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DESIGN OF THE REGENERATION METHOD OF HYDROXYL-CONTAINING ZIRCONIUM COMPOUNDS IN PROCESSES OF WATER PURIFICATION FROM BORON

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Abstract. The regeneration method of zirconium hydroxide sorbent spent in the boron sorption process by diluted solution of acids as well as the principle recycling diagram of the formed regenerating solution by the nanofiltration process with the OPMN-P membrane were proposedin this work. The permeate obtained can be used as a boron-containing microfertilizer (ammonium salt + boron) after it has been neutralised with ammonium hydroxide. Zirconium-containing concentrate may be reused for sorbent preparation. The effectiveness of separation of the regenerating solution components by nanofiltration is demonstrated by high values of zirconium rejection coefficient in this process (R_{Zr} ~98– 99%) and low values of boron rejection coefficient (R_B ~12%). In this case the specific performance of the membrane is about 50 $dm^3/m^2 \cdot h$.

Keywords: boron, water purification, zirconium hydroxide, regenerating solution, recycling.

Introduction

The natural factors (such as leaching from the boron-containing rocks, volcanic activity, etc.) are the main origin of boron entry into the aqueous environment, although lately the role of the human factor has significantly increased due to the great importance of the boron compounds for the national economy (Tkachev, Plyshevskiy 1983). The complex of various valuable physicochemical and other properties of boron compounds is the basis providing their extensive and varied usage virtually in all sectors of the national economy. Boron compounds are the second most used substance (the carbon compounds take the first place) in the world. The main producers of boron-containing compounds are the USA, Turkey, Russia, whereas there is no national production thereof in Ukraine (Melnik *et al.* 1998).

The boron compounds are included in the list of the priority toxicological water quality parameters (StStofUa 4808:2007). The maximum permissible boron concentration in drinking water in Ukraine is equal to 0.5 mg/dm^3 (StStofUa 7525:2014). The WHO in 2011 revised the guideline value of boron to 2.4 mg/dm^3 (WHO 2011). However, only a few of countries follow the WHO recommendation because the value of 2.4 mg/dm^3 exceeds the tolerated concentration of many crops, especially in the low annual rainfall regions, where a large quantity of irrigation water is provided by desalination plants (Guan *et al.* 2016).

Ezechi *et al.* (2011) emphasizes that taking into account the environmental challenges related to the negative impact of boron compounds on the environment and also the economic importance of these compounds it is advisable to consider the boron-containing water purification not from the boron removal point of view but from the boron extraction and recovery one.

Thus, the search of effective, available and economically feasible purification methods of boron-contaminated fresh water as well as permeates and dialyzates from membrane equipment (which often contain elevated boron concentration) with simultaneous recovery of valuable boron-containing compounds and averting of secondary environmental pollution constitutes a considerable practical interest in the world.

The most effective method of boron removal from aqueous solutions with relatively low boron content (up

to 100 mg/dm^3) is the sorption process using hydroxyl-containing synthetic organic boron selective sorbents of N-methylglucamine type (Kabay *et al.* 2008). The above-mentioned sorbents can remove boron selectively even from highly mineralized solutions with boron removal degree in this case reaching 93–98%. The boron selective sorption with the N-methylglucamine sorbents is caused by interactions typical for this element, i.e. the formation of stable complexes like ethers or complex anions with polyoxicompounds. The significant drawbacks of these sorbents are their high cost (about $ 19,000 per ton), the necessity of two-stage (acid, alkali) regeneration as well as the significant reagent consumption in the process in question.

Nowadays the adsorption with inorganic materials, particularly hydroxides of some metals, is a competitive method of water purification from boron (Guan *et al.* 2016), and the investigation in the field of design of modern and cheap inorganic sorbents as well as the technologies of their usage is very important.

Hydroxyl-containing zirconium compounds have the biggest sorption capacity in relation to boron compounds among such inorganic sorbents as slow-soluble metal hydroxides. Considering the sorption efficiency value some investigated metal hydroxides were arranged as follows (Atamanuk, Trachevskyi 2002):

$$ZrO_2 > La_2O_3 > TiO_2 > Fe_2O_3 > Al_2O_3.$$

The ability of zirconium hydroxide to remove boron effectively from aqueous solutions was discovered long ago and described in works (Ryabinin *et al.* 1972; Pospelov *et al.* 1980).

