

The use of zirconium oxy-hydroxide for removing anions from liquid industrial waste

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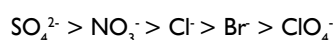
Introduction

Environmental requirements necessitate the implementation of the so-called clean technology, whose main determinants are: sustainable use of raw materials, improvement of energy efficiency and action in the broad sense of environmental protection. Important role in this type of technologies play a zirconium compounds, such as zirconium dioxide and zirconium oxy-hydroxide. Physicochemical nature of these compounds determines that they are mainly used in catalysis and in ion exchange. They have amphoteric properties, they are practically insoluble in water, their estimated solubility is $1.1 \cdot 10^{-54}$ [1]. They are well soluble in strong mineral acids and in highly concentrated alkali. Moreover, they have specific surface and structural properties [2].

Zirconium compounds play a significant role in many branches of industry. It is due to their mechanical and chemical properties, including the absence or low toxicity as compared with compounds replaced by them [3, 4, 1, 5–22].

The use of ion exchange properties of zirconium oxy-hydroxide

According to the literature, insoluble hydrated oxides of polyvalent metals, including Zr(IV) are characterized by ion exchange properties. They belong to a group of synthetic inorganic exchangers with high efficiency and selectivity. Ion exchange properties of zirconium oxy-hydroxide are dependent on synthesis process conditions (pH, precipitation temperature, concentration and type of final compound). Using during synthesis an excess of a strong base (eg. NaOH) and using the high final pH of the solution, a hydroxy compound in the form of cation is precipitated. However, in the precipitation processes of zirconyl nitrate or chloride solutions with ammonia at pH~9, a material with a good anion-exchange properties is obtained. The ion exchange of zirconium oxy-hydroxide affinity to anion decreases in series:



The process removing of sulfate ions from brines can be carried out by ion exchange, using an ion exchanger comprising zirconium oxy-hydroxide with active centers, able to OH⁻ groups exchange to SO₄²⁻ ions. In the ion exchange column both can be used: cation and anion zirconium exchangers, after following application of a zirconium compound on a synthetic resin matrix or on an inorganic carrier.

The Japanese company Kaneka Corporation as the first used zirconium anion exchanger for the removal of sulfate ions from industrial brines [2]. The process takes place in a system of two reactors and two rotary vacuum filters. The presented method is more economic than previously used (barium method). It allows the elimination of prior methods used to remove unwanted components (eg. sulfate precipitation in the form of barium sulfate transmitted to the landfill).

US patent [23] presents a method of anions removing from brine using hydrated zirconium oxide, carried on a granulated activated carbon or activated carbon impregnated with organic resins. The adsorbent with a preferred particle diameter of 0.5–5 mm, has a high ion exchange capacity and a high mechanical strength, allowing the usage of the material in both: adsorption processes carried out in a continuous column and in the tank adsorbers with agitators.

Sulfate ions are removed by adsorption through hydrated zirconium oxide of the general formula Zr(OH)₄·nH₂O (n in the range of 4–200) [24]. Ion desorption and adsorbent regeneration is carried out using alkali, such as solutions of carbonates, bicarbonates of alkaline earth, hydroxides of alkali metals. Temperature limits and duration of the desorption process are the same as for the adsorption. In the present removal process of sulfates from brine, the total or partial circulation of repeatedly regenerated and not dried adsorbent is provided.

The phenomenon of the ion exchange was used to develop the invention for the recovery of sulfates from sea water or other brine, using zirconium adsorbent of amorphous, polymerized structure, carried on an organic carrier [25]. The use of adsorbent allows the removal of not only the sulfates, but also borates, bicarbonates, phosphates and fluorides. In another work of the same authors [26] a method of sulfates removal from brine using ion exchanger deposited on a synthetic resin was disclosed. The process is carried out continuously (solution pH in the range of 2–3, temperature 40–60°C or higher 100–120°C). The column performance is strongly dependent on temperature.

Purification of brines from sulfate and borate ions is also possible thanks to the Dow Chemical Company product, called MSC-1, where zirconium oxy-hydroxide is supported on activated carbon [27]. Both the adsorption and desorption processes take place at a temperature of 65°C in a column, where a solution with a pH = 2 is passed through a bed of ion exchange. The adsorbed sulfates and borates are removed by washing with specified amount of water, sodium hydroxide and hydrochloric acid to give regenerated zirconium ion exchanger able for further work.

