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Ion Exchange Method for Removal and Separation of Noble Metal Ions

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Abstract

Ion exchange has been widely applied in technology of chemical separation of noble metal ions. This is associated with dissemination of methods using various ion exchange resins which are indispensable in many fields of chemical industry. Due to small amounts of noble elements in nature and constant impoverishment of their natural raw materials, of particular importance are physicochemical methods of their recovery from the second sources e.g. worn out converters of exhausted gases, chemical catalysts, dental alloys, anodic sludges from copper and nickel electrorefining as well as waste waters and running off waters from refineries containing trace amount of noble metals. It should be stated that these waste materials are usually pyro- and hydrometallurgically processed. Recovery of noble metals, from such raw materials requires individual approach to each material and application of selective methods for their removal. Moreover, separation of noble metals, particularly platinum metals and gold from geological samples, industrial products, synthetic mixtures along with other elements is a problem of significant importance nowadays. In the paper the research on the applicability of different types of ion exchangers for the separation of noble metals will be presented. The effect of the different parameters on their separation will be also discussed. The examples of the removal of noble metals chlorocomplexes will also be presented in detail.

Keywords: noble metals, ion exchangers, sorbents, separation

1. Introduction

General characteristics of ion exchangers

Ion exchangers are high molecular substances, most frequently solid, organic or inorganic, insoluble in water and many other solvents and capable of exchange of their own active ions into those coming from the surrounding electrolyte. From the chemical point of view, they are

polyacids, polybases or both polyacids and polybases (polyampholyte, amphoteric ion exchangers). Those which exchange cations are called *cation exchangers* and those which exchange anions are called *anion exchangers*. Generally, those exchanging ions are called *ion exchangers*. Some ion exchangers prepared by modification of various types of substances, particularly natural ones, besides capability of exchanging ions exhibit distinct sorption properties [1–5]. The cation exchangers occurring most frequently possess functional groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$ and $-\text{OH}$, whereas the anion exchangers possess the primary, secondary and tertiary amine ones and quaternary ammonium ones, quaternary phosphate ones and tertiary sulfone ones. Selective (chelating) ion exchangers and those strongly basic and weakly basic of the polymerization type of the functional trimethylammonium (type 1) and dimethylhydroxyethylammonium (type 2) groups are most widely applied in exchange chromatography. Their affinity mostly depends on the structure, size and change of anion exchanger. Type of functional groups in ion exchangers is decisive about the character of exchange reaction and its applicability.

Besides the general division of ion exchange materials due to the material (organic and inorganic) the skeleton is built, there are many others whose classification is based on the methods of preparation, type of functional groups and skeleton structure. There is still another basis of ion exchangers division conditioned by historical development of this area, i.e. according to their origin – natural, semi-synthetic and synthetic [1–5].

2. Application of ion exchangers of various types in recovery of platinum metal ions from secondary sources

Small amounts of noble elements in nature and constant impoverishment of their natural resources result in significant importance of physicochemical methods used for platinum metal ions recovery from secondary resources e.g. worn car exhaust gas convertor, chemical catalysts, stomatology alloys as well as waste waters and waters of refinery origin. Noble metals recovery from such raw materials requires individual approach and application of selective methods of their removal. Moreover, worse quality of these raw materials makes removal of pure noble metals more difficult. Determination of noble metals, particularly platinum ones in the above-mentioned materials, geological samples and synthetic mixtures together with other elements is of significant importance nowadays. Liquid–solid phase extraction (SPE) has some advantages compared to liquid–liquid extraction. Among others, it is faster, cheaper, uses small amounts of reagents and above all its automatization is easier. Moreover, its simple performance and high enrichment coefficients decide about its common laboratory application. SPE uses solid sorbents which should be characterized by not only high capacity towards metal ions under determination but also large selectivity and suitable sorption and desorption kinetics.

Synthetic ion exchange resins are widely applied in platinum metal ions enrichments. Among them of particular interest are cation exchangers, chelating ion exchangers and anion exchang-

ers of different basicity of functional groups. Ion exchange selectivity depends on the kind and number of functional groups of ion exchanger as well as cross-linking and composition of external electrolyte solution composition from which concentration proceeds. Of these types of ion exchangers, the most effective are monofunctional ones, which ensure the same strength of bonding ions with the ion exchanger surface due to the presence of one type of groups which does not make equilibrium establishment difficult. Complexity of platinum carrying samples for enrichment makes it necessary to separate a component under determination due to large interference of components present in the analyte. In the chloride systems, ion exchange enables platinum metal ions separation not only from their mixtures but also from other metals. In the hydrogen chloride acid solutions, most platinum metal ions are present in the form of anion chloride complexes; therefore they are retained by strongly basic anion exchangers. Anion exchangers enable selective removal of platinum metal ions from solutions of other metals; however, there appear some problems with their elution due to strong sorption of platinum metal ions. It can often occur that recovery is not quantitative or rendered difficult. Such situation arises because of stable ion pairs formation between anionic complexes and the quaternary ammonium groups of the anion exchanger. Reduction of noble metal ions can proceed in the ion exchanger phase which also affects incomplete recovery. Some difficulties with determination can result from different behaviour of new and 'old' solutions which is connected with the hydrolysis process in the solution. This reflects mainly to rhodium or iridium chloride complexes because they have the greatest tendency towards hydrolysis. Using cation exchangers, rare earth elements, transient metals as well as alkali metals and alkaline earth family form weakly anionic or stable cationic complexes therefore they are retained on the cation exchange deposit whereas platinum metals go through the column not being retained by the cation exchangers making separation of the above-mentioned metal ions possible.

3. Application of cation exchangers in concentration and removal process of platinum metals

There are numerous reports in the literature about cation exchangers application in concentration and separation of trace amounts of platinum metal ions. Ion exchange is widely applied also for control of bound and free platinum contents in the serum added in the cis-platinum form. After ultrafiltration, ethylenediamine was added to form complexes which are sorbed on cation exchange disks. Platinum ions were desorbed from the disks by means of 5 M HCl and determined using the AAS method. The detection limit was 35 µg/dm³ [6].

Besides the above-described procedures, there are separation methods using cation exchangers. As commonly known platinum metals tend to form anion complexes in the chloride systems, therefore partition coefficient values should not be high [7–9]. Much higher values of partition coefficients of platinum metal ions can be obtained by the addition of thiourea which results in cation complexes formation [9].

