

REMOVAL OF DISSOLVED OXYGEN FROM WATER USING THE SULPHITE FORM ANION EXCHANGE RESIN

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ABSTRACT

Deoxygenation is an important step in the preparation of high-quality industrial water for a wide variety of commercial-scale processes. Ultrapure water is used in various industries, including heat power plants (boilers), food industries (beer making), microelectronics (semiconductor fabrication), and oil and gas industries (as injection water). The present-day industries impose stringent requirements on the concentration of dissolved oxygen in process water.

The removal of dissolved oxygen (DO) from water was studied experimentally using anion exchange resin AV-17-8 in sulphite form. The effects of various operating conditions, such as water flow rates, height of the resin bed, mineralization of water and run time on the removal of DO have been studied extensively. The possibility of efficient water deoxygenation at ambient temperature has been demonstrated.

Key words: dissolved oxygen, anion exchange resin, sulphite, capacity

INTRODUCTION

Pollution of water bodies - the sources of drinking water - in the absence of effective technologies of water treatment and with unsatisfactory condition of water supply systems creates a risk to public health in many regions of Ukraine.

In the industrial regions natural water bodies' contamination occurs due to sewage discharge of the industrial enterprises, power plants and mines. In some regions potable water has unacceptably high salinity and hardness and groundwater used for drinking is contaminated with ions of iron and manganese, nitrites and nitrates. This adversely affects the health of the population.

The only correct approach to solve the complex problem of protecting water from contamination is the widespread adoption of closed systems of water use in industry and energy. Therefore, the development of modern low-waste technologies for high-quality water for the transition to the closed systems of water use, and their reliable operation is an urgent and important issue.

The corrosion of metal pipes in water distribution networks is a complex electrochemical and physicochemical phenomenon between a metal surface and corrosive water, which cannot always be eliminated but can usually be controlled in a cost-effective manner (Do-Hwan Kim et al., 2009). Corrosion of system pipes has economic, hydraulic and aesthetic impacts, including water leaks, corrosion product build up, increased pumping costs, and water contamination.

The corrosiveness of the water depends on chemical factors, such as pH, alkalinity, buffer intensity, dissolved oxygen and carbon dioxide and total dissolved solids (TDS), and physical properties, such as temperature, flow and velocity, as well as the nature of the pipe material (Do-Hwan Kim et al., 2009).

In neutral aqueous medium in power plants corrosive processes are usually caused by the presence of dissolved oxygen (Kudinov et al., 2009).

Thus, during operation of these plants considerable attention is devoted to the water chemical regime, one indicator of which is low oxygen content.

There are physical, chemical, and catalytic methods for water deoxygenation, and all of them have drawbacks. Physical deoxygenation methods, such as vacuum degassing and the inert-gas scavenging of oxygen, are incapable of reducing oxygen to the desired level. Furthermore, the physical methods are very energy-intensive. Chemical methods employ reducing agents (hydrazine hydrate, sulfites) contaminating both the environment and the water being purified (V. I. Lebedeva et al., 2006).

Methods for the removal of oxygen from water using polymer materials are currently under development. These methods include oxidation-reduction and catalytic techniques.

When using redox ion exchangers the required degree of oxygen removal is achieved through appropriate choice of the redox material, its fractional composition, the column height, and the flow rate of the water (Kravchenko et al., 1982).

MATERIALS AND METHODS

The objective of this research is the creation of modified ion-exchange materials on the basis of strongly basic anion exchange resin AV-17-8 in SO_3^{2-} and determination of the conditions for the effective removal of dissolved oxygen from water, exploring the influence of the type of oxidizing agent on the reducing ability of obtained reducing-oxidizing ion exchange resin.

Removal of dissolved oxygen (DO) from the water on anion exchange resin in sulfite form is described in (Shatalov et al., 2002). It mainly concerns desalted water or condensate. However it is unknown how deoxygenation will happen while using water without desalting. In this case, the process primarily will be affected by anions. Therefore application of redox ion exchange resin of this type can be problematic both in cooling systems, which use natural water without treatment or partially softened and in water-heating straight through boilers which use softened water. Partial decrease in hydrocarbonates is possible using reagent softening, while sodium cation softening usually doesn't influence the concentration of anions in water.

