausz, Synthesis of glycosylated porphyrins and their complexes with Cu(II) as new potential compounds of biological importance in photodynamic therapy. In: *Diagnostyka i terapia fotodynamiczna*, (eds. H. Podbielska, A. Sieroń, W. Stręć), Wydawnictwo Urban&Partner, Wrocław 2004.
- [94] M. Makarska, K. Polska, S. Radzki, General properties of water-soluble porphyrins as photodynamic therapy agents. In: *Acta of Biomedical Engineering: Aspects of Photodynamic Medicine I*, (eds. H. Podbielska, A. Sieroń, W. Stręć), Kriotechnika Medyczna, Wydawnictwo Indygo, Wrocław 2007, vol. 2, 1-46.
- [95] J. Dargiewicz, M. Makarska, S. Radzki; *Colloids Surf. A: Physicochem. Eng. Aspects*, 208, 159 (2002).
- [96] J. Dargiewicz-Nowicka, M. Makarska, M.A. Villegas, J. Legendziewicz, S. Radzki; *J. Alloys Comp.*, 380, 380 (2004).