The polystyrenesulfone cation exchanger Dowex 50Wx8 in the hydrogen form was used for the determination of metals from the platinum group in ores and concentrates. Before ion exchange stage, noble metals in metallic copper were collected. The obtained alloy was digested in *aqua regia*. The pH of the solution was made 1 using hydrochloric acid. Ions of metals such as Cu(II), Ni(II) and Fe(III) were sorbed on the cation exchangers, whereas noble metals were not retained. The deposit was washed in HCl solution of pH = 1. The separated noble metals were determined gravimetrically and spectrophotometrically [10–14]. A similar technique was applied for the determination of noble metals and for the collection of Cu-Ni-Fe and ferronickel alloys [15–24]. Also the cation exchanger Dowex 50Wx8 was used for noble metal ions removal. Before the ion exchange stage, collection was made using fused tin. The obtained alloy was digested in the HCl-H₂O₂ solution. Tin(IV) was removed by evaporation from the HCl-HBr solution, and the obtained solution was evaporated dry several times in the presence of 12 M HCl [25]. The removal of noble metals from ores, the cation exchange followed by anion exchange method was applied. Cu(II), Ni(II) and Fe(III) ions are adsorbed at pH = 1.5 on the cation exchanger Dowex 50Wx8, whereas the noble metal ions pass on the column filled with the strongly basic anion exchanger in the chloride form Amberlite IRA-400. Before sorption on the anion exchange column, the solution is evaporated dry in the presence of sodium chloride, then it is dissolved in 12 M HCl and diluted to weakly acidic reaction. Under such conditions, rhodium(III) ions pass through the column, and the ions of other noble metals are retained on the anion exchanger bed [26]. A similar method was applied for the determination of iridium in the flotation concentrate [27]. The application of cation exchange for the determination of platinum metals on the meteorites is quite interesting. In this method, two-stage adsorption on the cation exchanger was used. Non-noble metal ions were adsorbed at pH 1.5 on the first column. Then they were desorbed by means of 3 M HCl. The obtained eluant was evaporated dry and the residue was dissolved in diluted HCl and the pH value was brought to 1.5. The other stage of non-noble metal ions adsorption was conducted in the same way as the first one. Application of the second stage allows avoiding errors connected with co-adsorption of noble metal ions [28, 29]. For determination of platinum and palladium in the copper and nickel stone, there were used two ion exchangers: the cation exchanger Dowex 50 in the hydrogen form and the anion exchanger Amberlite IRA-400 in the chloride form. Before the ion exchange process, the sample was melted with SnO₂ to collect noble metals. Tin(IV) was evaporated from the mixture of HCl and HBr acids. After bringing the solution to pH 1.5, Cu(II), Ni(II) and Fe(III) cation were adsorbed on the cation exchanger bed. The obtained eluant containing Pt(IV) and Pd(II) was evaporated from NaCl and dissolved in HCl, next it was passed through the anion exchanger bed. At first, there were eluted Pd(II) ions by means of 12 M HCl and then Pt(IV) ions using 2.4 M HClO₄. Both elements were determined using the spectrophotometric method [30]. The residue in the copper-nickel stone was determined using the cation exchanger Bio-Rad AG50W-x8 and the chromatographic column Porasil C impregnated by means of TBP (tri-n-butyl phosphate). The sample was melted with Na₂O₂, then digested in HCl and the acid concentration was brought to 0.1 M. Non-noble metal ions were separated on the cation exchanger and platinum metals were sorbed on the chromatographic column. Pt(IV) and Pd(II) ions were eluted by means of TBP in toluene but Rh(III) and Ir(IV)

ions using water. Noble metals were determined gravimetrically and by means of AAS [31, 32]. Platinum alloys were determined in a two-stage separation process of noble metal ions. The sample was digested in *aqua regia*, next it was evaporated dry and the residue was diluted with HCl up to concentration about 0.1 M. The weakly acidic cation exchanger Amberlite IRC-50 of carboxylic groups in the sodium form was used in the first column. Palladium(II) ions were sorbed (probably precipitated in the hydrated oxide form [33]) on this ion exchanger, whereas Rh(III) and Pt(IV) passed to the eluant which was next put through the column with the strongly basic anion exchanger Dowex 2 in the chloride form. The adsorbed Rh(III) and Pt(IV) ions were eluted with 2 M HCl and 7 M HCl, respectively. The ion exchange technique was also applied for the determination of trace amounts of noble metals in common metals of high purity such as Fe, Ni, Cu, Mn and Al. The sample can be digested or melted with alkalis depending on its kind. The two-column cation–anion exchanger system was used for separation of noble metal ions. On the cation exchanger Dowex 50x8, there were adsorbed ions of metals such as Fe(III), Ni(II), Mn(II), Cu(II) and Al(III) from the 90% v/v ethanol + 10% v/v 1 M HCl solution. Then by evaporation, the medium changed from chloride to nitrate(V) one. In the other column on the anion exchanger Dowex 1x 8 in the nitrate form, there were sorbed noble metal ions from the aqueous solution of pH 6. Noble metals were analyzed in the resin phase by means of the radioisotope technique [34]. The similar method was used for the determination of noble metals in atmospheric dusts melting them with Na₂O₂ [35]. The cation exchanger Dowex 50x8 was used for the separation of copper(II) from the 0.03 M hydrochloric acid solution from the noble metal ions such as Pt(IV), Pd(II), Au(III) and Rh(III) [36, 37]. Ion exchange combined with extraction was applied for the determination of noble metals present in uranium alloys which can be uncoupled. Uranium can be separated from rhodium by extraction with 30% solution of TBP in CCl₄. Then after complete removal of chlorides, fluorides and nitrates by evaporation with chloric acid, rhodium(III) cations were sorbed by cation exchanger Dowex 50Wx8 from 0.3–0.9 % HClO₄ solution. Rhodium(III) was eluted from the cation exchanger by washing the column with 6 M hydrochloric acid solution and then determined spectrophotometrically using the method with SnCl₂ [38].

Separation of noble metals can be conducted on the cation exchangers from the thiourea systems. Separation of microquantities of various pairs of noble metal ions was made using the polystyrene sulfone cation exchanger Bio-Rad AG 50Wx4 in the hydrogen form. Pd(II) and Au(I), Pd(II) and Pt(II) ions as well as the Rh(III), Au(I), Pt(II) and Ag(I) mixture were separated using the acetate-thiourea solutions in the hydrochloric or hydrobromic acid medium [39]. Platinum(II) and palladium(II) ions were separated from aluminium ions using also the cation exchanger Bio Rad AG50Wx4 in the hydrogen form. Aluminium ions as well as Fe, Zn, Pb, U, Ni, Co and Sr ones do not form cationic complexes under experimental conditions, therefore only noble metals are sorbed from 0.1 M thiourea solution in 1.5 M hydrochloric acid solution. 2% Br₂ and 1.5 M HCl solution was used for elution of Pt(II) and Pd(II) ions. 0.87 M HBr–0.01 M thiourea solution in 90% acetone proved to be the best eluant towards Pt(II) ions. The presence of Cu(II) and Hg(II) ions is not recommended because of possible co-adsorption with noble metals [40]. It is relatively difficult to separate rhodium(III) ions from platinum(IV) ones in the chloride medium, therefore in some cases it is necessary to change the medium into the

nitrate one. Before the separation of platinum(IV) and rhodium(III) ions on the polystyrene-sulfone cation exchanger Varion KS in the hydrogen form, the chloride complexes were in contact with sodium hydroxide at pH 13 for four hours. Then the obtained solution was acidified with 4 M HNO_3 to pH 2. Under such conditions, rhodium(III) ions occur in the cation form and platinum(IV) ions in the anion form. Platinum(IV) ions are not retained by the cation exchanger. Rhodium(III) ions can be eluted with 1 M hydrochloric acid from the cation exchanger [41].

4. Application of chelating ion exchangers for concentration and removal of platinum metal ions

Chelating ion exchangers also called complexing ion exchangers are formed by building organic reagents containing organic groups into the ion exchange resin skeleton. Owing to that they possess active chemical groups capable of selective/specific interactions with metal ions in the solution forming chelating complexes when a metal ion can bind with two or a larger number of donor atoms of their functional groups. These ion exchangers are characterized by high selectivity and their sorption capacities depend, among others, on the kind of functional groups, their reciprocal position and spatial configuration (steric effects) and also on physicochemical properties of the polymer matrix [42, 43].

On the huge number of chelating ion exchangers, on a large laboratory and industrial scale, there are produced ion exchangers of functional dithizone, thiourea, isothiurea, aminophosphonic, phosphonic, thiol, amidooxime, aminoacetate, dithiocarbamate, iminodiacetate, thiosemicarbamate groups as well as chelating ion exchangers containing triisobutylphosphine sulfides [44-64].

5. Chelating ion exchangers of functional dithizone groups

Chelating ion exchangers of functional dithizone (diphenyl carbamate) groups are widely applied in concentration, separation and recovery of noble metal ions [44-54].