The amorphous zirconium hydroxide was found to have a better sorption capacity in relation to boron in comparison with the crystalline form of sorbent. This is due to the fact that amorphous zirconium hydroxide has a large surface area for the sorption and availability of active centers. That is why current investigations are focused on the use of amorphous zirconium compounds for water purification from boron and other elements (Kluczka 2015; Fedenko 2014).

It should be emphasized that in the case of separate use of amorphous zirconium compounds as a boron sorbent, particularly in (Kluczka 2015) the investigation of its regeneration was not conducted. However, in the context of environmental safety and sustainable development it is very important to ensure the regeneration and reuse of the sorbents in water purification processes.

The regeneration method of hydroxyl-containing zirconium compounds which are used as sorbents in processes of water purification from boron with subsequent regenerating solution processing and recovery of its components is suggested in this work. The use of the proposed method provides the closed-loop and low-waste technology of water purification from boron compounds as well as reduces the risk of secondary environmental pollution.

Materials and methods

This work considers the use of amorphous zirconium hydroxide as a sorbent for boron removal from water. As mentioned above, the advantage of using amorphous forms is better sorption capacity, and also there is no need for sorbent granulation hence simplifying the process of its preparation.

The sorption process was carried out in batch mode.

At the initial stage the boron sorption capacity of zirconium hydroxide was determined considering different pH values.

The solution (V = 1 dm^3) with zirconium concentration ~630 mg/dm^3 ($Zr(OH)_4$ content in an alkaline solution ~1.0 g/dm^3) was prepared and pH value was set by NH_4OH. The basic requirement was a full conversion of dissolved zirconium ($ZrOCl_2$) into the amorphous precipitate represented in the form of flakes, which then were used as a sorbent for boron removal.

The boric acid solution (C_B = 1000 mg/dm^3) was added to prepared zirconium-containing solution in such a way that the initial boron concentration before the sorption process was equal to1.4–1.5 mg/dm^3.

The concentration at the level of 1.4–1.5 mg/dm^3 was chosen taking into account the fact that such boron concentrations are often achieved in sea water after its desalination by reverse osmosis treatment.

The prepared solution was intensively stirred during 20 minutes to ensure the effective sorption process. Then the solution was filtered through the paper filter “Blue ribbon” using the Buchner funnel for the purpose of sorbent separation. The obtained filtrate was taken to determine the residual boron concentration, and the precipitate was removed from the filter with a scalpel and placed in a 100 cm^3 flask for further regeneration.

The possibility of spent sorbent regeneration using diluted acid (HCl, HNO_3) solutions was investigated in static conditions. The amount of regenerating solution was chosen as 10% from purified water volume.

The regeneration process was carried out on a phased basis by four portions of acid solution (25 cm^3 each) using two methods:

Method "a". After each regeneration stage (stirring with the water bath shaker type 357 (200 r.p.m., amplitude 8) for 10 minutes) the solution with precipitate was filtered through the paper filter "Blue ribbon" using the Buchner funnel, the filtrate was taken to determine the amount of eluted boron and the precipitate was removed from the filter and placed in a flask for the next regeneration stage.

Method "b". Continual stirring with the water bath shaker type 357 (200 r.p.m., amplitude 8) for 20 minutes in such a way that after each 5 minutes the new portion of fresh acid solution was added.

Thus, using the raw acid solution in each stage the data of the phased basis regeneration was obtained.

The obtained regenerating solutions were processed in two stages. At the first stage the filtration process was used to separate the disperse zirconium phase. At the second stage in order to separate the boron compounds from dissolved zirconium compounds the regenerating solution was processed using a nanofiltration method. Experimental runs were performed in the dead-end cylindrical cell (348 cm^3), which was equipped with a stirring rod and placed onto a magnetic stirrer (in order to minimize the concentration polarization effect). The stirring rate was controlled at around 300±5 rpm.