During the studies anion exchange resin AV-17-8 was used in Cl^- -form and SO_4^{2-} -form with bed volume 20-50 ml. Exploring the properties of modified ion exchanger water solutions were infiltrated through the resin bed at a flow rate from 1-5 to 20-50 ml/min. The sample's volume ranged from 100 ml to 2 l. The samples were analyzed for outlet DO content, sulfites, sulfates, chlorides, hydro carbonates, and chlorates content. During deoxygenation process samples were collected in the measuring flask fully filled with water. The water was supplied to the bottom of the flask through the thin pipe with water ousting. It prevented samples from ingress of atmospheric oxygen.

For assessment of reducing ability of redox ion exchange resin test solutions were used: tap water (Total hardness=4.0-5.1 meq/l, Alkalinity=3.9-5.0 meq/l, $[\text{Cl}^-]=50-62$ mg/l; $[\text{SO}_4^{2-}]=17-20$ mg/l),

sodium chloride solutions in tap water ($[Cl^-]=70-1500$ mg/l), sodium chlorate solutions in tap water ($[ClO_3^-]=100-300$ meq/l).

To evaluate reducing ability of redox ion exchange resin under static conditions sodium chloride solutions at a volume of 500 ml ($[ClO_3^-]=20-150$ meq/l) were added to 10 ml of the anion exchange resin.

DO in samples was determined by Winkler's titrimetric method.

RESULTS AND DISCUSSION

Exchange capacity of ion exchange resin for sulfite ions in dynamic conditions ranged from 0.4-1.2 eq/l when using 5% solution of sodium sulfite to 1.7-2.1 eq/l when using 10% solution.

Reducing ability of obtained redox ion exchanger for DO was investigated in dynamic conditions using tap water. According to the Figure 1 reducing ability of anion exchanger rises with the increase in exchange capacity for sulfites. However, even in tap water that has relatively low content of irrelevant ions ($[Cl^-]=62$ mg/l, $[SO_4^{2-}]=20$ mg/l, $[HCO_3^-]=3.9$ mg/l) reducing ability run up to 63.4% of theoretically possible with exchange capacity for $SO_3^{2-}=1,83$ eq/l and 74.8% with exchange capacity for $SO_3^{2-}=0.642$ eq/l.

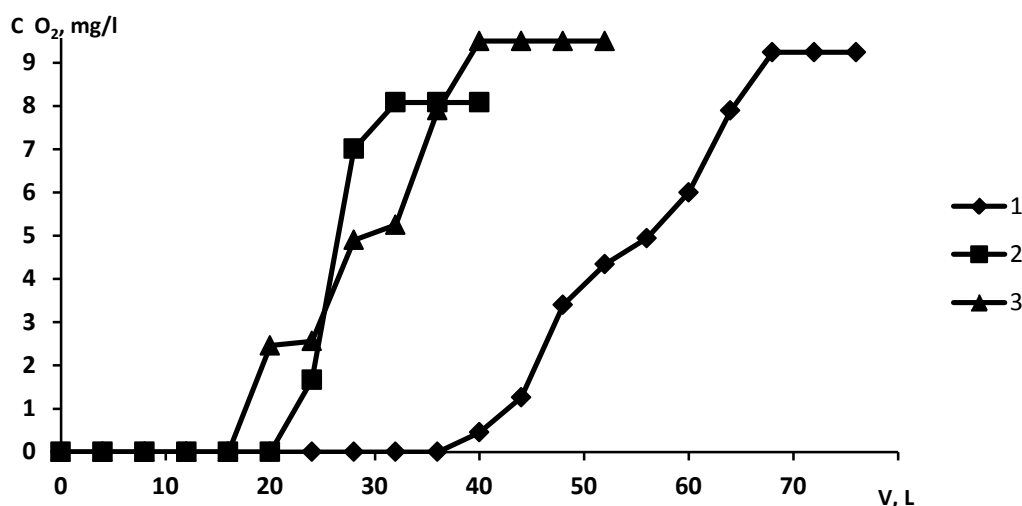


Figure 1. Dependence of outlet DO concentration on the volume of the tap water (1, 2) or sodium chloride solution in tap water ($[Cl^-]=956$ mg/l) (3) infiltrated through the anion exchanger AV-17-8 in SO_3^{2-} -form ($V=50$ ml) at the inlet DO concentration 9.24 mg/l (1), 8.08 mg/l (2), 9.50 mg/l (3) with exchange capacity for sulfites 1.83 eq/l (1), 0.642 eq/l (2), 1.99 eq/l (3) (Reducing ability₁=1.16 eq/l; Reducing ability₂=0.48 eq/l; Reducing ability₃=0.53 eq/l)

