Wastewater Treatment Using Plant Waste as Adsorbents

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Abstract. Adsorbents obtained from waste of plant origin are capable of replacing the traditional sorbents for removing of heavy metal ions from wastewater. The raw materials for the production of these sorbents are the chemically modified sunflower husks, as well as husk waste after industrial extraction of melanin. Experimentally determined the adsorption capacities and removal efficiency for copper and iron ions. Depending on the concentration, adsorption capacities varied from 5 to 25 mg of metal per gram of adsorbent. The use of the proposed adsorbents can also solve the problem of utilization of sorption material waste. The plant basis, and the neutral pH (in the order of 6-7) allows for the spent sorbents to be introduced into the soil as a component of the system of trace elements containing copper and iron.

1. Introduction

Purification of water from metal ions is vital in waste treatment, as well as in industrial, circulating or drinking water supply systems. Removing metal ions such as copper, iron, zinc is associated with the need to reduce pollutant concentration almost to trace amounts. With all the variety of existing methods, which include membrane, electrochemical, and reagent methods, the most practical are sorption solutions that achieve the required purification parameters at minimum costs. Modern industrial sorption materials have adequate processing characteristics, such as high sorption capacity, resistance to mechanical influences, and ability to regenerate. However, the issues of cost, accessibility, and the possibility of environmentally safe disposal of spent sorbents call for searching for new adsorbents that can reduce the cost and simplify water purification.

2. Relevance

Production of phytogenic (plant) waste-based sorption materials that can replace traditional adsorbents in the matter of extracting metal ions from sewage receives particular attention [1]. Phytogenic waste such as husks of sunflower, oats, buckwheat or rice chemically contains up to 30% of cellulose and up to 25% of lignin. Those substances are capable of physical sorption and chemisorption. The adsorption capacity of phytogenic materials is determined by the presence of cellulose, which has the ability to physical sorption. Therefore, foliage, sawdust, husks of sunflower, oats, buckwheat or rice are used as sorbents in unmodified form [2; 3]. Such materials are capable of adsorbing pollutants. However, their industrial effectiveness is low; while the ease of processing and preparation cannot compensate for this disadvantage. It is possible to increase the sorption properties of plant waste significantly and convert it to forms most effective for the extraction of metal ions with the help of chemical modification [4]. Various modifications are carried out to carbonize the material fully [5] or at least partially. The
carbonization improves their sorption activity, or else removes water-soluble and alkali-soluble substances, which allows chemisorption due to the interaction of ions with lignin [6].

Plant waste is currently used in not only sorbents production, but also in manufacturing various marketable products. For example, the sunflower husk is a promising raw material for the production of melanin - natural compound that is widely used as therapeutic and prophylactic medication, as well as dietary supplements [7]. Husks is an affordable low-cost high production volume waste of high antioxidant activity of isolated melanin-containing compounds [8].

Technologies for producing melanin from sunflower husks are distinguished by methods of extraction intensification, concentration and extraction processes. Yet, all of them include the stages of water flushing, drying, and extraction [9]. The husk waste remaining after extraction of melanin-containing matter can be used as sorbent to remove metal ions, since the extraction removes water-soluble and alkali-soluble substances such as hemicellulose. The removal of these substances make the functional groups of lignin accessible to ions, therefore intensifying the process of chemisorption [10].

3. Statement of problem
Developing sorbents from sunflower husk means selecting the optimum modification parameters to obtain a sorption material with a high efficiency of trapping metal ions while minimizing the reagent and energy costs. It also implies evaluating the possibility of using melanin waste from sunflower husks as a sorption material without additional processing operations – due to the similarity of the stages of preparation of raw materials and the production of sorbents.

4. Theoretical justification and experiments
4.1. Methods for obtaining sorbing agents
On the basis of theoretical appraisal of available techniques for modification of sunflower husks [11; 12] we developed an original technology to obtain a sorbing agent with a high sorption capacity which is due to enhanced sponginess [13; 14]. Obtaining the sorption agent includes a stage of soaking in alkaline agent, drying and size reduction. The following technological parameters were determined for this process. Soaking is performed in 0.5 M of sodium hydroxide solution for 45 min; to intensify the process, it is performed within a super-high frequencies field with 0.1–0.5 W/cm² power-weight ratio, where the husk to sodium hydroxide solution weight ratio is 1:5.

