Purification of Colored Aqueous Solutions in the Adsorption Process on Magnetite Modified with Polymers †

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Abstract: Colored industrial wastewater is a threat in many environmental aspects. As such, there is a need to find more effective methods for its purification. This article presents a brief overview of available methods for removing dyes from aqueous solutions, among them the adsorption process, which is the subject of this study. The course of preliminary tests on the process of cleaning dye solutions in the adsorption process is presented. Unmodified magnetite and magnetite modified with polymers were used as adsorbents. The synthesis of particular types of magnetite, the adsorption process, as well as the methods of further analyzes are described. As part of the work, the focus was put on a comparison of the effectiveness of the purification process for different types of adsorbents in relation to selected dyes. The varied conditions of the process were also analyzed. It has been shown that magnetite is an adsorbent that is easy to use, allowing effective separation of dyes of various chemical structures from aqueous solutions. The effectiveness of the process depends on the type of dye and on the pH value and can be increased in relation to some dyes by using magnetite modification with selected polymers.

Keywords: dyes; adsorption on magnetite; magnetite synthesis; magnetite modified with polymers

1. Introduction

Industries such as the textile, food, dyeing and cosmetics are constantly developing. As part of the activities of these industries, many different dyes are used. As a result of production processes, these dyes may get into the environment in the form of colored wastewater, whose presence is becoming more and more common and onerous. The dyes can cause the worsening of the phenomenon of oxygen deficit and disturbances in photosynthesis in water reservoirs. In addition, industrial wastewater is characterized by high chemical and biochemical oxygen demand (COD, BOD₅) values, as well as the presence of suspended solids. Due to the toxic and pathogenic properties of some dyes (muta- and carcinogenic effects), the dyes also pose a threat to living organisms. As such, there is a need to find more effective ways of achieving their separation. There are several different methods for separating dyes, including membrane techniques, deep oxidation processes, electrocoagulation, and adsorption [1–3]. Adsorption is a fundamental physicochemical process in the technology of water purification, which consists of the transfer and accumulation of substances between phases, and its driving force is surface affinity. In this process, many adsorbents with a developed surface are used, with adsorbents divided into natural and synthetic ones. Ashes, zeolites, and biomass can be distinguished in the first group. Synthetic adsorbents include silica gels and activated carbon. The adsorbents also include magnetic iron oxides, such as maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), or magnetite (Fe₃O₄), the latter of which was used in presented experiments.
The aim of this research was to compare the effectiveness of the adsorption process carried out with the use of unmodified magnetite and magnetite that was modified using two types of polymers. The solutions of five dyes with different characteristics were subjected to the purification and the impact of various pH values used in the process was analyzed.

2. Materials and Methods

2.1. Dyes, Magnetite, and Polymers Used for the Modification of Magnetite

For this study, the following dyes were used: methyl blue, methylene blue, methyl orange (POCH), Acid Green 16, and Acid Red 18 (Boruta-Zachem S.A., Bydgoszcz, Poland). They differ in chemical structure, which has a direct impact on the subsequent efficiency of the adsorption process. In the separation of dyes, Fe₃O₄ magnetite was used. This iron oxide works well as an adsorbent due to its well-developed surface. Magnetite belongs to ferrites and is commonly found in the Earth's crust as a natural mineral. It is used as a black pigment, an electrode material, and a material for absorbing microwaves. It is characterized by natural magnetic properties that disappear above 580 °C. The magnetic properties of Fe₃O₄ are also used in sorption processes, as they facilitate the subsequent separation of purified solutions from the adsorbent, which positively contributes to further analyzes. To improve adsorption efficiency, two magnetite modifications were carried out using sodium polyacrylate (PSA) and polyethyleneimine (PEI). These substances are not only surface modifiers, but they can also act as stabilizers that protect magnetite against reaction with oxygen.

