SORPTION OF METHYLENE BLUE BY ALTERNATIVE ADSORBENTS

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Abstract

The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. Dyes are generally removed by conventional sorbents. This article discusses the use of adsorbents from the waste metal production (low-cost sorbents), red mud (RM) and black nickel mud (BNM), to remove methylene blue solution (MB) under different test conditions, such as time and temperature of sorption and weight of sorbent samples. From the obtained data, we can claim that the highest achieved sorption efficiency was achieved by a RM sorbent at 60 °C after 48 hours of sorption with all three weights of samples (83.01 – 83.72%).

Key words

Red mud, black nickel mud, sorption efficiency

INTRODUCTION

Many industrial processes use a variety of synthetic chemical dyes for various uses. The industries like paper and pulp manufacturing, dyeing of cloth, textiles, leather treatment, printing, food products etc. used dyes and the effluents released from these industries bear large amounts of coloured wastes. It has been estimated that about 800,000 tons of synthetic dyes are produced annually and ~50% of these are azo dyes) [1].

It is estimated that approximately 15% of the dye stuffs are lost in industrial effluents during manufacturing and processing operations [2].

Dyes exhibit a complex aromatic molecular structure and are generally resistant to light, temperature and oxidizers. These characteristic features make the dye non-degradable, causing bioaccumulation in living organisms and leading to severe diseases and disorders.

Methylene blue (MB) is a cationic dye having various applications in chemistry, biology, medical science and dyeing industries. MB is the most commonly used substance for dyeing

cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [3].

Nowadays, great attention has been focused on elimination of the effluents bearing dyes, owing to their potential toxicity and visibility problems.

Colour is conventionally removed by chemical precipitation and biological oxidation. However, these processes are not always effective and economical where the solute concentrations are very low. Moreover, most of the synthetic organic dyes undergo a very slow biodegradation. Currently the sorption technique is proved to be an effective and attractive process for the treatment of the dye containing wastewater [2].

Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several researchers. These materials could be used as adsorbents for the removal of dyes from solution.

Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation [4, 5], sonochemical degradation [6], micellar enhanced ultrafiltration [7], cation exchange membranes [8], electrochemical degradation [9], adsorption/precipitation processes [10], integrated chemical–biological degradation [11], integrated iron(III) photo assisted-biological treatment [12], solar photo-Fenton and biological processes [13], Fenton-biological treatment scheme [14] and adsorption on activated carbon. [15, 16] As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, their adsorption on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater [17].

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [3].

MATERIALS AND METHODOLOGY OF EXPERIMENT

In the experiment described in this article, we applied sorption to remove MB using low-cost sorbents – red mud (RM) and black nickel mud (BNM).

Red mud is obtained from the Al_2O_3 production by the Bayer method, in which the bauxite is leached with sodium hydroxide under high pressure and temperature. Dissolved sodium aluminate is precipitated and calcined after cleaning in the next steps [18].

Red mud is a stable mixture of chemical compounds and a subject with a stable structure of a known and typical chemical composition [19]. In Slovakia, aluminium oxide was produced mainly by sintering in the aluminium mill in Žiar nad Hronom from 1957 to 1997 [20, 21]. The studied sample of the red mud sorbent came from the above-mentioned ash pond.

Black nickel mud represents the waste from the nickel and cobalt production process from the imported Albanian iron-nickel lateritic ore containing 1 % nickel. It is a fine material with a fraction mostly below 0.01 mm [22, 23].

Soldánová et al. (2009) state that the black nickel mud with a chromium and nickel residue is a substantially iron concentrate of a chemical composition [24].

Black nickel mud, which was used for the research purposes came from the waste landfill in Sered'. The Albanian iron-nickel ore has been processed in Niklová huta, š.p., Sered' since 1963 [22, 23]. This landfill lies at 125 m a.s.l. on the southern edge of Dolnovážska niva on the intersection of the cadastral areas of Sered' and Dolná Streda [22].

Pre-adjustment of the samples of red mud and black nickel mud was proposed to remove possible organic impurities that could have negative effect on sorption capacity of the sorbents.