In the experiment the nanofiltration OPMN-P membrane of polyamide type was used. The working pressure was set by compressed nitrogen over the range of 1.5 MPA and controlled with a manometer with an accuracy of ±0.01 MPa.

The boron solution concentration has been controlled by the photocolorimetric method with carmine and the ICP-MS method with Agilent 7500ce ICP-MS. The zirconium and acid solution concentration has been analyzed using titration method with trylon-B and alkali respectively.

Results and discussion

Figure 1 shows the effect of solution pH on boron sorption capacity using the fresh amorphous zirconium hydroxide (curve 1). The estimated sorption capacity (E) equals to 1 mg B/g $Zr(OH)_4$ at optimum pH value (pH ~8.5), adsorbent dose – 1 g/dm^3, and initial boron concentration – 1.5 mg/dm^3.

For comparison, Figure 1 shows the effect of pH on boron removal degree (RD_B) using amorphous zirconium dioxide, which was obtained during the research (Kluczka 2015) (curve 2). As it can be seen shapes of the curves are practically the same at pH range ~7–10.

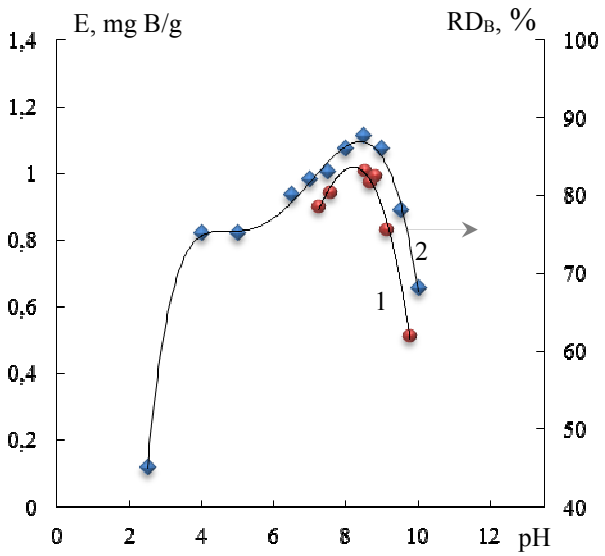

Fig. 1. The effect of pH on boron sorption capacity using zirconium hydroxide (1) and on boron removal degree using amorphous zirconium dioxide (2)

Previous research has shown that boron elution efficiency from hydrated zirconium oxide (Melnik *et al.* 2015) using 0.25 M sodium hydroxide solution is very low. As can be seen from Figure 1 (curve 2) (Kluczka 2015) the boron sorption process using amorphous zirconium dioxide is practically non-existent at pH < 2. So, in the current research the regeneration efficiency of zirconium hydroxide using the nitric and hydrochloric acid solutions was investigated. According to the data obtained both methods of the phased basis regeneration listed in the experimental part ensure the same boron elution degree (ED) which equals to ~50% (Fig. 2). However, in case of method "b" the regeneration process is simplified significantly and takes less time (due to the reduction of filtration time). Furthermore, during the regeneration process less amount of zirconium is dissolved in solution if method "b" is followed.

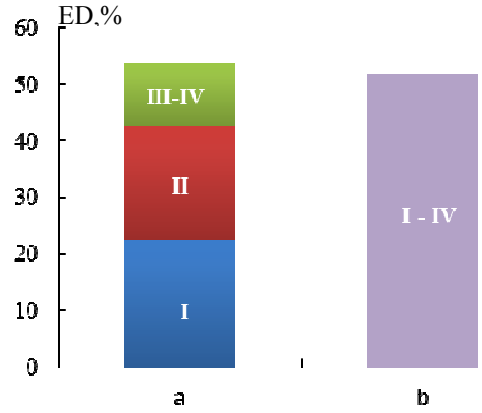

Fig. 2. The boron elution degree from the spent sorbent during the regeneration process using methods "a" and "b"; I, II, III, IV – the order number of regenerating solution portion

The efficiency of boron elution from sorbent using different portions of regenerating solution is shown in Figure 3.