2.2. Magnetite Synthesis

For each test, magnetite synthesis was carried out separately. It was obtained by the reaction of chemical co-precipitation from a solution of iron(II) sulfate and iron(III) chloride using a 25% ammonia solution, according to the reaction (1):

\[
\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 \downarrow + 8\text{NH}_4^+ + 4\text{H}_2\text{O} \quad (1)
\]

Iron salts in the amounts of 4.2 g of FeSO₄ · 7H₂O and 6.1 g of FeCl₃ · 6H₂O were dissolved in distilled water heated to 30 °C. This mixture contained a reduced content of iron(III) in relation to the stoichiometric quantity, as a result of having conducted a synthesis reaction in the ambient temperature and the resulting possibility of iron(II) oxidation to iron(III), in accordance with the methodology used by Bobik et al. [4]. To initiate the precipitation of magnetite, 20 cm³ of 25% aqueous ammonia solution was added to the prepared salt solution followed by the addition of 50 cm³ of deionized water (unmodified Fe₃O₄) or 1% polymer solution (modified Fe₃O₄). The resulting magnetite was subsequently subjected to mixing for 30 minutes, pH measurement, and then the precipitate was washed three times with distilled water. All reagents used in the synthesis were provided by Stanlab Poland.

2.3. Adsorption Process, Separation, and Analysis of Purified Solutions

A suitable amount of suspension containing 50 mg of adsorbent was dosed into dye solutions of 50 mg/dm³ and pH was corrected to the appropriate value of 3 or 8. Mixtures prepared in this way were shaken for 8 hours (260 rpm, shaker LCD digital orbital, SK-O330-Pro, ChemLand, Stargard Szczeciński, Poland). After the adsorption process, the pH value was re-measured and the magnetite and the solution remaining after sorption were separated. This process was quick and simple due to the magnetic properties of the adsorbent and because its sedimentation was assisted via the use of a neodymium magnet. The starting solutions used in the research and the collected solutions without magnetite after the adsorption process were subjected to spectrophotometric measurements (spectrophotometer DR 500, HACH LANGE) at the following wavelengths for each dye: methyl blue—590 nm; methylene blue—665 nm; methyl orange—465 nm; Acid Green 16—640 nm; Acid Red 18—505 nm. On the basis of the measured absorbance values and the standard curves, the concentrations of dyes in solutions were determined.
The percentage efficiency of the adsorption process was calculated based on the value of the concentration of pigments before and after sorption, according to formula (2):

$$\eta = \frac{C_i - C_f}{C_i} \cdot 100\%$$  \hspace{1cm} (2)

where \(\eta\) is the process efficiency, \%; \(C_i\) is the initial concentration of dye, mg/dm³; and \(C_f\) is the final concentration of dye, mg/dm³.

In addition to the percentage efficiency of the process, the sorption capacity was calculated for each of the sorbents. Sorption capacity determines the amount of dye that has been removed in the purification process per unit mass of the adsorbent. The values were calculated according to formula (3):

$$q_e = \frac{m_i - m_f}{m_a}$$  \hspace{1cm} (3)

where \(q_e\) is the sorption capacity, mg/g; \(m_i\) is the initial amount of dye, mg; \(m_f\) is the final amount of dye, mg; and \(m_a\) is the adsorbent mass, g.

3. Results and Discussion

The observed efficiency of dye separation is influenced by several factors, mainly the surface charge of the adsorbent and the type of functional groups present in the dye molecule. Magnetite molecules in the solution undergo hydration, which makes the surface covered with hydroxy groups (~Fe−OH). As a result of the acid–base balance, these groups can achieve a positive charge (~Fe−OH₂⁺) at low pH values and a negative charge (~Fe−O⁻) under alkaline conditions.