Japanese patent [28] presents a method for the brine purification from sulfate ions using hydrated zirconium oxide. The first step is adsorption of sulfate from the brine contaminated with an alkali, on the resin-zirconium ion exchanger. The pH of ions desorption process is higher than pH of adsorption.

Another patent [29] describes the purification of aqueous solutions of alkali metal chlorides from sulfate ions, using the zirconium adsorbent with a particle diameter of 1–20 microns. Preferred conditions for the adsorption step are: pH = 3–6, and the temperature not lower than 50°C. Desorption of ions is performed at the same temperature and pH = 9. To achieve it, an aqueous solution of ammonia, alkali metal hydroxides, tetra-alkyl-ammonium hydroxide, etc. may be used.

Sulfates from the contaminated brine can also be removed using ion exchanger – zirconium oxy-hydroxide supported on material

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compatible with brine solution [30]. The ion exchange takes place in a column filled with ion exchanger with a particle diameter of not less than 30 microns (preferably diameter $> 50 \mu\text{m}$). According to the authors, 1 mole of hydrated zirconium oxide of formula $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (wherein $n = 0.3-7$), adsorbs 1 mole of sulfate ions.

Mesoporous ion exchange adsorbent can be used to remove arsenic(V) ions, fluoride and phosphate ions [31]. It is obtained by applying to the porous polyacrylic-styrene ion exchanger the zirconyl nitrate or chloride ion exchanger from alcohol solution. Followed by evaporation of alcohol and contact of the porous material coated with a zirconium compound with an alkali, zirconium salt changes into zirconium oxy-hydroxide, constituting the active phase of ion exchanger.

Phosphates(V) can be selectively adsorbed from seawater or wastewater, using as adsorbent amorphous zirconium oxy-hydroxide $\text{ZrO}(\text{OH})_2 \cdot (\text{NaO})_{0.05} \cdot 1.5\text{H}_2\text{O}$ [21]. The studies show that the adsorption of phosphates(V) increases with increasing pH of solution to 6, then it begins to rapidly decline. In case of the adsorbent used, much greater tendency to adsorb phosphates(V) was observed compared to other adsorbents based on layered double hydroxides. The effective desorption of adsorbed phosphates may be carried out, using 0.1 M NaOH.

In the sorption of phosphates(V) mesostructural zirconium synthesized from aqueous zirconium sulfate using as a matrix surfactant (heksadecyltrimetylo-ammonium bromide) [32]. It is characterized by a pore size of 2–50 nm, high surface area ($> 1000 \text{ m}^2 \text{ g}^{-1}$) and 2–3 times higher sorption capacity of phosphates, as compared with commercial anion exchange resins.

In US patent [33] there is presented a method for the preparation and use of a zirconium complex of formula $\text{Zr}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ or $\text{ZrO}_2 \cdot A \cdot n\text{H}_2\text{O}$ (wherein A is an anion, eg. arsenic, chromium, selenium, fluoride, borate, perchlorate, $n = 1-10000$) for cyanide removal from industrial media. The adsorption is carried out at a pH of 7.5–11. Its efficiency is above 80%. NaOH solution of 1% is applied for desorption. Regeneration of the zirconium ion exchanger is possible through the use of hydrochloric acid (pH = 3), and rinsing with slightly acidified water.

Another patent [34] presents a method of anionic ground water treatment from arsenic, iron or perchlorates ions. The presented invention, in an economic way, allows treatment of drinking water, using activated carbon, coated with a hydroxide of rare earth metals, including zirconium, with a surface area of $850 \text{ m}^2/\text{g}$. Adsorption efficiency depends on conditions under which the coal is subjected to activation, for example with sulfuric acid, nitric acid or a mixture of them, at a temperature above 100°C and for 24 h.

The method for preparation of the zirconium ion exchanger, used for the purification of sea water, is described in the following U.S. patent [35]. The porous, inorganic base such as activated carbon, silicon or aluminum oxide, is coated with an active substance – zirconium, titanium oxy-hydroxide, etc. Created amphoteric ion exchanger, depending on the process conditions, enables the exchange of cations or anions.

Zirconium oxy-hydroxide doped with Fe(III) and Fe(II) oxides, of a molecular formula $\text{ZrO}(\text{OH})_2 \cdot 1.6\text{Fe}_3\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ can be used to remove arsenates(V), which are reduced to arsenates(III) [36]. The sorbent has a surface area equal to $151 \text{ m}^2/\text{g}$. It characterizes by a small average pore diameter (543.7 nm). Sorption equilibrium can be achieved over 25 hours. The better adsorption effect is obtained at lower pH values.