For a solution of sodium chloride in tap water at a concentration of chlorides 956 mg/l reducing ability appeared to be 0.53 eq/l with the capacity for $SO_3^{2-}=1.99$ eq/l. Thus, it reached only 26.6% of theoretically possible.

As for the two first mentioned cases we can talk about random oxidation of sulfites on the anion exchanger with atmospheric oxygen (although the process was carried out using reliable rubber seals, water was fed to the bottom of the volumetric flask with a narrow neck, with a constant displacement of water from a volumetric flask), in the third case, there is a negative effect of chlorides, which obviously cause desorption of the sulfite from anion exchanger.

The quantity of displaced sulfite ions is significantly higher than the concentration of DO in the water, causing a significant reduction in the time of protective action of anion exchanger (decrease in reducing ability).

In this connection it was interesting to determine the effect of chlorides concentration on the efficiency of their sorption on the anion AV-17-8 in SO_3^{2-} -form. Also, desorption of sulfite was a question of importance. Since the low concentrations of sulfites in water because of sulfite oxidation by atmospheric oxygen the results of their concentration determination are significantly understated. Therefore the control was mainly carried out by chlorides concentration using ion meter I-160 MI.

Figures 2 and 3 illustrate the dependence of outlet concentration of chlorides and sulfites on the flow volume of sodium chloride solutions. As can be seen in figure 4 the increase in the concentration of chlorides from 453 to 955 mg/l leads to the rise in exchange capacity of anion exchanger for chlorides from 0.790 to 1.458 eq/l. At the chlorides' concentration of 110 mg/l exchange capacity decreases to 0.33 eq/l while chlorides at the concentration of 70 mg/l almost don't sorb on the anion exchange resin and don't displace sulfite anions.