The zeta potential value can be a measure of the resultant surface charge of magnetite nanoparticles in the solution. The characteristic point in the assessment of this charge is the isoelectric point, the pH at which the zeta potential takes the zero value (pH_{iep}). The pH_{iep} value for synthesized magnetites usually found in the literature ranges from 6 to 6.6 [5], although there are publications in which the authors point to lower (pH_{iep} = 5 [5]) and higher (pH_{iep} = 8 [6]) values. At pH < pH_{iep}, the resultant surface charge of the magnetite particles is positive, whereas at pH > pH_{iep} the negative charge prevails on the adsorbent surface. In addition, the type of the modifier used may affect the position of the magnetite isoelectric point. The pH of the solution will also be of great importance with regard to the type of adsorbate and functional groups that are contained in its structure. The sodium polyacrylate has carboxylic groups that are capable of dissociation so that it can get a negative charge. Polyethylenimine contains primary, secondary, and tertiary amino groups that can undergo protonation under acidic conditions, resulting in a positive charge. Using these two different modifiers, modified magnetites with different properties are obtained.

Table 1 presents the obtained results of the adsorption efficiency of each type of dye for unmodified magnetite (M_NM), magnetite modified with sodium polyacrylate (M_PSA), and magnetite modified with polyethylenimine (M_PEI).

|          | Efficiency of the Adsorption Process, % |
|----------|-----------------------------------------|
|          | Methyl Blue    | Methylene Blue | Methyl Orange | Acid Green 16 | Acid Red 18 |
| **M_NM** | pH 3 98.45    | 36.74         | 80.59        | 91.04        | 86.84       |
|          | pH 8 86.48    | 54.70         | 35.56        | 38.06        | 18.71       |
| **M_PSA**| pH 3 96.17    | 67.75         | 41.91        | 46.52        | 49.72       |
|          | pH 8 58.27    | 98.10         | 18.96        | 41.65        | 3.92        |
| **M_PEI**| pH 3 99.35    | 41.78         | 85.20        | 74.50        | 71.45       |
|          | pH 8 97.70    | 35.79         | 82.60        | 82.48        | 97.54       |
Based on the results obtained, it can be seen that the values of the process efficiency are determined by the type of adsorbent used. An example is the Acid Red 18 dye, whose separation efficiency at pH 8 was 3.92% for magnetite modified with PSA and 97.54% for magnetite modified with PEI. This is directly related to the functional groups of these polymers. Another significant factor was the pH value of the process. Its effect is visible, for example, in the case of the Acid Green 16 dye in the process using unmodified magnetite. Under acidic conditions (pH 3), the separation efficiency of this dye was 91.04%, and under alkaline conditions (pH 8) the separation efficiency was 38.06%. Under the conditions of the experiment, the highest (more than 90%) removal of individual dyes from solutions was obtained in the following systems:

- methyl blue—unmodified magnetite (pH 3), magnetite modified with PSA (pH 3), and magnetite modified with PEI (pH 3, 8),
- methylene blue—magnetite modified with PSA (pH 8),
- Acid Green 16—unmodified magnetite (pH 3),
- Acid Red 18—magnetite modified with PEI (pH 8).

Sorption capacity was in the range of 0.78–19.87 mg/g and depended on the type of dye, type of magnetite, and the pH value.

4. Conclusions

This work presents the possibility of using adsorbents, obtained on the basis of magnetic iron oxides, for the separation of dyes from aqueous solutions. It was shown that magnetite synthesized in laboratory conditions by co-precipitation from iron(II) and iron(III) salts, as well as its modifications carried out using sodium polyacrylate and polyethyleneimine, can be effective adsorbents in relation to such dyes as methyl blue, methylene blue, methyl orange, Acid Green 16, and Acid Red 18. Adsorption processes carried out at two different pH values (3 and 8) confirmed that the pH of the solution is an important parameter that exerts a strong influence on the efficiency of the process. In addition, it was found that the effectiveness of dye separation was dependent on the type of adsorbent used. Depending on the pH and the type of dye, it was possible to obtain a very high efficiency (>90%) of the separation process using both unmodified and modified magnetites.

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Conflicts of Interest: The authors declare no conflict of interest.

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