Grote and Kettrup [45-48], by conversion of the ion exchanger of functional dehydrodithizone groups, prepared a chelating resin containing dithizone groups. It was used on both sorption and separation of 27 noble and non-noble ions from acids (HCl , HNO_3). They showed very high values of partition coefficients of noble metal ions of the order 10^4 - 10^6 (Pd(II) - 7.7×10^5 ; Pt(IV) - 3.4×10^5 ; Au(III) - 2.1×10^5 (0.01 M HCl)) in the whole range of hydrochloric acid (0.01-6 M) as well as Ag(I) (1.1×10^3) and Hg(II) (5.8×10^4) ions in diluted nitric(V) acid solutions compared to the values of partition coefficients for non-noble metal ions. Also high values of ion exchange capacities of platinum metals and gold (Au(III) 0.74; Pd(II) 0.68; Pt(II) 0.39; Pt(IV) 0.31; Os(IV) 0.12; Ir(IV) 0.14; Ir(III) 0.02; Ru(III) 0.14; Rh(III) 0.16 mmol/g of the dithizone resin) indicate large selectivity of the resin with dithizone functional groups towards noble metal

ions as well as possibility of their application in separation from other non-noble metals. Satisfactory results were obtained using the chelating ion exchanger with dithizone functional group in concentration and recovery of Au(III), Pt(IV) and Pd(II) ions originating from the extraction of sulfide ores, stones and enriched ores. Elution of the above-mentioned ions was conducted by means of 2 M chloric(VII) acid and 5% thiourea solution [44]. There was also made a thorough analysis of desorption of single noble metal ions and their mixtures from the resin with the dithizone functional groups using the following eluents: HCl, HClO₄, NH₄NO₃, NaSCN, (NH₂)₂CS. Palladium(II) and platinum(IV) ions retained on this resin can be qualitatively desorbed using the thiourea solution [46].

Similar investigations using polyvinylpyridine resin of functional dithizone groups in Pd(II) and Pt(IV) ions concentration in the presence of Au(III), Ni(II) i Hg(II) ions were carried out by Shah and Devi [49]. The values of maximal ion exchange capacities towards palladium and platinum ions were 100 and 250 mg/g of resin, respectively. Separation of the above-mentioned ions from nickel, gold and mercury ions (Pd(II)-Ni(II); Pt(IV)-Au(III); Pt(IV)-Ni(II); Pd(II)-Pt(IV)-Ni(II); Pt(IV)- Au(III)-Hg(II)) was conducted using various eluants 0.1 M HCl + 1% (NH₂)₂CS (elution of Pd(II)), 0.1 M HCl + 5 % (NH₂)₂CS (elution of Pt(IV)), 0.2 M CH₃COOH (elution of Ni(II)), 5 M HCl + 1 M HNO₃ (elution of Au(III)) and 0.5 M HNO₃ + 2 % NH₄NO₃ (elution of Hg(II)).

Modification of the commercially available polyacrylate matrix Diaion HP-2MG with dithizone resulted in the preparation of the selective sorbent towards Pd(II) and Pt(IV) ions. Chwastowska et al. [51] used the above-mentioned sorbent for removal of Pd(II) and Pt(IV) ions from the environmental samples, among others, from road dusts, soil and grass collected from fast traffic routes. After proper preparation, among others, drying (673 K, 1 h) and digestion in *aqua regia*, the geological samples were analyzed using the GF AAS technique. The detection limit (LOD) for the determined metal ions was 1 ng/g for Pt(IV) and 0.2 ng/g for Pd(II). Metal ions desorption was run in two ways: using thiourea solution (possibility of determination of both elements in the eluant by the GFAAS technique) and concentrated HNO₃ solution (possibility of directed determination of only Pd(II) ions in the eluant). The obtained ion exchange capacity towards both metal ions was about 0.16 mmol/g of resin.

Chelating resin formed by immobilization of sulfonated dithizone on the anion exchanger Amberlite IRA-400 was applied in concentration of heavy metal ions, i.e. Pd(II), Ni(II), Co(II), Cu(II) and Pb(II) in the water samples collected in Japan. The first four elements were determined by the GFAAS technique but Pb(II) by HGAAS. The affinity series of the studied ions towards the present resin is as follows: Pd(II) > Cu(II) > Co(II) > Pb(II) > Ni(II) [52].

6. Ion exchangers of functional thiourea and phosphonic groups and their derivatives

Of significant importance are the results of studies on the application of commercial ion exchangers Tulsion of the functional isothiurea and phosphonic groups for removal of Pd(II)

ions from nitric(V) acid solutions (0.1–4 M). High values of partition coefficients (particularly in diluted HNO_3 (0.1 M) solutions) decreased with the increasing concentration of nitric(V) acid for the ion exchangers Tulsion CH-95, Tulsion CH-96 and Tulsion CH-97. The values of partition coefficients (particularly in diluted HNO_3 (0.1 M) solutions) which were $>10\,000\text{ cm}^3/\text{g}$, $1650\text{ cm}^3/\text{g}$, $5210\text{ cm}^3/\text{g}$ for Tulsion CH-95, Tulsion CH-96 and Tulsion CH-97, respectively, decreased with the increasing nitric acid(V) concentration. The selectivity series of the Tulsion ion exchangers towards Pd(II) ions is as follows: *Tulsion CH-95* $>$ *Tulsion CH-97* $>$ *Tulsion CH-96*.

The ion exchangers of the functional thiourea and isothioureia groups, commercially known as Srafion NMRR, Lewatit TP-214 and Purolite S-920, are widely used for the concentration of platinum metal ions [53–61]. Srafion NMRR (Ionac SR-3) exhibits great affinity for Au(III) and Ag(I) as well as Pd(II), Pt(IV), Rh(III), Ru(III), Ir(III) and Os(VI) ions [53–61]. It is applied in the separation of noble metal ions [57], similar to the ion exchangers Monivex which develop high sorption capacity values particularly in the largely acidic solutions (2–6 M HCl) [67]. Lewatit TP-214 was used for the removal Pd(II) ions from two component Pd(II)–Zn(II); Pd(II)–Cu(II)) and multicomponent (Pd(II)–Cu(II)–Zn(II)) chloride solutions [61] and for the removal of Pd(II) ions from chloride solutions (0.1–8.0 – 0.001 M Pd(II)) and chloride–nitrate ones (0.1÷0.9 M HCl – 0.9÷0.1 M HNO_3 – 0.0011 M Pd(II))) [55]. The total ion exchange capacity of Lewatit TP-214 towards Pd(II) ions was from 0.97 mmol/g–3 M HCl to 1.16 mmol/g–0.1 M HCl [55].

Zuo and Muhammed prepared a large number of ion exchangers of the functional thiourea groups by modification of macroporous polystyrene matrices of Bonopore, Amberlite XAD-2, Amberlite XAD-4 as well as the weakly basic anion exchanger Amberlite IR-45 [62]. Newly prepared ion exchangers were used in sorption of Au(III), Ag(I), Cu(II) and Fe(III) ions from one-component chlorides solutions (2 M HCl) and their mixtures (Au(III), Ag(I), Fe(III), Cu(II)), as well as in sorption of platinum metal ions e.g. Pd(II), Pt(IV), Rh(III), etc. The studied ion exchangers are characterized by high selectivity towards noble metal ion, particularly gold and silver in the presence of Cu(II) and Fe(III).

Separation of Pd(II), Cu(II) and Zn(II) ions using the melamine-formaldehyde-thiourea (MFT) resin was presented in [63]. There was proved high selectivity of this resin towards Pd(II) ions, and the obtained values of sorption capacity were 15.29 mg Pd(II)/g (static method) and 1580 μg Pd(II)/g resin (dynamic method). Desorption of ions with studied resin was conducted using 0.5 M thiourea, 0.5 M HCl solutions and the acidified thiourea (0.5 M $(\text{NH}_2)_2\text{CS}$ –0.5 M HCl).

7. Ion exchangers of functional thiol groups

The chelating ion exchangers of functional thiol and methylene thiol groups with the commercial names: Chelate S, Duolite GT-73, Imac GT-73, Duolite GT-74, Purolite S-924, Spheron Thiol 1000 and Tulsion CH-97 are widely applied in sorption and separation of noble metal ions [55, 56, 64–69]. Introducing 8-hydroxcholine (HOxn) and sodium salicylate groups to the methacrylate polymer matrix generates two new chelating ion exchangers Spheron Oxine 1000 and Spheron Salicyl 1000, respectively, which similar to Spheron Thiol 1000 are applied

in the separation of Pd(II) and Cu(II) ions. From the determined ion exchange capacities, the affinity series of Spheron ion exchangers towards Pd(II) ions is as follows: *Spheron Thiol 1000* (0.949 mmol/g) > *Spheron Oxine 1000* (0.536 mmol/g) > *Spheron Salicyl* (0.094 mmol/g) [68]. Elution of Pd(II) and Cu(II) ions from the ion exchanger Spheron Oxine 1000 was conducted using 0.5 M thiourea solution (pH = 2) and 2 M HCl [70].