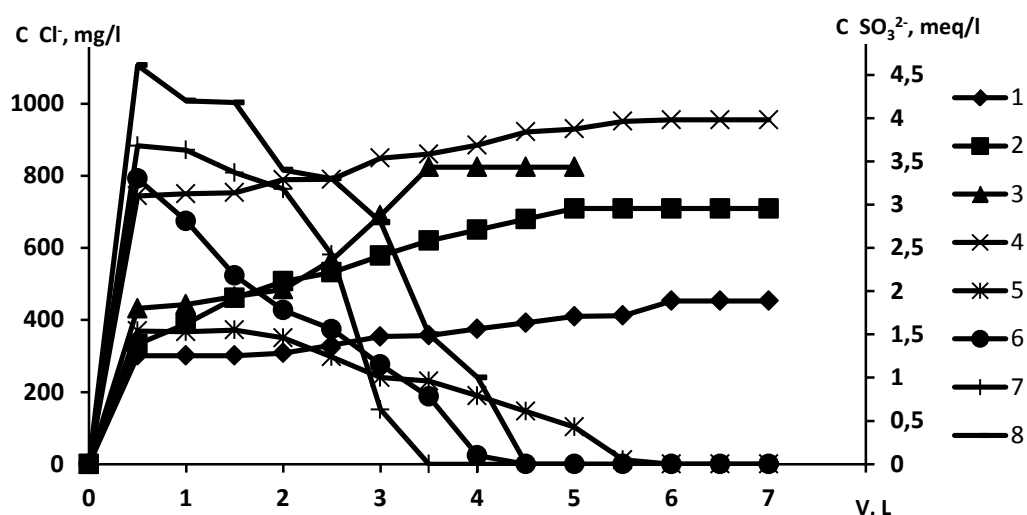


Figure 2. Dependence of the outlet concentration of chloride (1, 2, 3, 4) and sulfite anions (5, 6, 7, 8) on the volume of the sodium chloride solutions with concentration of 453(1, 5), 709 (2, 6), 824 (3, 7) and 956 (4, 8) mg/l infiltrated through anion exchange resin AV-17-8 ($V = 20$ ml) in the SO_3^{2-} -form with exchange capacity for sulfites 2.06 (1, 5), 1.78 (2, 5), 1.83 (3, 7) and 1.99 meq/l (4, 8) (Capacity for $\text{Cl}_1 = 0.790$ eq/l, Capacity for $\text{Cl}_2 = 1.15$ eq/l, Capacity for $\text{Cl}_3 = 1.312$ eq/l, Capacity for $\text{Cl}_4 = 1.458$ eq/l).

Concerning the results decrease in the reducing ability of modified anion exchanger in sodium chloride solution (Fig. 1, curve 3) can be easily explained. Chloride caused leaching of the anion of sulfites in amounts far exceeding the oxygen content in water which led to a decrease in reducing ability. But why there was a decrease in reducing ability up to 25-37% in tap water, in which the total content of chlorides and sulfates reached only 82 mg/l. Displacement of sulfite anions by the hydrocarbonates is unlikely due to the low selectivity of the resin for the latter. However it was determined that hydrocarbonates can displace sulfite anions at a concentration of 6 meq/l.

With increasing concentrations of hydrocarbonates their sorption on the anion exchanger AV-17-8 in the sulfite form increases. Taking into account that alkalinity of tap water reaches 3.9 meq/l, content of chlorides is 1.75 meq/l and sulfates - 0.42 meq/l (total anions content is 6.07 meq/l), it is quite possible that displacement of sulfite anions from anion exchanger takes place. At the

concentration of hydrocarbonates of 6 meq/l concentration of ions driven out rises up to 1.3-1.5 meq/l. With the concentration of DO at level of 1.0-1.1 meq/l the loss of sulfites at 20-35% becomes quite possible.

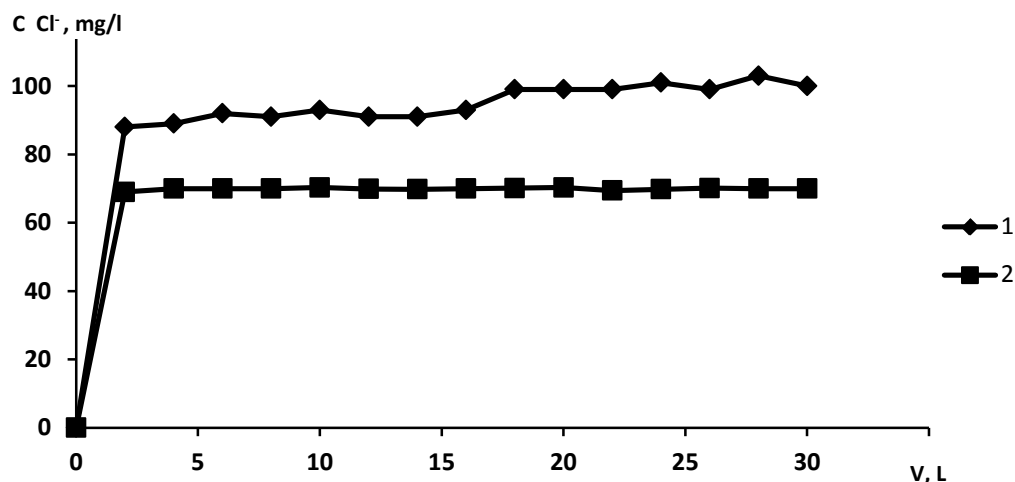


Figure 3. Dependence of the outlet concentration of chlorides (1, 2) on the volume of sodium chloride solutions at the concentrations of 110 mg/l (1) and 70 mg/l (2) infiltrated through anion exchange resin AV-17-8 in SO_3^{2-} -form with the exchange capacity for sulfites 1.800 eq/l (1) and 1.760 eq/l (2) (Capacity for $\text{Cl}^- = 0.330$ eq/l)

Assessment of reducing capacity of redox ion exchangers for water deoxygenation is quite a challenge. Even when using the exchange resin in small quantities - 20-50 ml at a relatively high capacity for reducing agent causing high reducing ability, determination of the total reducing ability requires dozens of litres of tap water to be infiltrated through the resin bed because of the low concentration of dissolved oxygen (6-14 mg/l). And at the rate of 20-50 ml/min it takes a long time. Therefore concentrated solutions of oxidant such as sodium chlorate may be used for the quick test to determine the reducing ability of redox ion exchanger.

