REMOVAL OF HYDROGEN SULPHIDE FROM SULPHUROUS GROUND WATERS

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ABSTRACT

The most efficient and cost-effective treatment option will depend primarily on the concentration of hydrogen sulphide. Activated carbon removes a variety of water contaminants, including hydrogen sulphide, by adsorbing and oxidation of the hydrogen sulphide species on the carbon particles surface. This work deals with experimental investigation related to the removal of hydrogen sulphide from sulphurous underground water by adsorption/oxidation on copper modified activated carbon, in both laboratory and field conditions. The performance of carbonaceous adsorbents synthesized from peach and plum stones by the physical-chemical activation method and modified by oxidation following impregnation with Cu$^{2+}$ by ion-exchange method in both laboratory and field conditions have been investigated. Comparative analysis of adsorbents highlights the performance of carbonaceous adsorbents obtained by impregnation with copper (II) ions using ion-exchange method, being recommended for practical purposes to remove hydrogen sulphide from natural waters. The capacity of copper modified carbonaceous adsorbents for removal of hydrogen sulphide in dynamic field conditions (expressed as the ratio of volumes of adsorbent : water at breakthrough point) achieved a ratio up to 1:5500.

Keywords: removal, active carbon, hydrogen sulphide.

1. INTRODUCTION

Hydrogen sulphide in drinking water is a problem of considerable importance in Republic of Moldova, especially in small communities that have no alternative sources of available water (Bernardini et al., 2011; Garaba, 2005). Hydrogen sulphide can be effectively removed from water using a number of treatment processes (Dalai et al., 1999; Delzer et al., 1993; Levine et al., 2004; Nastas et al., 2012; Rusu et al., 2011). Among various methods used to remove hydrogen sulphide, adsorption/oxidation on activated carbons is considered as a very efficient and cost effective approach. This is the result of unique surface properties of carbonaceous adsorbents such as large surface area, and high pore volume, along with particular surface chemistry (Puri, 1970), which promotes catalytic oxidation of H$_2$S. Impregnation with transition metals changes catalytic properties of activated carbons. An essential influence on selectivity of formation of sulphur species has the form of the immobilized metal on the surface. Metals presented on the surface in the form of ions favour the formation of sulphur species with higher degree of oxidation (SO$_3^{2-}$ and SO$_4^{2-}$), while metals presented in the form of oxides promote oxidation of sulphide ions up to elemental sulphur (Bagreev and Bandosz, 2001; Mikhalovsky and Zaitsev, 1997; Nastas et al., 2012). Previous researches pointed out carbonaceous adsorbents modified with copper ions having good abilities for removal of hydrogen sulphide from water, in this case the sulphide oxidation products are thiosulphate, sulphite and sulphate ions, and there is no present elemental sulphur (Nastas et al., 2012).
This work deals with experimental investigation related to the removal of hydrogen sulphide from sulphurous underground water by adsorption/oxidation on copper modified activated carbon, in both laboratory and field conditions.

2. MATERIALS AND METHODS
In these studies carbonaceous adsorbents obtained from peach and plum stones by the physical-chemical activation method and modified by oxidation following impregnation with copper (II) ions by ion-exchange method (Rusu et al., 2010) have been used.

Testing of carbonaceous adsorbents for removal of sulphur species from solutions was performed by using lab installation provided with an air bubbler and recovery flask for aerated hydrogen sulphide at appropriate parameters, i.e. solid/liquid ratio, aeration flow rate, pH of the medium, initial concentration of sulphur species (Nastas et al., 2013). Elemental sulphur, thiosulphate, sulphite and sulphate ions, and aerated hydrogen sulphide from recovery flask were determined in the equilibrium solutions by standard methods (APHA, 1999). All sulphur species were recalculated as H₂S, and removal of hydrogen sulphide from solutions, expressed as sulphur demand (SD, %) was calculated as (Eq. 1):

\[
SD = \frac{C_0 - C_e}{C_0} \times 100\% 
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium concentrations (mg/L) of hydrogen sulphide in the solution, respectively.

Dynamic adsorption/oxidation of hydrogen sulphide from water was conducted in a glass column filled with activated carbons (Nastas et al., 2013). The concentration of hydrogen sulphide in the effluent was monitored using pH/mV/ISE/T meter HI 121 (HANNA Instruments) with H₂S electrode WT-573-H₂S (WATER TEST CO., Thailand). The efficiency of adsorbent (Q, mg/g) (integral on effluents) was calculated as (Eq. 2):

\[
Q = \frac{(C_0 - C_{eff})}{m} \times V_{eff}
\]

where \(C_0\) is influent hydrogen sulphide concentration (mg/L), \(C_{eff}\) is effluent hydrogen sulphide concentration (mg/L), \(V_{eff}\) is the volume of solution passed through column (L) and \(m\) is the mass of adsorbent (g).

Field experiments/tests of copper impregnated carbonaceous adsorbents for removal of hydrogen sulphide from underground waters have been performed in two locations from Republic of Moldova, the village Bulboaca, Anenii Noi (underground water having initial concentration of hydrogen sulphide under range 0.5÷1.7 mg/L and pH value 8.60÷8.75) and the town Hincesti (underground water having initial concentration of hydrogen sulphide under range 6÷9 mg/L and pH value 8.2÷8.3).