Zirconium oxy-hydroxide with ethylenediamine in a ratio of 3:1 of the formula $[\text{ZrO}(\text{OH})_2]_3[\text{NH}_2(\text{CH}_2)_2\text{NH}_2] \cdot 3\text{H}_2\text{O}$, can be used for molybdates separation [37] from the specific circuits: $\text{Cl}^- \cdot \text{MoO}_4^{2-}$, $\text{Br}^- \cdot \text{MoO}_4^{2-}$, $\text{I}^- \cdot \text{MoO}_4^{2-}$, et al.

US patent [38] illustrates the preparation method of new material used in the dialysis process, wherein the sorbent is composed of acidic zirconium phosphate and basic hydrated zirconium oxide. Zirconium phosphate absorbs such cations: NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , and zirconium oxy-hydroxide enables the exchange of anions (P, F, CH_3COO^-). The common use of those two compounds takes place in the system REDY, in which the zirconium phosphate is responsible for cations exchange and zirconium oxy-hydroxide for anion exchange. The invention is characterized by the possibility of ion exchange, without the need to separate the acidic zirconium phosphate (AZP) and alkali zirconium oxy-hydroxide (NaHZO).

The process of sulfates removing from contaminated chloride solutions is possible through the exchange of OH^- ions to SO_4^{2-} . For example, in a process carried out in a column of bed ion exchanger, reduction of sulfate ions in 26% NaCl solution, from 970 ppm to 110 ppm is possible [39]. However, in the process of desulfurization of industrial solutions containing 0.037% SO_4^{2-} , the use of zirconium ion exchanger makes a possibility to reduce sulfate ions to 0.001%.

Conclusions

The ion exchanger comprising zirconium oxy-hydroxide may be used to remove anions and cations from liquid technological waste. Both the zirconium cation and anion exchangers can be used in the ion exchange column after application of zirconium oxy-hydroxide on organic or inorganic matrix. The zirconium ion exchanger is capable to remove sulfate ions, borates, bicarbonates, phosphates, fluorides, arsenates, cyanides, etc. Anion exchange properties of zirconium ion exchanger among others depend from:

- a method of zirconium oxy-hydroxide preparation (pH, precipitation temperature, the concentration and type of raw materials purity),
- type of carrier, on which the active substance is applied,
- conditions of ion-exchange process.

According to the literature, conducting of desulfurization process is preferred in the range of pH of 1–6 at a temperature above 50°C during 0.5–3 h. It is advisable to carry out the desorption of zirconium ion exchanger by washing with warm water, using an alkalizing agent, which is sodium hydroxide, aqueous ammonia, etc., (temperature $> 50^\circ\text{C}$, pH > 7). According to different authors grain size is in the range from $0.01 \mu\text{m}$ to 5 mm. The speed of ion exchange increases with decreasing of ion exchanger grain size and with increasing of the temperature. It should be noted that for small grain size, there is the risk of clogging the pores of ion exchanger during filtration.

In the process of liquid industrial waste treatment in a similar manner borates, bicarbonates, phosphates and fluorides can be removed. Using zirconium oxy-hydroxide ground water can be purified from arsenic ions, iron or perchlorate, at a temperature above 100°C and for 24 h. It has been reported that for certain anion exchanger sorption speed is very low and obtaining of equilibrium state requires even several days. Moreover, the use of certain derivatives of zirconium oxy-hydroxide ($[\text{ZrO}(\text{OH})_2]_3[\text{NH}_2(\text{CH}_2)_2\text{NH}_2] \cdot 3\text{H}_2\text{O}$, $\text{ZrO}(\text{OH})_2 \cdot 1.6\text{Fe}_3\text{O}_4 \cdot 2.5\text{H}_2\text{O}$) enables efficient removal of contaminants from liquid industrial waste.

The available literature data indicate that the adsorption efficiency depends on the physicochemical properties of the exchanger, operating conditions and equipment solutions.

The use of zirconium oxy-hydroxide or its derivatives in ion exchange processes is preferred because of the possibility of:

- applications in the environmental protection through its use in the process of industrial waste treatment,
- elimination of previously used methods of unwanted components removal,
- application of new ways of reduction of the content of harmful substances discharged with waste water.

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