8. Ion exchangers of functional imidazole groups

Many authors prove high reactivity of imidazole groups and their derivatives towards metal ions, particularly noble metals ions. For example, VBC-DVB (VBC – vinylbenzene chloride, DVB – divinylbenzene) – recovery of Pd(II) and Pt(IV) ions from chloride solutions (1–2 M HCl) and their separation from Cu(II), Zn(II) and Ni(II); sorption capacity, 1.6–1.7; 1.4–1.5 and 1 mmol of metal/g for the 0.1 M HCl, 1 M HCl and 2 M HCl solutions, respectively; desorption of Pd(II) and Pt(IV) ions, 0.1–0.3 M thiourea solution (desorption effectiveness >98% for Pd(II); 85% for Pt(IV)) [71, 72]; epoxide resin of the functional imidazole groups concentration of trace (20 ng/dm³) amounts of Au(III), Pd(IV) and Ru(III) ions. Noble metal ions can be enriched in a quantitative way (recovery 94.5–100%, pH = 4), desorption: acidified thiourea solutions (16 cm³ 6 M HCl, 0.2 g thiourea), recovery 96–99.5% [73], polystyrene-divinylbenzene resin of functional benzimidazole group – separation of heavy metal ions that is Pd(II), Ag(I) and Hg(II) from medical alloys, geological materials, different kinds of waste waters and sludges; sorption capacity: 1 mmol/g for Ag(I) (pH = 4–6), 0.62 mmol/g for Pd(II) (pH = 5–6) and 0.83 mmol/g for Hg(II) (pH = 4–6); desorption: 5% thiourea solution in 0.1 M HClO₄ (recovery: Ag(I) and Hg(II) – 100%, Pd(II) – 60%) and 12 M hydrochloric acid solution (recovery: Ag(I) – 45 %, Pd(II) – 100 %, Hg(II) – 65 %) [74]; polystyrene-divinylbenzene resin of Im-NO₃ (Im-imidazole) groups – removal of Pd(II) (0.00062 M) from nitric(V) acid solutions (1–5 M HNO₃); sorption capacity depends, among others, on the molar ratio of initial reagents of chloromethylated resin (I) and 1-methylimidazole (II) at the reagents ratio I:II = 1:1.5 this capacity is the highest (4.06 mmol/g), the total capacity determined from the Langmuir 88 mg/g (3 M HNO₃) [75]; resin of functional aminoethylene imidazole (IEA) – concentration of trace amounts of Au(III), Pt(IV), Ir(IV), Pd(II) ions and their separation from Cu(II), Fe(III), Zn(II), Ni(II), Mn(II), Cr(III), Ca(II) and Mg(II) ions; sorption capacity in 2 M HCl solution: 4.0 mmol/g – Au(III), 1.57 mmol/g – Pt(IV), 2.26 mmol/g – Pd(II) and 1.85 mmol/g – Ir(IV) [76].

9. Ion exchangers of functional thiosemicarbazide, piperazine and tetrazine groups

Table 1 presents the characteristic of chosen chelating ion exchangers of thiosemicarbazide, piperazine and tetrazine functional groups widely applied in the concentration and removal of platinum group ions [77–80].

Ion exchanger	Application	Additional Information	Ref.
Resin of thiosemicarbazide functional groups	Separation of Pd(II), Rh(III), Pt(IV), (pH = 0) and increase with increasing solution Ru(III), Ir(III), Au(III), Os(VI), as well as Cu(II), Bi(III), Hg(II), Fe(III) and Al(III)	Sorption capacities (mmol/g): Pd(II) – 0.78 (pH = 0); Pt(IV) – 0.71 (pH = 0); Ru(III) – 0.685 (1.5 M HCl); Rh(III) – 0.615 (2 M HCl); Ag(I) – 0 pH, Ir(III) – 0 (pH = 0); Au(III) and Os(VI) are reduced during the contact with the resin; Cu(II), Bi(III), Hg(II), Fe(III) and Al(III) are not retained by the resin; Desorption: 4 M and 9 M HCl as well as 5 % N,N-diphenylthiourea in ethanol	[77]
Resin of amine and 1,2,4,5-tetraazine functional groups	Preconcentration and separation of noble metal ions in the amount of 0.001 M in the presence of Zn(II), Co(II), Cu(II), Fe(III), Ni(II) and Cd(II) from acidic solutions of the proportion of noble metal to base metal: 1:1, 1:10, 1:100	Selectivity series: Pd(II) > Au(III) >> Ir(IV) > Os(IV) > Pt(IV) > Ru(III) > Rh(III); Desorption: acidified 5% (NH ₂) ₂ CS	[79]
Resin of 1-(2-aminethylene)-piperazine functional groups	Pre-concentration and recovery of Au(III), Pd(II), Ru(III), Os(VI), Pt(IV) and Ir(IV) in the presence of Zn(II), Fe(III), Cu(II) and Ni(II) from chloride solutions	Sorption capacities for Au(III), Pd(II), Ru(III), Os(VI), Pt(IV) and Ir(IV) equalled to 5.38, 3.67, 3.46, 3.10, 2.46 and 2.24 mmol/g, respectively	[80]

Table 1. Examples of the chelating ion exchangers of thiosemicarbazide, piperazine and tetrazine functional groups and their characteristic.

10. Ion exchangers of functional (amino)pyridine groups

Resins of pyridine [81] and α-aminopyridine groups on the polyphenylethylene support [82] were successfully used for the separation of technetium and platinum metals from diluted chloride solutions and in concentration of Pt(IV), Pd(II) and Ir(III) (*on-line* FAAS). Technetium ions were eluted using concentrated solutions of hydrochloric acid but platinum metals (Ru(III), Rh(III) and Pd(II)) by means of 0.1 M NH₂CSNH₂ in 1 M HCl [81] or 0.5 M HCl – 0.5 M HClO₄ – 0.5 M Mg(ClO₄)₂ [82]. Most interferences coming from noble-metal ions were eliminated using 2 M HCl and those from iron (> 200 mg Fe/dm³) adding 0.2 M EDTA [82].

11. Ion exchangers of functional amine and guanidine groups

Resins of functional amine and guanidine functional groups were successfully used in sorption of Pd(II), Pt(IV) and Au(III) ions from chlorides solutions (initial concentration of each metal

was 24 mM). The highest selectivity towards the above-mentioned ions and the possibility of practical application of their recovery are exhibited by the ion exchangers A2 (Au – 99.7; Pt – 108; Pd – 54.3 mg/g), B2 (Au – 94.1; Pt – 104.8; Pd – 48.7 mg/g) and AG2 (Au – 85.1; Pt – 64; Pd – 49.2 mg/g) and BG2 (Au – 74.3; Pt – 76.2; Pd – 48.5 mg/g). The sorption mechanism of Pd(II), Pt(IV) and Au(III) chloro complexes is the combination of coordination interactions of electron nitrogen pair and electrostatic interactions of these ions with the protonated group $-\text{NH}_2$ [83].

In the case of the ion exchangers of the same functional groups: amine (D1, D2, D3, D4) and guanidine (D1G, D2G, D3G, D4G) but on the basis of copolymer VBC/AN/DVB (copolymer D), the studies of Pd(II), Pt(IV), Au(III), Cu(II), Ni(II) and Fe(III) ion removal from single and multi-component chloride solutions (0.1–3.0 M HCl) showed that the highest selectivity towards metal ions is exhibited by the resin D4 (sorption capacity 190 mg Au(III)/g, 245 mg Pt(IV)/g and 280 mg Pd(II)/g of the resin), and the selectivity series towards Pd(II) ions is as follows: D4 (117 mg/g) $\gg$ D1 > D4G > D1G > D2 = D3G > D2G > D3 (25 mg/g). Recovery of noble metals from multi-component solutions with ten greater excess of Cu(II), Ni(II) and Fe(III) ions was > 95 % [84].