3. RESULTS AND DISCUSSION

3.1. Lab experiments for removal of hydrogen sulphide from solution
Testing of carbonaceous adsorbents for removal of sulphur species from solutions was performed by using lab installation provided with an air bubbler and recovery flask for aerated hydrogen sulphide. Impregnation of oxidized activated carbon with copper (II) ions greatly influences the formation of sulphur species of higher oxidation level, the products being thiosulphate, sulphite and sulphate ions, without formation of elemental sulphur (Table 1). The effectiveness of CAPO23Cu(ce) for hydrogen sulphide elimination from model solution is demonstrated during four contact cycles (Table 1).
Column adsorption/oxidation experiments were performed in order to evaluate capacity of carbonaceous adsorbents to remove hydrogen sulphide from water. The performance of carbonaceous adsorbent obtained from peach stones and modified by oxidation following impregnation with Cu$^{2+}$ (CAPO23Cu(ce)) was investigated in comparison with unmodified activated carbon (CAPO23). Hydrogen sulphide breakthrough curves and the efficiency (Q, mg/g) of adsorbents (CAPO23 and CAPO23Cu(ce)), to eliminate/oxidize of hydrogen sulphide species in dynamic conditions are shown in Figures 1 and 2. The results emphasize high capacity for carbonaceous adsorbent CAPO23Cu(ce) of elimination/oxidation of hydrogen sulphide obtained from peach stones modified with copper ions by ion-exchange method. The capacity of adsorbent (expressed as the ratio of volumes of solid:solution at breakthrough point) achieved a ratio up to 1 : 3000. Also, the formation of colloidal sulphur was not observed in this column.

Table 1. Quantity of H$_2$S aerated and oxidized to sulphur species in the presence of catalysts (C$_0$= 10 mg/L, pH=8.5, ratio mgO$_2$/mgH$_2$S = ¾, mass of catalyst 1.0 g).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Quantity aerated, %</th>
<th>Quantity oxidized %</th>
<th>Quantity (%) of H$_2$S oxidized to sulphur species:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>S$^0$ colloidal $\sum$(S$O_3^{2-}+SO_3^{2-}$) SO$_4^{2-}$</td>
</tr>
<tr>
<td>CAPO23</td>
<td>4.3</td>
<td>95.6</td>
<td>6.1 27.1</td>
</tr>
<tr>
<td>CAPO23Cu(ce)</td>
<td>First - Fourth contact cycles 10.3 - 16.0</td>
<td>84.0 - 89.7</td>
<td>0 50.6 - 61.3</td>
</tr>
</tbody>
</table>

Figure 1. Breakthrough curves of hydrogen sulphide elimination/oxidation in dynamic conditions on oxidized active carbon CAPO23 (curve 1) and adsorbent CAPO23Cu(ce) (curve 2).

Figure 2. The efficiency (Q, integral on effluents) of oxidized active carbon CAPO23 (curve 2) and adsorbent CAPO23Cu(ce) (curve 1) to eliminate/oxidize of hydrogen sulphide species in dynamic conditions.

3.2. Field experiments for removal of hydrogen sulphide from ground water
In these studies, the experiments for evaluation the removal efficiency, capacity, and monitoring of hydrogen sulphide concentration were conducted in a continuous operation, using columns with carbonaceous adsorbent obtained from plum stones and modified by oxidation following impregnation with Cu$^{2+}$ (CAPrO36Cu(ce)). The raw water has been passed through columns with a flow rate of 80 to 90 mL/min. Data (the concentration of
hydrogen sulphide, pH and temperature) were automatically analyzed every 10 minutes and stored by the computer software.

Variation of hydrogen sulphide concentration, pH value in the effluents and the efficiency (Q, mg/g) of adsorbent CAPrO36Cu(ce) to eliminate/oxidize of hydrogen sulphide species in field dynamic conditions (the village Bulboaca, Anenii Noi) are presented in Figures 3 and 4. The capacity of carbonaceous adsorbent CAPrO36Cu(ce) to eliminate/oxidize of hydrogen sulphide species was not exhausted at crossing through column a volume of about 1450 L of natural sulphurous water. There were not found species of hydrogen sulphide in the effluents and the pH value of the treated water was about 8.

Field experiments for removal of hydrogen sulphide from underground water with a higher initial concentration of hydrogen sulphide have been performed in the town Hincesti. Hydrogen sulphide breakthrough curve and the efficiency (Q, mg/g) of adsorbent CAPrO36Cu(ce)) to eliminate/oxidize of hydrogen sulphide species in dynamic conditions are shown in Figures 5 and 6. The capacity of carbonaceous adsorbent CAPrO36Cu(ce) (expressed as the ratio of volumes of adsorbent : water at breakthrough point) in dynamic condition achieved a ratio up to 1:5500.

The developed copper modified carbonaceous adsorbents were found to be effective adsorbents for treatment of sulphurous waters.
4. CONCLUSIONS

The performance of carbonaceous adsorbents synthesized from peach and plum stones by the physical-chemical activation method and modified by oxidation following impregnation with Cu$^{2+}$ by ion-exchange method in both laboratory and field conditions have been investigated.

Comparative analysis of adsorbents highlights the performance of carbonaceous adsorbents obtained by impregnation with copper (II) ions using ion-exchange method, being recommended for practical purposes to remove hydrogen sulphide from natural waters.

The capacity of copper modified carbonaceous adsorbents for removal of hydrogen sulphide in dynamic field conditions (expressed as the ratio of volumes of adsorbent : water at breakthrough point) achieved a ratio up to 1:5500.

Shortcomings observed during field conditions experiments have been pointed out and will be considered for further field experiments.

REFERENCES


