Industrial pollution of the hydrosphere and problems of water treatment in Russia

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Abstract. The statistical data of water use by various industries in Russia were presented and analyzed for the years 2010 to 2016. The problems of saving water resources and developing market for environmental services in Russia were considered. The dynamics of industrial water consumption and water treatment was estimated. The structure of water use and the wastewater disposal for different branches of economy is represented. The constructive proposals for industrial water treatment systems were made. It was shown that sorption method is one of the most promising and environment friendly. The composite sorbents were synthesized from reagents being produced in Russia. For comparison the use and effectiveness of the composite sorbent and imported ion-exchanger was investigated. The developing closed water systems based on the composite sorbents was suggested.

1. Introduction
Currently in the world there is no country, which would have not affected by environmental problems. Compared with other countries, especially with Europe, Russia has huge water resources [1]. Unfortunately, it is for this reason the problem of saving water resources has not been given proper attention for a long time. After long ignoring problem at the end of the 20th century Russia has become a consumer in the global market for environmental goods and services, but such a way of development is not in the interests of our country.

Firstly, this way contributes to the economic growth only of the exporting countries.

Secondly, many imported building materials and reagents which use in the water treatment cannot withstand severe climatic conditions. These can be successfully used only in the southern regions of our country. On the other hand, most of the companies are in the Urals and Siberia, so before start-up of the imported equipment it needs to be retrofitted (covered space, additional heating, etc.). This requires additional costs instead of resource and energy saving. In addition, after about two years, our country must to purchase spare parts, materials, etc. from a foreign supplier for a hefty price.

Thirdly, data about principle of the equipment action are commercial secrecy of the exporting countries. Our engineers often use imported equipment and do not understand well how it works.

This situation may have very undesirable consequences for economic development of Russia. Today the changing situation is important, a way out of it is new scientific developments in the field of ecology.
Sorption method is one of the most promising among the known methods of water treatment. The sorption efficiency is comparable to the same value for complex and expensive methods as electrodialysis and vaporization. However, sorption systems consume little power. These are environment friendly and have simple working mechanism. The main problem is making effective sorption materials. The search for the optimal sorbent is frequently carried out according to the approach that «each physicochemical system needs its own sorbent» [2].

Modification of carbon matrices by micro- and nanodispersed metal hydroxides is upcoming direction for synthesis of effective sorbents. The authors [3] synthesized the composite sorbent based on ion exchangers and polyvalent metal hydroxides. All reagents used for synthesis are produced in Russia. To modify the ion exchanger in optimal conditions the authors investigated and modeled complexation in solutions containing ions of polyvalent metals [4].

A polyvalent metal (iron, tin, titanium, etc.) dispersed in the composite sorbent has a large specific surface area, due to the stabilizing action of the porous carrier, and, thus, high reactivity. The composite sorbent has pronounced physicochemical properties conforming to the operating requirements. Possible application areas of composite sorbents being synthesized are the drinking water preparation, the wastewater treatment and the elimination of emergencies.

The aim of the present study was analyzing statistical data of water use by various industries in Russia in the past seven years (from 2010 to 2016) and investigating the use, effectiveness of the composite sorbent for the water treatment in comparison with imported ion-exchangers.

2. Analysis of statistical data
In 2015 there was a decline in branches of economy by 3.4–5.4%. Manufacturing has suffered the most [5]. However, it practically did not affect the dynamics of water intake because the agricultural sector has increased water use.

In 2015 the total volume of water intake from natural sources was 68.6 km$^3$ (line 1, figure 1a). This is 3.1% less than in the previous year. The volume of fresh water used to the level of 2015 was 97.5% from the 2014 level (line 3, figure 1a). There are small decreases, but they are not significant [6].

The consumed volume of water for industry consists of fresh water (line 3, figure 1a) and water of consecutive and closed water systems (line 2, figure 1a). Saving of fresh water for production needs due to consecutive and closed water systems is on the average 78%.

![Figure 1](image)

**Figure 1.** Dynamics of main indicators of water use in Russia from 2010 to 2016

a) intake, b) disposal

1 – water intake from natural sources, 2 – consumption in water recycling and reuse systems, 3 – using fresh water, 4 – total wastewater volume, 5 – wastewater discharge without treatment
A different situation is observed with the wastewater disposal. The volume of wastewater discharged into natural water bodies gradually decreased from 2010 to 2014 and began to grow in 2015 (line 4, figure 1b). In 2016 the volume of wastewater discharge without treatment is 13.5% above this value in 2013 (line 5, figure 1b).