12. Ion exchangers of functional hydrazone and hydrazine groups

Modification of the macroporous copolymer ACR/ST/DVB (where ACR – acrolein, ST – styrene, DVB – divinylbenzene) using isonicotinic acid hydrazide and hydrazine hydrate results in preparation of new chelating ion exchangers: P-NHZ and P-THZN, respectively [85–87]. These resins exhibited high selectivity towards noble metal ions which allows their separation from common metal ions. The maximal values of sorption capacities obtained in 0.1 M HCl are 3.77 mmol Au(III)/g, 1 mmol Pt(IV)/g, 0.79 mmol Pd(II)/g, 0.72 mmol Ir(III)/g, 0.51 mmol Ru(III)/g, 0.39 mmol Rh(III)/g for the resin P-NHZ and 4.2 mmol Au(III)/g, 1.36 mmol Pd(II)/g, 0.5 mmol Pt(IV)/g, 0.4 mmol Ir(III)/g, 0.31 mmol Rh(III)/g, 0.29 mmol Ru(III)/g for the resin P-THZN, whereas the sorption capacities for common metal ions (Cu(II), Fe(III), Co(II), Ni(II), Cr(III), Zn(II), Mn(II) and Al(III)) are small, in the range 0–0.13 mmol/g for the resin P-NHZ and 0.03–0.32 mmol/g for the resin P-THZN. Desorption of the above-mentioned ions from the P-NHZ and P-THZN was achieved using a 5% thiourea solution in 0.1 M HCl. Quantitative desorption was possible only in the case of Au(III) and Pd(II) from the resin P-NHZ. Another advantage of the ion exchanger P-NHZ over P-THZN is fast kinetics of sorption and easy elution of adsorbed ions [87].

Ge et al. [86] proved high selectivity of the P-NHZ resin towards noble metal ions and possibility of its exploitation for separation and concentration of trace amounts of Pd(II) and Pt(IV) contained in road dust samples. Sorption of the above-mentioned ions on the P-NHZ resin can be conducted also from the HNO_3 , HF and H_3BO_3 solutions of the concentration 0.08–1.2 M.

13. Ion exchangers of functional formazane groups

Chelating ion exchangers of functional formazane groups [88–91] based on the styrene divinylbenzene skeleton [58], amino- and chloromethylated polystyrene [91], cellulose [58, 91], saccharose [65] and methacrylate [58] were applied for sorption and separation of platinum metals, gold, mercury, silver and copper. The sorption capacity towards Pd(II), Ag(I) and Hg(II) ions was in the range 0.05–0.06 mmol/g, 0.4–0.9 mmol/g and 0.6–0.8 mmol/g, respectively, for formazane ion exchanger based on cellulose, aminomethylated polystyrene; however, their sorption capacity towards Cu(II) ions was close to zero.

14. Ion exchangers of functional cyclane groups

For separation and recovery of Pd(II), Pt(IV) and Au(III), Jermakowicz-Bartkowiak [92] used the resin A7C prepared by the reaction of cyclane (1,4,8,11-tetraazacyclotetradecane) with the copolymer of vinylbenzyl and divinylbenzene chloride (VBC/DVB) obtaining the following sorption capacities: 47.4 (S0), 47.4 (S1) mg Au(III)/g, 48.1 (S0), 47.5 (S1) mg Pt(IV)/g, 26.0 (S0), 25.6 (S1) mg Pd(II)/g resin, where S1 – the multifunctional system, S0 – the single component system (static method) and 0.92 mmol Au(III)/g, 0.66 mmol Pt(IV)/g, 0.9 Pd(II) mmol/g dry resin (dynamic method). Desorption of Au(III), Pt(IV) and Pd(II) ions from the resin was made using a 5 % thiourea solution in 0.1 M hydrochloric acid with the yield 98, 97 and 98%.

15. Ion exchanger Metalfix Chelamine

The studies of the use of the ion exchanger Metalfix Chelamine of tetraethylenepentamine ligands (1,4,7,10,13 – pentaazatridecane) in the process of recovery, concentration and separation of platinum metal ions, gold and their accompanying elements from the environmental samples, anodic sludges from the electrorefining of copper ores, spent car exhaust gas catalysts, etc. [93–98].

16. Polyorgs ion exchangers

Polyorgs type chelating ion exchangers [58, 99–103] are used for separation, concentration and removal of palladium(II) ions and other noble metals from deposits, rocks, ores, minerals and industrial waste waters. The Polyorgs sorbents were prepared by introducing e.g. imidazole, pirazole, mercaptobenzothiazole, amidooxime groups to the macroporous copolymers (polystyrene, polyvinyl, polyacrylonitrile) and other matrices. Sorbents of this type are characterized by high chemicals stability in strong acid and alkaline solutions as well as high thermal resistance and can be applied in the whole pH range. The sorbents of Polyorgs type (11-n, 15-n, 17-n and 33-n) were also used for filling fibres e.g. polyacrylonitrile (PAN),

cellulose, polyvinyl (PVA) ones. In the literature, such sorbents are called filled fibrous sorbents (FFS) [99, 102, 103]. Main advantages of FFS are good kinetics of sorption and ease in their separation from solution which make them more attractive than sorbents in the form of powder or grains.

17. Ion exchangers of functional iminodiacetate groups

Recovery of palladium ions from chloride and chloride-nitrate(V) solutions using the ion exchanger Amberlite IRC-718 of functional iminodiacetate groups and polystyrene skeleton was conducted by Hubicki et al. [104]. The largest total ion exchange capacities of Amberlite IRC-718 were obtained in the 0.1M HCl (1.099 mmol/g) and 0.9M HCl–0.1M HNO₃ (0.693 mmol/g) solution. The additional of 1M AlCl₃, 1M CuCl₂ or 1M NiCl₂ results in significant drop of ion exchange capacity.

Studies of Amberlite IRC-718 selectivity towards Pd(II), Pt(IV) and Au(III), Ti(IV), Ag(I), Al(III), Co(II) and Fe(III) were carried out also by Park and co-workers [105]. The optimal sorption conditions for Pd(II), Pt(IV) and Au(III) ions are pH = 0.1–4 and a flow rate ≤ 2 cm³/min. Quantitative desorption of noble metal ions was conducted using 20 cm³ of 0.25 M thiourea and a flow rate 1 cm³/min. The ion exchange capacity of the studied ion exchanger was 0.34 mmol Pt(IV)/g; 0.69 mmol Au(III)/g and 0.55 mmol Pd(II)/g of the resin. From a practical point of view, the chelating ion exchanger Amberlite IRC-718 can find application in removal, concentration and separation of noble metal ions from the solutions originating from hydrometallurgical processing of car exhaust gas catalysts, anodic sludges, wastewaters as well as in removal and determination of gold(III) ions in printed computer plates PCP [105].

18. Copolymers modified with triisobutylphosphine sulfide

Of special importance are the studies by Sanchez et al. [106–109] of building triisobutylphosphine sulfide (TIBPS, Cyanex 471X) into the styrene-divinylbenzene (4% DVB) copolymer in order to obtain a resin concentrating noble metal ions. Polymers are characterized by high selectivity towards Au(III) and Pd(II) ions (sorption from chloride solutions) as well as a lack of selectivity towards Ir(IV), Rh(III), Pt(IV) and Fe(III), Cu(II) or Ni(II) [106]. Based on the obtained values of sorption capacities (mmol/g) towards Pd(II) ions, the affinity series of the studied resins is as follows: Pd(II): Polymer 2 (0.07 mmol/g) < Polymer 1 (0.11 mmol/g) < Polymer 5 (0.17 mmol/g) < Polymer 3 (0.51 mmol/g) < Polymer 4 (0.72 mmol/g) [106].

With the temperature increase in the range 298–333K, there is observed the increase in Au(III) ions sorption compared to that of Pd(II) ions. The sodium nitrate(III) and thiourea solutions were used as eluents. Sodium nitrate(III) (2 M, pH 4.7) desorbs 75% of Pd(II) practically not washing out Au(III) from the ion exchanger, whereas thiourea (0.5 M, [H⁺] 0.1 M) enables almost quantitative recovery of gold(III) containing trace amounts of palladium (II) ions.