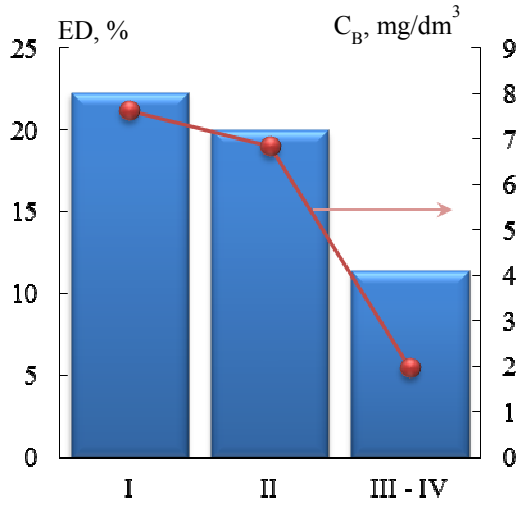

Fig. 3. The boron concentration in different portions of regenerating solution and boron elution degree in different regeneration phases (the regeneration method "a")

During the secondary use of zirconium hydroxide precipitate (after its regeneration), the boron removal degree was reduced and amounted to 34% of boron removal degree using fresh zirconium hydroxide (Fig. 4). This fact is evident because the sorbent was regenerated only partially (50%), furthermore, apart of zirconium sorbent was lost due to the dissolution.

Since during the regeneration process the spent zirconium hydroxide is partially dissolved (Fig. 5), it is necessary to separate the dissolved zirconium compounds from boron compounds after the separation of disperse zirconium phase from aqueous solution.

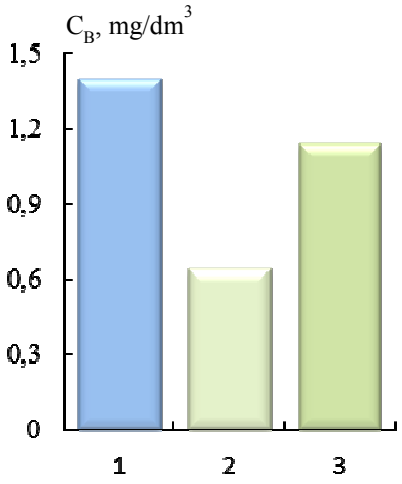

Fig. 4. The boron concentration: in the initial solution (1), in the solution after the sorption using the fresh precipitated $Zr(OH)_4$ (2) and after the sorption using $Zr(OH)_4$ regenerated by 50% (3)

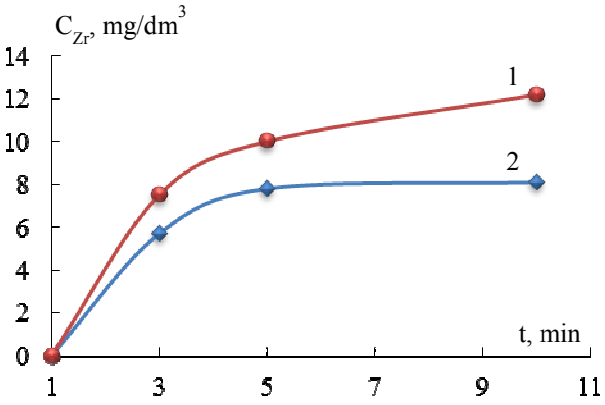

Fig. 5. Changes in the dissolved zirconium concentration in the acid regenerating solution in relation to the contact time of regenerating solution with the spent sorbent: 1. regenerating solution – 0.1 M acid; 2. regenerating solution – 0.01 M acid

This work suggests separating the boron and zirconium compounds present in acid regenerating solution by nanofiltration using the OPMN-P membrane.

As it was shown previously (Goncharuk *et al.* 2011) the boron rejection coefficient (R_B) of OPMN-P membrane does not exceed 10% (permeate recovery (PR) 50%). The rejection coefficient of Zr (IV) ions (R_{Zr}) of this membrane apparently stands at 98–99% as the rejection coefficient of divalent ion Mg^{2+} of this membrane equals to ~98.5% (Vladipor 2017). Taking into account the possibility of the impact of zirconium presence on the boron rejection during the treatment of regenerating solution by nanofiltration method using the OPMN-P membrane, the model solution was prepared (C_B ~1 mg/dm^3 and C_{Zr} ~345 mg/dm^3) for the purpose of its nanofiltration treatment and the investigation of the efficiency of components' separation.