The structure of water use and wastewater disposal for different branches of economy is shown in Figure 2. Pie charts were plotted on averaged data for the years 2014 to 2016 [6]. Agriculture and forestry are the second largest economic sector on water consumption and in last place on wastewater disposal. Water use of manufacturing is only 6% due to consecutive and closed water systems, but wastewater disposal is 18%. Portion of production and distribution of electricity, gas and water in the total water use and disposal is maximal. Mining and manufacturing has most toxic wastewater because of heavy metals.

![Figure 2. Structure of water use (a) and wastewater disposal (b) for branches of economy: 1 – agriculture and forestry, 2 – mining, 3 – manufacturing, 4 – production and distribution of electricity, gas and water, 5 – household and drinking water and other needs](image)

The structure of wastewater disposal in 2016 are represented on Figure 3 [6]. It was shown that only 11.86% of wastewater are treated to normative values. The rest of 88.14% must be treated, 20.48% of wastewater are discharged into natural reservoirs without treatment. The wastewater treatment can be achieved by means of sorption technologies.

![Figure 3. Structure of wastewater disposal in 2016 1 – insufficiently treated, 2 – without treatment, 3 – normative treated](image)
3. Investigating the sorption materials

3.1. Experimental

The composite sorbents based on cation exchanger KU-2-8 and iron(III) hydroxide were made according to the methodology of stepwise synthesis [3]. For comparison determining the sorption capacity were carried out in parallel on the composite sorbent and the imported cation exchanger Dowex Marathon C which is often used in industry.

Heavy metal pollution of wastewater is one of the most important environmental problems throughout the world. In this regard, the investigated liquid phase was selected solutions of heavy metals. The certain volume of the test solution with known initial composition in the range pH from 5 to 14 was used for sorption processes. The pH value was adjusted by addition of ammonia solution and was monitored with the pH meter (pH 410 Akvilon). Experiments was carried out under dynamic conditions at 297±0.1 K in specially made glass column with stopcock. The equilibrium solutions were analyzed for heavy metals by the spectrophotometric method [7].

3.2. Sorption results

The results of sorption experiments are represented on Figure 4 and Table 1. It was found that the capacity of composite sorbents for heavy metals is about twice as large as imported cation exchanger Dowex Marathon C. The largest differences are observed in the alkaline pH range of the test solutions.

![Figure 4. Dependence of the total dynamic exchange capacity for copper(II) of the composite sorbent and the cation exchange Dowex Marathon C on the pH](image)

| Metal   | pH solution | Dynamic exchange capacity before breakthrough, mg-equiv/g | Total dynamic exchange capacity, mg-equiv/g |
|---------|-------------|----------------------------------------------------------|-------------------------------------------|
|         |             | Composite sorbent | Dowex Marathon C | Composite sorbent | Dowex Marathon C |
| Copper  | 5.20        | 2.10             | 0.18            | 4.27             | 3.87            |
|         | 11.20       | 4.55             | 1.59            | 6.73             | 3.14            |
| Zinc    | 5.53        | 2.01             | 1.55            | 4.24             | 3.82            |
|         | 11.50       | 4.15             | 2.09            | 6.10             | 3.31            |
| Nickel  | 5.66        | 3.02             | 1.74            | 4.67             | 3.08            |
|         | 11.50       | 3.72             | 2.58            | 5.72             | 3.82            |
| Cadmium | 5.47        | 1.50             | 1.00            | 4.05             | 2.10            |
|         | 11.80       | 2.80             | 1.72            | 5.18             | 2.40            |
Wastewater of many industries contain ammonia complexes of heavy metals. Removing complexes is very difficult [8]. The main method is thermal decomposition that requires a large energy consumption. The high capacity in the alkaline pH range allows using the composite sorbent to remove heavy metals from wastewater and to save energy. Due to the sorption degree is over 98% treated wastewater may be recycled into the production. Based on the experimental results closed water system in industries may be created.

4. Conclusions
Dynamics of the main indicators of water use in Russia from 2010 to 2016 hardly changed. There are small changes for branches of economy, but they are not significant. Saving of fresh water due to consecutive and closed water systems is about 78%. This value should be increased. Around 88% of the total wastewater must be treated.

Problems of saving of fresh water and wastewater treatment can be solved with the help of sorption technologies.

The composite sorbents were synthesized from cation exchanger KU-2-8 and iron(III) hydroxide which were made in Russia. The capacity of composite sorbents for heavy metals is about twice as large as imported cation exchanger Dowex Marathon C. Closed water systems based on the composite sorbents may be developed.

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