19. Ion exchangers of cyclic ligands

Kałędowski and Trochimczuk [110, 111] synthesized polymers containing calixpyroles preparing among others the resin B4 (covalently bonded thiophene kalix[4]pyrol[2] with the vinylbenzene chloride and divinylbenzene (VBC-DV, 0.5% DVB) of the expanded gel structure) selective towards noble metal ions. The maximal sorption capacity values determined from the Langmuir adsorption isotherms are 0.26 mmol/g; 0.55 mmol/g; 0.6 mmol/g; 0.61 mmol/g and about 1.7 mmol/g for Ag(I), Pt(II), Pt(IV), Pd(II) and Au(III), respectively. The resin B4 can be applied for the selective removal of Au(III) from the solutions originating from processing of ores, galvanic sludges containing other noble metals. The metals adsorbed on the resin are quantitatively washed out using 2 M solution of HCl or 2 M HNO₃-Pt(IV), 0.5 M thiourea + 0.1 M HCl-Ag(I) and 5% solution of KCN-Au(III). In the case of palladium(II), the recovery was not quantitative (>57%, 0.5M thiourea in 0.1M HCl).

Garcia et al. [112] used the polystyrene-based resin of 15-membered triolefinic azamacrocyclic rings in Pd(II) and Pt(IV) ions sorption from aqueous and aqueous dioxane solutions. The addition of dioxane (10% v/v) results in increasing polymer swelling and effectiveness of palladium(II) ions sorption from 48% to 73%. The total sorption capacities for Pd(II) and Pt(IV) ions were 0.36 mmol/g and 0.28 mmol/g of the resin, respectively. The presence of Cu(II) and Ni(II) ions affects insignificantly the selectivity of the resin towards noble metals. 0.5 M thiourea in 0.1 M HCl was used as an eluent of Pd(II) and Pt(IV) ions with 100% and 79% recovery, respectively.

20. PAN-ATAL, PS-BMT ion exchangers

Chen and Zhao [113] prepared the chelating resin PAN-ATAL by immobilization of cross-linked polyacrylonitrile (PAN) (7% DVB) with 2-amino-2-thiazole (ATAL) selective towards noble metals, i.e. Pd(II), Ru(II), Ir(IV) and Rh(III) ions, for which the sorption capacity values were 230.7 mg Pd(II)/g, 147.1 mg Ir(IV)/g, 137.6 mg Ru(IV)/g and 72.1 mg Rh(III)/g of the resin. The affinity of chelating macroporous resin PS-BMT (where PS – the cross-linked chloromethylated polystyrene (10% DVB), BMT – 2,5-dimercapto-1,3,4-thiadiazole) for Pd(II), Au(III) and Pt(IV) ions from chloride solutions was studied by Qu et al. [114]. The sorption capacity for Au(III) ions 5.8 mmol/g is much higher than for Pd(II) ions 0.19 mmol/g and Pt(IV) ions 0.033 mmol/g which is associated with gold(III) chlorocomplexes coordination by two donor N and S atoms of the resin and reduction of gold(III) to a metallic form. However, in the case of PdCl₄²⁻ and PtCl₆²⁻ complexes, only one donor atom – sulfur atom takes part in bonding.

21. Chelating fibres

It is worth presenting also the studies of using chelating fibres for the removal of platinum elements, for example, those Gong [115] and Li et al. [116] on application of fibres of functional

imidazole groups in noble metal ions sorption. Bilba et al. [117] used chelating polyacrylamidoxime fibres in concentration and recovery of Pd(II) ions from chloride solutions. The attention should be also paid to the investigation by Gong and Wang [118, 119] as well as Chang et al. [120] on concentration of trace amounts of Au(III), Pd(II), Pt(IV) and Ir(IV) by means of chelating polyacrylacylaminothiurea fibres. Poly (acrylamidrazonehydrazide) [121] and poly (acryl-p toluenesulfonamideamidine-p-toluenesulfonylamide) [122] fibres were applied in quantitative concentration and separation of Au(III) and Pd(II) as well as Ru(III), Rh(III), Au(III) and Pd(IV) ions in the column system.

22. Amphoteric ion exchangers and anion exchangers

Of a large group of ion exchangers, anion exchangers of different basicity (strong, average and weak basic) of functional groups are applied in ion exchange chromatography of noble metal ions. Strongly basic anion exchangers possessing well-dissociated functional groups capable of anion exchange of even weak acids, e.g. quaternary ammonium groups, are widely applied in the whole pH range. This group includes types 1 and 2 strongly basic anion exchangers of functional trimethylammonium groups (type 1) and dimethylhydroxyethylammonium groups (type 2). Weakly basic anion exchangers possess poorly dissociated functional groups i.e. primary-, secondary- and tertiary amine groups. There is also a group of amphoteric ion exchangers which, depending on solution pH, are able to exchange anions or cations. They are polyacids and polybases so-called polyampholites, e.g. of COO^- and $-\text{N}^+(\text{CH}_3)_3$ groups (snake in cage polymers).

Application of amphoteric ion exchangers for removal of trace amounts of Pd(II), Pt(IV) and Au(III) ions, among others, geological materials was studied by Chajduk-Maleszewska and Dybczyński [123], Dybczyński et al. [124] and Samczyński et al. [125] and Hubicki et al. [104]. Duolite ES 346 containing the functional amidoxime groups was successfully applied for recovery and separation of noble metal ions. There was proved high selectivity of amphoteric ion exchange Duolite ES 346 in Pd(II) ions sorption from the chloride (0.1–6M HCl–0.0011M Pd(II) and chloride-nitrate(V) (0.1–0.9 M HCl–0.9–0.1M HNO_3 –0.0011M Pd(II)) systems. The total sorption capacity towards Pd(II) ions is 1.099 mmol/g (0.1 M HCl) and 1.545 mmol/g (0.1M HCl–0.9M HNO_3). The processes of sorption and separation of trace amounts of Pd(II), Au(III) and Pt(IV) from ammonium and aqueous-non-aqueous solutions on Duolite ES 346 were also conducted [123, 124]. Also high selectivity of this ion exchanger towards noble metal ions was proved. Ions desorption was achieved using the solutions: 2 M HCl (elution of Pt and other metal ions, 8 M NH_4OH –0.01 M NH_4Cl – CH_3OH (1:5), desorption temperature 323 K (elution of Au(III) and 0.3 M $\text{CS}(\text{NH}_2)_2$ in 2 M HNO_3 (elution of Pd(II)).

The amphoteric vinylpyridine ion exchangers VP-14K, ANKF-5 and the anion exchanger AN-251M were used for recovery of Pd(II) ions from spent car exhaust gas convertors subjected to extraction with the NaCl (2–2.3 M) solution acidified with hydrochloric acid (0.5–2 M) at 353 K, the extraction time was 4h. These ion exchangers were characterized by high affinity towards palladium(II) ions and their recovery was 98–99%. The sorption capacity of the anion

exchanger AN-251M towards Pd(II) ions and the aminophosphonic ion exchanger ANKF-5 was comparable (2.4–2.5 mmol/g) and much larger than that of the ion exchanger VP-14K (1.4 mmol/g) so the ion exchangers AN-251M and ANKF-5 can be recommended for this type of application.

The strongly basic gel anion exchanger Dowex 1x10 (Cl⁻ form, grain size 100–200 mesh) was successfully applied for removal of Pd(II) and Pt(IV) ions from the dust collected in Germany from street and fast traffic roads (Saarbrücken, motorway A-1, A-61, road B-262). Quantitative desorption of sorbed metal ions took place using the 0.1 M thiourea solution in 0.1 M HCl at the increased temperature 333 K enabling reduction of the eluent volume by half. The matrix ions, i.e. Cd, Cu and Fe, were not retained on the anion exchanger but Ni, Pb and Zn sorbed at 8–15 %. Elimination of interferences during noble metals determination was achieved by using the reagents masking the matrix ions even before the sorption process, e.g. xylene orange (C₃₁H₃₂N₂Na₄O₁₃S) [126]. Application of ion exchange technique for the determination of platinum(II) ions in biological tissues gives interesting results. The tissues with the cis-dichloro-diamineplatinum(II) were irradiated with neutron in the reactor. The sample irradiation was mineralized by means of HNO₃–H₂SO₄–H₂O₂ mixture. Then platinum ions were sorbed on the anion exchanger Dowex 1x8 in the chloride form with 6 M hydrochloric acid solution. Platinum was determined using the radiometric method [127]. Platinum and rhodium contained in ores were determined after separation on the anion exchanger Dowex 1x8 in the chloride form. The ore was digested in *aqua regia*. Next the solution was passed through two columns. In the first one, platinum ions were sorbed from 9 M HCl solution. In the other one, rhodium was sorbed in the form of a complex with zinc(II) chloride from 0.5 M HCl solution. ¹⁰⁴Rh was determined directly in the ion exchange phase using the radiometric method [128].