The results of this experiment are presented in Table 1. According to the results obtained the zirconium presence has practically no impact on the boron rejection coefficient using nanofiltration membrane and the separation process of regenerating solution components (Zr and B) is running effectively.

Table 1. The results of model solution separation by OPMN-P nanofiltration membrane (C_{Zr} = 345 mg/dm^3; C_B = 1 mg/dm^3; P = 1.5 MPa, pH ~1.5)

Permeate recovery, %	Permeate flux, dm^3/m^2·h	R_B, %	R_{Zr}, %
23	48.1	–	–
47	43.6	–	–
70	44.4	–	–
90	44.2	11.8	98

The results of nanofiltration treatment of regenerating solution are demonstrated in Table 2. The data from Table 2 shows that zirconium rejection by OPMN-P membrane is considerable and there is practically no rejection of acid. The average concentration value of acid both in the permeate and in concentrate is practically the same and equals to 0.065–0.07 mol/dm^3.

Table 2. The results of nanofiltration treatment of the acid regenerating solution using the OPMN-P membrane (P ~1.5 MPa, PR ~75–85%)

№ of regenerating solution portion	1	2	3	4
C_{Zr} in concentrate, mg/dm^3	100.1	250.3	477.8	1305.9
C_{Zr}, in permeate, mg/dm^3	6.0			
C_{HNO3} in concentrate, mol/ dm^3	0.029	0.072	0.085	0.092
C_{HNO3} in permeate, mol/ dm^3	0.027	0.067	0.080	0.084

The low acid concentration in the initial portions of the regenerating solution is caused by binding of acid by zirconium hydroxide. The mechanism of this process is shown in Figure 6.

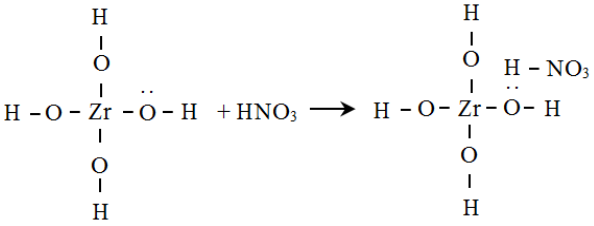

Fig. 6. The mechanism of acid binding by zirconium hydroxide precipitate

The permeate flux of OPMN-P membrane in the process of separation of acid regenerating solution on average equals to ~50 dm^3/m^2·hour (see Fig. 7).

The principle technological scheme of acid regenerating solution utilization suggested in this work is shown in Figure 8.

The nanofiltration permeate consisting of nitric (hydrochloric) and boric acids and also small amount of zirconium can be neutralized with the ammonium hydroxide to pH ~8, filtered and used as a microfertilizer. It should be mentioned that boron is the most effective microelement for many plants.

The zirconium-containing concentrate can be used for preparation of boron sorbent.

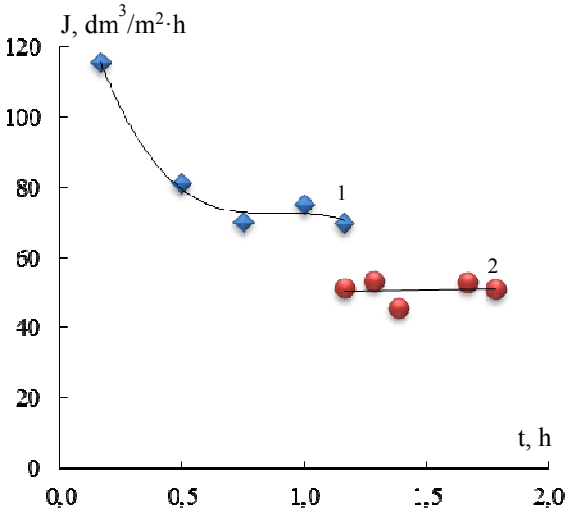

Fig. 7. The permeate flux of OPMN-P membrane during its compression setting with distilled water (1) and during the nanofiltration treatment of the acid regenerating solution (2) (P = 1.5 MPa)