Soaking sunflower husks in 0.5 M of sodium hydroxide solution provides for a faster swelling of the raw material and a considerable increase in the portion of bound water (water adsorbed by cellular walls of the raw material) in it, which ensures a greater destructive effect of super-high frequencies on cellular walls upon drying followed by an increase in the number of pores which, therefore, enhances the sorption activity. Besides, the alkaline medium resulting from the presence of sodium hydroxide enhances dissociation of ionogenic groups of melanin and lignin in the sunflower husks. At the same time, the hydrophilic ionogenic groups are oriented outwardly, while the hydrophobic portions are oriented inwardly of the particles, which ensures their greater availability for interaction with heavy metal ions, and increases the sorption activity.

Exposure of raw material to the impact of alkaline solution also results in rupture of bonds in cellulose-lignin-hemicellulose complexes, which ensures a greater number of pores in the raw material and a greater sorption activity. Reducing the concentration of sodium hydroxide solution below 0.5 M fails to promote a greater sorption activity, but results in inefficient use of sodium hydroxide.

Sunflower husks treated with sodium hydroxide show an alkaline pH of the medium, which elevates the pH of waste water when interacting with the sorbing agent. If there are heavy metal compounds in the waste water, they undergo hydrolysis yielding insoluble hydroxides of heavy metals that are absorbed by the surface of the sorbing agent.

If the stage of sunflower swelling in sodium hydroxide solution continues for less than 45 min, the process remains incomplete, that is, the raw material fails to swell in full measure. On the other hand, duration of longer than 45 min is ineffective as further swelling of the raw material slows down considerably.
Drying the raw material in super-high frequencies field provides for three-dimensional heating. At the first stage of drying the emission of thermal energy by oscillating movement of molecular dipoles results in boiling intracellular solution and rupture of the cellular membrane under the impact of excessive pressure from the heat in a closed intercellular space, which ensures a greater porosity of the raw material and a greater sorption activity. The solubility of water-soluble and alkali-soluble components increases as well, the rate of diffusion processes intensifies, which ensures a fast redistribution of components moving from the depth of raw material particles to the surface due to their carrying away by the boiling extractant, which also increases the porosity and sorption activity of the resulting sorbing agent.

If sunflower husks are processed in super-high frequencies field with power-weight ratio below 1.3 W/cm³, the duration of the process increases while the desired effect is not attained. If sunflower husks are processed in super-high frequencies field with power-weight ratio above 1.3 W/cm³, the energy consumption is much higher while increasing the product’s prime cost.

Another material was tried as adsorbing agent; melanin was isolated by extraction, which was performed as a two-stage process of extracting the reduced sunflower husks in a vibration extraction plant at conventional settings for 20 min at each stage, by 0.1–0.5 M sodium hydroxide solution at the 1:(4÷5) weight ratio between raw material and extracting agent [15].

4.2. Assessment of sorption properties of sorbing agents

To assess the sorption capacity of sorbing agents we used the conventional technique based on measuring the optical density of marker substance solution (methylene blue, iodine) obtained after interaction with a sample for a precisely set period of time. To assess how well the obtained material can absorb iron and copper ions, we prepared model solutions containing Fe²⁺ ions (ferrous ammonium sulfate) and Cu²⁺ ions (copper sulfate) at a concentration of 0.6 and 1.0, as well as 250.0 mg/l, respectively, in which the samples of metals under study were steeped for 1 hour (0.5 g per 50 ml of solution). The residual content of iron ions in the exhausted solution was estimated by subjecting a complex compound of iron with sulfosalicylic acid, stained bright yellow, to photocolorimetry in a weakly acidic medium (pH=9, ammonium buffer solution). The residual content of copper ions was estimated by subjecting a complex compound of copper, stained blue, to photocolorimetry with 10% ammonia solution.

Table 1. Parameters of obtained sorbing agents are presented in the table.

| Type of sorbing material          | Absorption I₂, % | Methylene blue absorption, mg/g | Activity in relation to metal cations, % |
|----------------------------------|-----------------|---------------------------------|-----------------------------------------|
| Modified husks sorbing agent     | 42.4            | 211.0                           | Cu²⁺ 100 98.2 100 97.4                   |
| Melanin production waste         | 34.1            | 108.2                           | Cu²⁺ 93.5 85.6 90.8 83.1                 |

Cu²⁺ - initial concentration 1.0 mg/l,
Cu²⁺ - initial concentration 250.0 mg/l,
Fe²⁺ - initial concentration 0.6 mg/l,
Fe²⁺ - initial concentration 250.0 mg/l.