For removal and determination of platinum from geological materials, a technique using the anion exchanger Rexyn 201 was proposed. Sorption was performed from 0.5 M of hydrochloric acid solution containing Ir(IV), Pt(IV), Pd(II) and Au(III) ions. Elution was carried out by means of 0.1 M solution of thiourea in 0.1 M HCl. Ir(III) was eluted using 6 M HCl. Platinum metals and gold were determined radiometrically [129]. The same methods were applied for the determination of platinum in carbons [130]. Somewhat modified technique was used for the determination of platinum metals in meteorites. Modification consisted in the change of the anion exchanger Rexyn 201 on Deacidite FF in the chloride form [131].

Bio-Rad AG1x8 (100–200 mesh) was characterized by high selectivity for Pd(II), Pt(IV) and Au(III) ions (the partition coefficient values were 10⁶, 10⁴, 10³ for Au(III), Pt(IV) and Pd(II) ions, respectively), and therefore it could be applied for removal of noble metal ions from the environmental and geological samples, among others, from rocks, ores as well as dust and road dust [132].

Similar studies of application of anion exchangers Amberlite IRA-900 (macroporous, polystyrene, strongly basic anion exchanger of type 1, 16–50 mesh) [133–135] and Amberlite IRA-410 (gel, polystyrene, strongly basic of type 2, 16–50 mesh) [135] for recovery and removal of trace amounts of Pd(II), Pt(II), Ru(III), Rh(III), Au(III) and Ir(IV) ions from chloride and radioactive nitrate waste waters were carried out by the Els et al. [133, 134] and El-Said et al.

[135]. Selectivity of the anion exchanger Amberlite IRA-900 for Pd(II) ions depends on the concentration of Cl^- ions in the solution. Quantitative sorption of palladium(II) ions from the chloride solutions is obtained at $[\text{Cl}^-] < 0.25 \text{ M}$. Sorption capacity of the anion exchanger Amberlite IRA-900 for Pd(II) ions in 0.2 M HCl solution was 0.0017 mmol/dm^3 ($[\text{Pd}^{2+}]$ 350 ppm) [133]. Selectivity of the anion exchanger Amberlite IRA-900 towards noble metal ions changes in the series: $\text{Au(III)} > \text{Pt(II)} > \text{Pd(II)} > \text{Ru(III)} > \text{Ir(IV)} > \text{Rh(III)}$ [134].

Satisfactory results were obtained using the above-mentioned anion exchanger for separation of Pd(II) and Ni(II), Sr(II), Rh(III), Eu(III), Ce(III), Ru(III), U(VI), Fe(III), Cr(III), Al(III), Ca(II) and Cs(I) from the radioactive nitrate waste waters [135].

The anion exchangers of quaternary ammonium groups: Purolite A-850 and Amberlite IRA-958 of polyacrylate skeleton, Lewatit MP 500A of polystyrene-divinylbenzene skeleton as well as Varion AP of functional pyridine groups and polystyrene-divinylbenzene skeleton exhibit high selectivity for Pd(II) ions from chloride and chloride-nitrate(V) solutions. Sorption capacities towards Pd(II) ions are 0.0282 g/cm^3 (in 0.1 M HCl) and 0.0005 g/cm^3 (in 6 M HCl) for Amberlite IRA-958 as well as 0.0408 g/cm^3 (in 0.1 M HCl) and 0.005 g/cm^3 (in 6 M HCl) for Purolite A-850. The addition of Zn(II) and Al(III) to the solution largely decreases selectivity of most anion exchangers for Pd(II) ions. The exception is Varion AP, whose selectivity changes insignificantly despite the presence of Al(III) ions [136, 137].

Due to modification of the macroporous polystyrene-divinylbenzene resin Amberlite XAD-1, the ion exchanger containing functional tertiary amine groups was obtained. This ion exchanger was used for separation of noble metal ions. Separation of Rh(III), Pd(II) and Pt(IV) ions mixture was achieved using suitable eluents:

Rh(III) – 1M HCl or 1M NaCl in 0.1 M HCl

Pd(II) – 0.05 M NaClO_4 in 1 M HCl or 1 M NaCl + 0.025 M NaClO_4

Pt(IV) – 0.1 M NaClO_4 in 1 M HCl or 1 M NaCl + 0.15 M NaClO_4 .

The method is quick (about 30–40 minutes) and allows separation of 1.18–11.8 μg amounts of noble metal ions [138].

Among weakly basic anion exchangers of special interest is the macroporous polystyrene-divinylbenzene anion exchanger of functional dimethylamine groups Amberlite-93 used for recovery of Pd(II), Pt(II) and Rh(III) ions from spent car exhaust gas converters. Rhodium(III) was desorbed from the anion exchanger as the first using 6 M hydrochloric acid solution, then palladium(II) was desorbed using 1% ammonia solution at room temperature. Platinum(II) was washed out with the ammonia solution of the concentration 5% (at increased temperature). Separation of palladium from platinum from the eluant solution can be achieved reducing to the metallic form or precipitating $(\text{NH}_4)_2\text{PdCl}_4$ and $(\text{NH}_4)_2\text{PtCl}_6$ using hydrochloric acid. The presented method of selective removal of platinum metals using Amberlite IRA-93 can be regarded as an effective technique for separation of these ions on a laboratory and commercial scale [139].

The weakly basic Amberlite IRA 67 is applied for selective removal of microquantities of platinum(IV) ions from the acid solution containing CuCl_2 , FeCl_3 , NiCl_2 , AlCl_3 and ZnCl_2 . In

chloride solutions, the above components can partly form anions, which reduces the sorption capacity of weakly basic anion exchangers. The effect of the above-mentioned macrocomponents on decrease of sorption capacity towards platinum(IV) ions can be presented in the series: $\text{CuCl}_2 \approx \text{FeCl}_3 \approx \text{NiCl}_2 < \text{AlCl}_3 < \text{ZnCl}_2$ [140, 141]. A similar series can be determined for the anion exchanger Duolite S 37, which contains secondary and tertiary functional groups added to the phenol-formaldehyde skeleton [142].

23. Low-cost sorbents

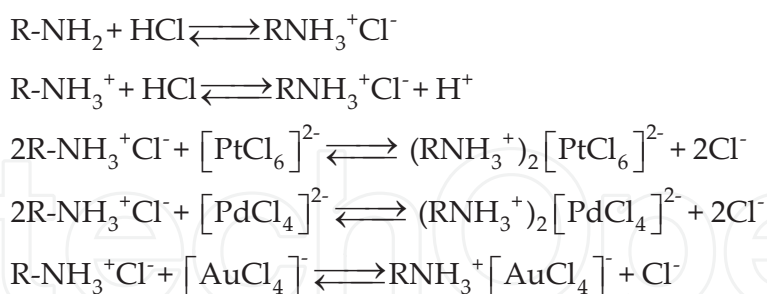
In the literature, there are many examples of the alternative sorbents for noble metals removal produced from renewable and low-cost resources [143]. Among them, those based on bacteria, fungi and algae as well as agriculture and seafood wastes (coffee, green tea, tea, yuzu, aloe, wheat and barley straw, maize crop, coconut shell, rice husk, etc.) have been investigated. One of the low-cost sorbents is chitosan (CS) [144-155]. It is a kind of abundant natural polysaccharide. Chitosan is produced by the alkaline deacetylation of chitin, the most abundant biopolymer in nature after cellulose. It is extracted from shrimp and crab shells. Due to large availability of functional groups such as amino and hydroxyl ones, CS has been proved to be very efficient for the recovery of several toxic metal ions such as Cu(II) , Cd(II) and Pb(II) and strategic metal ions such as Pt(IV) and Pd(II) [144]. It should be mentioned that sorption properties of CS are due to its composition and presence of active and functional groups. CS is characterized by its high percentage of nitrogen present in the form of amine groups, which are responsible for metal ion binding through chelation mechanisms. Due to the fact that it is protonated in acidic solutions, it is also capable of sorbing metal ions through anion exchange mechanisms. It should be mentioned that chitosan protonation in acidic solution causes the polymer to dissolve (except in sulphuric(VI) acid solutions). For the sorption of some metal ions (for example noble metals), sulphuric(VI) acid cannot be used for pH control due to reduction of sorption efficiency [145].