Another thing worth mentioning is that in the study of the reducing process of chlorate anions on modified anion exchanger in sulfite form in static conditions (Fig. 4), the reducing ability of the resin did not exceed 1.550 eq/l at capacity for sulfite - 1.945 eq/l. Decrease in the reducing ability of anion exchange resin compared with a capacity for sulfite anions is possible due to oxidation of sulfite anions with atmospheric oxygen during the experiment. In this case a certain volume of anion exchange resin was introduced with SO_3^{2-} in dynamic conditions, and then divided into samples of 10 ml each for research in static conditions.

Furthermore, after oxidation of sulfite anions anion exchange resin can be easily regenerated. In this case, sorption of chlorate anions was carried out on the anion exchanger. Anion exchanger was washed with 10% solution of sodium sulfate for the removal of adsorbed chlorate anions. After washing SO_3^{2-} anions were introduced to the anion exchange resin from the 10% solution of sodium sulfite.

It should be noted that the processing with sodium sulfate is eliminated after the oxidation of sulfite anions with dissolved oxygen. Under normal conditions without extraneous anions adsorption anion exchanger after oxidation of sulfite anions is transformed into sulfate form. Using anion exchanger both in SO_4^{2-} -form and in Cl^- -form its capacity for SO_3^{2-} reaches 1.7-2.0 eq/l after its regeneration with 10% solution of Na_2SO_3 .

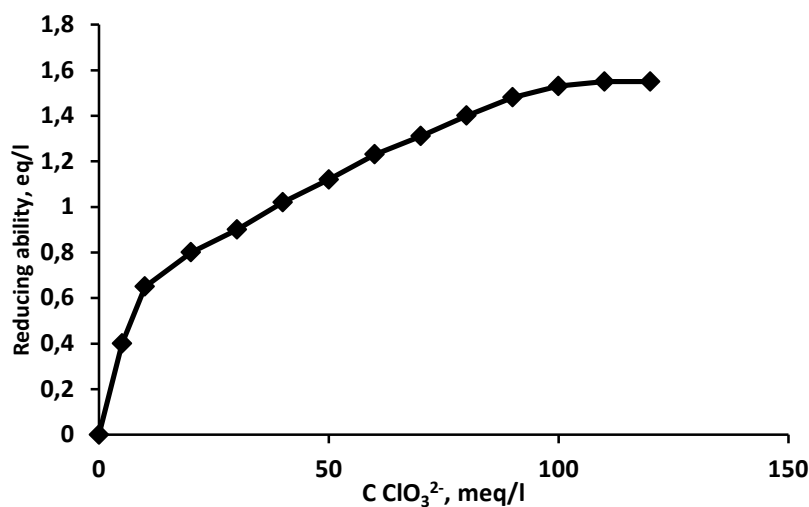


Figure 4. Dependence of reducing capacity of anion exchange resin AV-17-8 in SO_3^{2-} -form (Exchange capacity for $\text{SO}_3^{2-} = 1.945$ eq/l) for ClO_3^- on their equilibrium concentration in samples of 500 ml and the volume of ion exchange resin=10 ml.

CONCLUSIONS

The reducing ability of anion exchange resin AV-17-8 in the sulfite form depends on the capacity of anion exchange resin for sulfite anions and desorption of them in the presence of competing anions. In the case of sorption of chloride anions it was shown that the desorption of sulfite anions occurs at concentrations higher than 110 mg/l.

It was discovered that hydrocarbonates at concentrations exceeding 6 meq/l can cause a decrease in the reducing ability of redox ion exchanger up to 20-35%.

Anion exchange resin AV-17-8 in sulfite form should be used for deaeration of water containing anions at a concentration less than 6 meq/l.

An assessment of reducing ability of modified anion exchange resin was made with the help of model solutions of sodium chlorate. It was shown that highly basic anion exchange resin AV-17-8 can be easily regenerated with 10% solution of sodium sulfite.

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