Application of a Magnetic Composite Sorbent On The Basis Of Woodworking Waste for Sewage Treatment from Heavy Metals.

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ABSTRACT

On the basis of waste of wood fiber and magnetite the composite sorbent possessing magnetic properties has been received, its physical and sorption properties, possibility of use for sewage treatment from heavy metals have been investigated, the way of regeneration and utilization of the sorbent has been offered. Keywords: heavy metals, wood fibers, magnetite, sorbent.
INTRODUCTION

The most difficult object of cleaning is the sewage with impurity of heavy metal ions (HMI). The majority of the compounds that contain HMI which are discharged with wastewater have carcinogenic and mutagenic effects. The problem of HMI extraction is connected with the imperfection of the existing methods of sewage treatment.

According to literary sources [1,2,3] a lot of different wastewater treatment processes such as flocculation, coagulation, cementation, chemical sedimentation, electrochemical and biological ways are most effective for high concentrated wastewater treatment. These methods are effective to extract most part of pollutants from water phase. But reached purification efficiency of HMI, as a rule, is insufficiently high. A number of ways, such as the ionic exchange, liquid extraction, adsorption, ultrafiltration and return osmosis allow to reach deep purification efficiency of HMI. However, they are usually unsuitable for high concentrated water treatment because of cyclicality of hardware schemes of cleaning processes and low productivity of one cycle. As a result, using a combination of a various methods of water treatment is more expedient.

One of the most perspective methods, economic and simple in hardware registration, that allows to carry out deep cleaning of low concentrated HMI polluted water objects, is adsorption. Sorption materials (SM) from residuals, containing cellulose, are of special interest. The advantages of these reagents in comparison with synthetic materials are determined by chemical nature of the polymer matrix, its physicochemical properties and its various functional groups. Economic expediency of application such reagent is defined by large supplies, low cost, renewable source of raw materials, possibility of utilization [4].

On the basis of the above, the aim of this work to increase of purification efficiency of galvanic production sewage from ions of $\text{Cr}^{6+}$, $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$ by using magnetic composite sorbents based on wood fiber waste (WFW) and magnetite ($\text{Fe}_3\text{O}_4$). The main advantage of such sorbent in comparison with common (not magnetic) is using of magnetic sorbents significantly simplify adsorption by carrying out sorption at big speeds and easy separation of sorbent from solutions by magnetic separation [5,6].

MATERIALS AND RESEARCH METHODS

Magnetic composite sorbent (MCS) has been received by sedimentation on the WFW surface of $\text{Fe}_3\text{O}_4$ nanoparticles that are formed in water solution as a result of exchange reaction:

$$\text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O}.$$  

Sedimentation has been made under ultrasonic vibration at optimum temperatures – not more than $25^\circ\text{C}$ at one-and-a-half of excess of precipitant– ammonium hydroxide. Fiber was used as a waste, it is formed in production of Medium Density Fiberboard (MDF) made from various wood breed (a pine, a birch, an aspen). WFW is formed at fiber formation stage in MDF production cycle and it is unsuitable for further use. Fiber is the system of chaotically, freely distributed in space threads, having spatially focused structure which allows pollutants to contact with bigger surface per unit of time. Bioassay has been used to identify hazard class of wood fiber waste [8, 9]. Analysis of chemical composition of magnetite powder that had been synthesized on the fiber surface was carried out on X-ray fluorescence, energy dispersive, spectrometer “BRA-18”. Specific surface area of MCS was measured by BET method on a BET Surface Area Analyzers “Nova1000e”. To determine particle size and $\zeta$-potential we used “NanoBrook Omni” analyzer. Changes in the structure of wood fibers fixed by electron microscopy.

To evaluate the effectiveness of the received SM at water purification from HMI we used sewage from galvanic production. Adsorption has been carried out on laboratory filtration system by sewage transmission with metering rate through glass columns (diameter is 10 mm, length of perforated bottom is 150 mm. The height of reagent layer was 100 mm, weight – 2 g. Some quantity of sewage was filtered through the adsorptive layer. Initial and final concentration of HMI has been defined by atomic emission spectroscopy on “Agilent 720 ICP-OES” spectrometer. Absorbent carbon “BAU-A” with particle size of 0,5-1 mm has been used for comparison sorption ability of the studied materials. Regeneration of magnetic composite sorbents (MCS) has been carried out by using 0,1 M aqueous solution of nitric acid.
RESULTS

According to literary sources [10] and researches, the main components of WFW are cellulose (more than 60%) and a lignin (25-30%). WFW also is composed of carbamide pitches modified by melamine (to 20 mg / 100 g), applied as binding elements, length of fibers is 0.5–3 mm. Hazard class of WFW determined by biotesting is IV. The analysis of chemical composition of magnetite powder synthesized on a fiber surface has shown that the main component of the received powder is Fe$_3$O$_4$.