In the case of chitosan derivatives obtained by glutaraldehyde cross-linking (GA), poly(ethyleneimine) grafting through glutaraldehyde linkage (PEI) or thiourea grafting (T), noble metal ions can be sorbed. The reasons for grafting new functional groups are (i) to increase the density of sorption sites, (ii) to change the pH range for metal ions sorption and (iii) to change the sorption sites and/or the uptake mechanism in order to increase sorption selectivity for the noble metals [146]. Such derivatives were used for palladium and platinum removal [147]. It was found that the maximum adsorption capacity occurred at pH 2.0 for both Pt(IV) and Pd(II) species. The material selectively adsorbs Pt(IV) and Pd(II) from binary mixtures with Cu(II) , Pb(II) , Cd(II) , Zn(II) , Ca(II) and Mg(II) . The isotherm adsorption equilibrium was well described by the Langmuir isotherms with the maximum adsorption capacity of 129.9 mg/g for Pt(IV) and 112.4 mg/g for Pd(II) , which was relatively high compared with the glycine chitosan derivative (122 mg/g for Pt(IV) and 120 mg/g for Pd(II)). The results show that 0.5 M EDTA-0.5 M H_2SO_4 solution can effectively desorb Pt(IV) and Pd(II) (>97%) metal ions from the adsorbent material. The high percentage of desorption obtained when the 0.5 M EDTA-

0.5 M H₂SO₄ solution was used and can be explained by both stable complexes and the electrostatic interactions between the Pt(IV) and Pd(II) species.

In the paper [143], rubeanic acid was grafted on chitosan through the reaction with glutaraldehyde as the linker to obtain the sorbent for Au(III) with the thiol functional groups. It was found that the maximum sorption capacity was high and equal to 600 Au(III) mg/g. The speciation of gold in the chloride and hydroxide chloride systems appears to be a predominant parameter influencing the removal process. The optimum pH range was between 2 and 3 for glutaraldehyde cross-linked chitosan. However, the sorption capacity strongly decreases with the increasing pH. It was found that in the case of the grafting of sulfur compounds on chitosan derivatives, the partial change in the sorption mechanism occurs. In this case, metal ion chelation with sulfur compounds is weakly sensitive to the pH change [148]. Sorption capacity in the HCl system reaches 2 mmol/g (180 mg/g) and is slightly lower than for the chitosan derivatives obtained by grafting of pyridyl groups (6 mmol/g). Increasing chloride concentration involves a significant decrease in sorption capacity.

The removal of Au(III), Pt(IV) and Pd(II) onto the glycine modified cross-linked chitosan resin was investigated in the paper by Ramesh et al. [146]. The results show that the optimum pH appeared to be 1.0–4.0, and the maximum percentage removal was obtained at pH 2.0 for Au(III), Pt(IV) and Pd(II). The pH_{ZPC} was found to be 5.1. At pH < pH_{ZPC}, the surface of modified chitosan resin is positively charged, whereas at a pH > pH_{ZPC}, the surface of modified chitosan resin is negatively charged. Due to the positive surface charge of sorbent at pH lower than pH_{ZPC}, it attracts the chlorocomplexes of platinum, palladium and gold, resulting in the greater amounts of adsorption at low pH. The authors proposed the following mechanism of the sorption process:



The results also demonstrated that the amount of adsorption was decreased with the increasing chloride ion concentration. This is because of strong interaction between the chloride ions and precious metal ions to form chlorocomplexes. The 0.7 M thiourea-2 M HCl solution was the most effective for the desorption of Au(III), Pt(IV) and Pd(II).

In the case of chitosan derivatives, noble metal ions are sorbed according to several kinetic models based on pure sorption, pure reduction and dual sorption-reduction mechanisms [149, 150]. Moreover, the optimum acid pH for noble metal ions sorption depends on the metal. For platinum and palladium, it was equal to 2. For CS cross-linked by glutaraldehyde (CS-GA) for

hydrochloric acid solutions of palladium at pH 2, sorption reached the same level as achieved at pH 1 (capacity strongly decreased) [151]. However, in the sulphuric(VI) acid solutions, the sorption capacity remains almost unchanged. It is well known that pH has a critical effect on the speciation of the metal in solution because the distribution of metal species depends on pH. Other parameters which affect the sorption efficiency are connected with the nature of the sorbent (ionic charge), chemistry of the metal ion: ionic charge, ability to be hydrolysed as well as metal concentration and the composition of the solution and the form of polynuclear species [151]. Sorption kinetics is controlled by particle size, cross-linking ratio and palladium concentration. In hydrochloric acid solutions, equilibrium is achieved at 24 h contact. For chitosan-cellulose fibres, it was found that incorporation of cellulose fibres improves the binding efficiency of chitosan towards Ag(I). The sorption capacity was close to 220 mg/g. This is much higher than for the pure chitosan (140 mg/g) [152]. The cellulose fibres contribute to dispersion of the chitosan chains that are more accessible and available for silver. It is also possible to modify the chitosan structure by introducing cross-linking structure, blending chitosan with synthetic polymers such as poly(vinyl alcohol) (PVA) – a non-toxic, water-soluble synthetic polymer with good physical and chemical properties and film-forming ability. It is also possible to apply the sol-gel process to develop organic–inorganic hybrid materials [153–155]. For this aim, clays and silicas are frequently used. Clays are composed of silicate layers which form three-dimensional structures after hydrated in water. They have negative charge and can interact with chitosan. Also silicas are characterized by several advantages which are among others surface stability in the acidic medium and highly developed surface, acceptable kinetics, thermal stability, resistance to microbial attack and low cost should be mentioned [156]. Chemically modified silicas (CMSs) with the functional groups covalently bound to the surface such as polyamines, particularly, linear polyhexamethylene guanidine (PHMG) with convenient amine group configurations and nitroso-R salt (NRS) were used in palladium sorption [157, 158]. Complex of palladium(II) with the ratio Pd:NRS = 1:2 formed the SiO₂–PHMG–NRS. The other examples are presented in Table 2.

Functional group	Metal ion	Ref.
Thiosemicarbazide	Pd(II)	[159]
Dithizone	Ag(I)	[160]
2-Amino-1-cyclopentene-1-dithiocarboxylic acid	Ag(I) and Pd(II)	[161]
N-(3-triethoxysilylpropyl)-4,5-dihydroimidazoleuene	Pd(II), Pt(II)	[162]
Amidinothiourea	Ag(I), Au(III) and Pd(II)	[162]
3-(1-thioureido)propyl	Ag(I), Au(III) and Pd(II)	[163]

Table 2. Organofunctionalized silicas in pre-concentration of noble metal ions.

24. Conclusions

Ion exchange has been widely applied in the technology of chemical separation of noble metal ions. This is associated with the dissemination of methods using various ion exchange resins which are indispensable in many fields of chemical industry. Due to small amounts of noble metals in nature and constant impoverishment of their natural sources, of particular importance are physicochemical methods of their recovery from the secondary sources as well as waste waters.

Recovery of noble metals, from such raw materials, requires individual approach to each material and application of selective methods for their removal. Moreover, separation of noble metals, particularly platinum metals and gold from geological samples, industrial products and synthetic mixtures along with other elements, is a problem of significant importance nowadays.

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