4.3. Determining the scope of use for sorbing agents

Experimental research was made to evaluate the technological capabilities of sorbing agent use, such as the optimum time of water processing and the permissible ranges of metal ion concentration in water. Three types of sorbing materials based on sunflower husks were used: 1 – sorbing agent obtained by special processing of husks by the method described above; 2 – husk waste after melanin extraction; 3 – husks that just underwent reduction, without any further processing.
In all samples, the fraction composition was 0.3–0.5 mm. Extraction media were solutions with 0.5 mg/ml concentration of copper \( \text{Cu}^{2+} \) and iron \( \text{Fe}^{2+} \) ions. In the purification process the sorbing agent to solution ratio was 1 g per 50 ml. The sorption process was carried out under static conditions. The effectiveness of the process was estimated by photocolorimetry. The curves of adsorption kinetics are shown in Fig. 1 and Fig. 2.

As the experimental data shows, the best result was achieved with the use of a sorbent produced by the proposed technology. Near-complete recovery of \( \text{Cu}^{2+} \) ions in two hours and \( \text{Fe}^{2+} \) ions in an hour and a half is observed.

The sorbent obtained from the husk waste of melanin production, produced less cleaning results; which is probably due to its porosity less than that of sorbent 1. Treatment of the solution with pulverized husk sorbent shows a low sorption capacity for this type of contamination because of the large amount of ballast substances in the material and encumbered access of ions to chemisorption agent (lignin) [16].

An analysis of the dependence of the metals extraction degree on the solution concentration was studied to evaluate the possible application of husk waste, see Fig. 3, 4. The amount of \( \text{Cu}^{2+} \) ions extracted from aqueous solutions can reach high values - around of 98.6 - 99.6% for solutions with a concentration from 0.1 mg/ml to 1 mg/ml. For highly diluted solutions, we observed a strong turbidity samples, discoloration of the liquid, and the impossibility to perform a photocolorimetric evaluation of the results. This is probably due to an increased alkalinity of the solution (\( \text{pH} = 9-9.5 \)) and dissolution of organic substances. High concentrations exceeding 5 mg/ml exceed the sorption capacity of the material and cannot capture qualitatively, which is typical for any kind of sorbents [17].

The range of optimal \( \text{Fe}^{2+} \) ion concentrations for extracting is somewhat wider and ranges from 0.08 mg/ml to 1.7 mg/ml, see Fig. 4.
The proposed study includes statistically processed results of the experiments with a confidence probability of $P = 0.95$, $n = 5$, where "$n$" is the number of experiments.

An important characteristic of industrial sorbents is the possibility to desorb and reuse. However, for this type of phytogenic waste material desorption is almost impossible, because it requires exposing materials to concentrated acids and high temperatures, which will destroy the cellulose (the basis of the material); with the extraction of the desired product from the resulting compounds economically unviable [18]. The problem of utilizing spent sorption materials can be solved by using them as a component of microelement fertilizer containing copper, iron, and zinc [19; 20]. Since the core of the sorbent is phytogenic with neutral pH (around 6-7) after the purification, it can be safely introduced to soil.

5. Conclusion

1. The results obtained allow us to conclude that obtaining sunflower husk-based sorbents, as well as the re-use of husk waste, is a promising enterprise. When combined with melanin production, complex processing of sunflower husk is proposed to manufacture adsorbents. It is also possible to obtain sorbents using the melanin extraction technology independently. Such technologies include alkaline extraction and intensification of the process by various types of physical impact, as well as a number of adjustments for the pH-medium selection and temperature conditions.

2. Optimal technological parameters for obtaining the adsorbent based on husk sunflower, according to the proposed method are:
   - treatment in 0.5 M sodium hydroxide solution for 45 minutes in a microwave field with a specific power of 0.5 W / cm$^3$;
   - 1:5 mass ratio of husk to hydroxide sodium solution.

3. When treating water with sunflower husks-base sorbents almost complete recovery of Cu$^{2+}$ ions within two hours and Fe$^{2+}$ ions within one and a half hours takes place. Adsorption capacity of the material ranges from 5 to 25 mg of metal per gram of adsorbent depending on concentration, as exemplified by copper and iron ions.

4. Utilization of spent sorption materials is also proposed. Because of the phytogenic nature of the sorbent base with neutral pH values after purification (around 6-7), it can be introduced to soil as a microelement fertilizer supplement containing copper, iron, and zinc.

5. The results of experimental studies show that the obtained sorption material is highly active to copper and iron ions. Sorption capacity of adsorbents based on melanin waste is somewhat lower, but still technologically acceptable. In addition, since it is possible to utilize the production waste without further processing, these materials are certainly advised for commercial use.
6. References

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