Particle size analysis by NanoBrook Omni, based on the principles of dynamic light scattering, has shown that received Fe$_3$O$_4$ on WFW surface according to the suspension characteristic on dispersion is polydisperse, the average size of Fe$_3$O$_4$ particles collected in associates of 400-500 nanometers is 20-50 nanometers. ζ–potential of particles at neutral pH is -8.5 mV. The specific surface area of MCS measured by BET method is 161 m$^2$/g. Microscopic pictures of the initial and modified by magnetite fiber shown in figure 1.

![Microscopic pictures of the initial and modified by magnetite fiber](image)

Figure 1: The wood fiber structure: a) initial fiber; b) modified fiber.

Final treatment results of sewage from HMI by MCS and separately its components, characteristics of SM are presented in the 1 and 2 table.

<table>
<thead>
<tr>
<th>Sorption material</th>
<th>Heavy metal concentration ±Δ, mg/l n=3, P=0,95 Before treatment After treatment</th>
<th>Purification degree, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Cr</td>
</tr>
<tr>
<td>WFW</td>
<td>1.32±0.26</td>
<td>6.89±1.37</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>0.07±0.01</td>
<td>0.36±0.07</td>
</tr>
<tr>
<td>MCS</td>
<td>0.20±0.04</td>
<td>0.35±0.07</td>
</tr>
<tr>
<td>BAU-A</td>
<td>0.07±0.01</td>
<td>0.36±0.07</td>
</tr>
<tr>
<td>Norm, mg/l</td>
<td>0.25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 1 – Degree Of Waste Water Purification From HM by Various Sorbents

<table>
<thead>
<tr>
<th>Sorption material</th>
<th>Particle size, mm</th>
<th>Specific surface area, m$^2$/g</th>
<th>Sorptive capacity, mg/g</th>
<th>Sewage flow rate, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WFW</td>
<td>0.5-3</td>
<td>112</td>
<td>14</td>
<td>20-25</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>0.004-0.005</td>
<td>75</td>
<td>39</td>
<td>0.01-0.02</td>
</tr>
<tr>
<td>MCS</td>
<td>0.5-3</td>
<td>161</td>
<td>32</td>
<td>18-23</td>
</tr>
<tr>
<td>BAU-A</td>
<td>0.5-1</td>
<td>740-800</td>
<td>20</td>
<td>0.1-0.3</td>
</tr>
</tbody>
</table>

DISCUSSION

To evaluate the effectiveness of the received SM at water purification from HMI we used waste water of galvanic productions. Today reagent methods which don’t provide full observance of standards for the residual HMI content are applied for HMI removal from wastewater. It was established by analysis data that
after chemical neutralization we observe excess of standards for Pb^{2+} ions more than 3 times, for Cr^{6+} ions - more than 2 times, for Cu^{2+} ions - more than 5 times. This necessitates to apply additional actions for deeper cleaning of sewage.

According to the results of experiments Fe_{3}O_{4} has the highest purification degree and sorption capacity. However at the same time filtration process is difficult due to small particle size and high bulk density of reagent. For absorbent carbon the speed of feed water consumption has made 0,1–0,3 ml/min, efficiency of cleaning on ITM has made 87%. MCS has shown high purification and sorptive capacity at a high speed of sewage (18-23 ml/ min); modifying of Fe_{3}O_{4} surface has allowed significantly increase the sorption capacity of WFW. It should be noted that WFW itself has high purification degree from Pb^{2+}.

According to the results of regeneration experiments it was found that on the 8th cycle of application, efficiency of Pb^{2+} ion sorption declined to 20%, on ions of Cu^{2+} and Cr^{6+} ions - to 30%. This may be because magnetite is oxidized and it was washed away from fiber surface.

CONCLUSION

Thus, researches allow to consider MCS as effective and inexpensive sorbent for purification of liquid wastes from HMI. After working off sorbent doesn’t need to be regenerated and after dehydration it is offered to make pressed fuel granules from used fiber.

There are several advantages of using pressed biofuel. The first one is big heating value in comparison with splinter and lumpy wood waste, the second advantage is low cost of equipment for boiler plant in comparison with burning waste wood.

REFERENCES