Sorbents were annealed in a muffle furnace, VEB ELECTRO Bad Frankenhausen LM 312.11 at 600 °C for four hours, followed by cooling in a desiccator. Requested fraction of the samples (< 500 µm) was obtained by sieve analysis.

In the experimental part, the efficiency of the sorption of the 3,5-dichlorophenol with the sorbents and the influence of the sorption conditions (Table 1) were observed. Homogenisation of the solution was performed by a HEIDOLPH Promax 1020 shaker, at a rate of 160 T min⁻¹. Tested samples were stirred throughout the whole time of sorption. During investigating the effect of temperature (using the MEMMERT 100-800 dryer) on sorption, the shaker was not used, and the homogenisation of the solution was performed manually. Subsequently, the samples were, at specified time, placed in a JANETZKI T30 centrifuge for 10 minutes, at a rotational speed of 2000 – 3000 g to sediment the small, undesirable, particles of sorbent. The loss of MB was determined by spectrophotometer GENESYS 8 in UV/VIS area (500 – 800 nm). The highest light absorbance (amount of light absorbed by the material) of MB is at 670 nm. The achieved value of absorbance (at 665 nm) was used to calculate the efficiency of absorbents according to (1):

$$\eta_t = \frac{A_0 - A_t}{A_0} \times 100 [\%], \quad (1)$$

where: η_t – sorption efficiency,

A_0 – detector response of MB sample concentration,

A_t – detector response after sorption.

Table 1 Test condition of chosen low-cost sorbents in the process of MB sorption (author)		
Sorbent weight (g)	Temperature (°C)	Time (h)
0.2	25	1
0.4	40	2
0.6	60	3
		24
		48

RESULTS AND DISCUSSION ON RESULTS

In Figure 1, we can see the sorbent efficiency of Red mud (RM) a Black nickel mud (BNM) at 25 °C, with three different weights of sorbent. The sorption efficiency of RM and BNM achieved in the first three hours of sorption was 0 % and 0.32 – 4.32% respectively. At the sorption time of 24 and 48 hours, the RM sorbent achieved a relatively low sorbent efficiency, at the range of 0.43 – 4.67%. Higher sorption efficiency was achieved by BNM (0.6 g) after 24 hours (19.31%) and after 48 hours (34.62%).

Fig. 1 Sorbent efficiency at 25 °C

Although no sorption occurred during the first three hours of sorption at 40 °C in any of the tested sorbents, the long-term sorbent efficiency was higher compared to the previous measurement, as shown in Figure 2. The highest sorption efficiency of BNM achieved at 0.6 g after 48 hours (40.28%) was slightly higher than that at 25 °C. Efficiency of RM was significantly improved at this temperature after 24 and 48 hours of sorption, and after 48 hours it reached 34.01% (0.2 g), 50.49% (0.4 g) and 55.38% (0.6g).

Fig. 2 Sorbent efficiency at 40 °C

Sorption efficiency of selected sorbents at 60 °C is shown in Figure 3. As in previous measurements, sorption efficiency of all samples during the first three hours was zero. After 24 hours, sorption efficiency of all sorbents exceeded 60% (except 0.2 g BNM, which reached 27.17%). Although the highest values were reached at 48 hours of sorption with RM sorbents (83.01 – 83.72%), efficiency of these sorbents after 24 hours is negligibly lower (80.28 – 80.9%), thus more effective in the economical way.

Fig. 3 Sorbent efficiency at 60 °C

CONCLUSION

Based on the results stated above, we can say that two of the tested parameters (time and temperature) have a significant impact on sorption efficiency. Time of the sorption is an important parameter as it influences the costs and simplicity of the operation. Our findings suggest that the sorption time should be at least 24 hours, as no (or negligible) sorption occurred in the first three hours of the sorption. After 24 hours, the sorption effectivity increased in both cases.

Temperature of the operation also has a positive influence on the sorption efficiency. The highest values of efficiency were achieved at 60 °C, particularly 80.28 – 83.72%. Weight of the sample has lower impact on the overall sorption efficiency.

From the two tested sorbents, red mud and black nickel mud, RM achieved higher sorption rates at increased temperature (40, 60 °C). We can assume that it is due to different chemical composition, and higher adsorption-active oxide content. However, as low-cost sorbents, they both are effective for methylene blue dye sorption under right conditions.

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