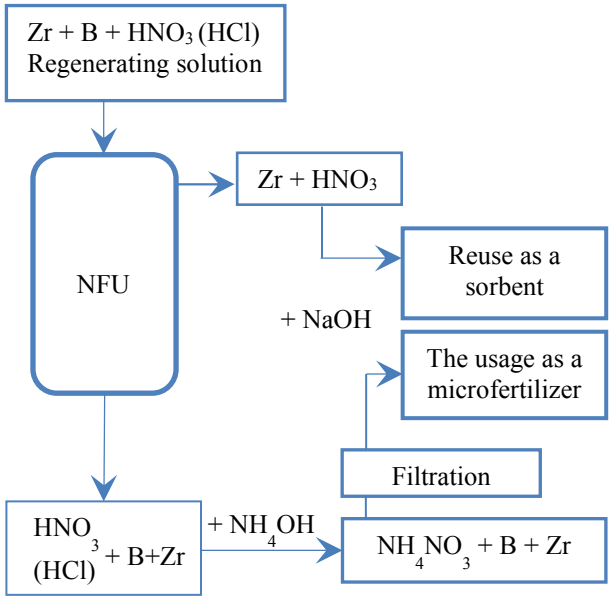

Fig. 8. The principle technological scheme of regenerating solution utilization

NFU – the nanofiltration unit of regenerating solution separation

Conclusions

1. It was established that the sorption capacity of hydrated zirconium oxide equals to 1.0 mg B/g $Zr(OH)_4$ at optimal pH value ~8.5.

2. The principle regeneration possibility of spent zirconium hydroxide by its treatment using diluted solutions of nitric and hydrochloric acids was shown.

3. The utilisation method of the acid regenerating solution by its nanofiltration treatment using the OPMN-P membrane was suggested. The obtained results (boron rejection coefficient equals ~12%, Zr-rejection coefficient – 98–99%) showed that the nanofiltration treatment allows to effectively separate boron from dissolved zirconium. The permeate flux of OPMN-P membrane during nanofiltration treatment of the acid regenerating solution on average equals ~50 $dm^3/m^2 \cdot h$.

4. The zirconium-containing concentrate obtained can be used for the sorbent preparation, and after the neutralization and filtration the boron-containing permeate can be used as a microfertilizer.

5. Thus, the possibility of creating a closed-loop and low-waste water purification technology from boron compounds was demonstrated. This technology allows both averting the danger of the secondary environmental pollution and utilizing the regenerating solution components.

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HIDROKSILO TURINČIŲ CIRKONIO JUNGINIŲ REGENERACIJOS METODŲ PARENGIMAS VANDENS VALYMO NUO BORO PROCESUOSE

D. Urbanas, L. Melnyk

Anotacija

Darbe siūlomas boro sorbcijos procese naudotų hidroksilo turinčių cirkonio junginių regeneracijos atskiestais rūgščių tirpalais būdas ir principinė susidariusio regeneracinio tirpalo utilizacijos nanofiltracijos būdų, panaudojant ОПМН-П membraną, schema. Tai užtikrina permeatų, kurie po neutralizacijos amoniaku gali būti panaudoti kaip mikroelementinė boro trąša (amoniako druska + boras), gavimą. Cirkonio turintis koncentratas gali būti pakartotinai panaudotas sorbentui gauti. Regeneracinio tirpalo komponentų skaidymo nanofiltracijos būdu efektyvumas užtikrinamas aukštomis cirkonio uždelsimo šiame procese koeficiento reikšmėmis (RZr ~98–99 %) ir žemomis boro uždelsimo koeficiento reikšmėmis – RB ~12 %. Šiuo atveju membranos lyginamasis našumas yra apie 50 $dm^3/m^2 \cdot val$.

Reikšminiai žodžiai: boras, vandens valymas, hidroksilo turintys cirkonio junginiai, regeneracinis tirpalas, perdirbimas.