MINING AND METALLURGY INSTITUTE BOR

and

TEHNICAL FACULTY BOR, UNIVERSITY OF BELGRADE

53rd International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:

Ana Kostov
Milenko Ljubojev

3 – 5 October 2022

Hotel "Albo" Bor, Serbia

53rd International October Conference on Mining and Metallurgy

Editors: Ana Kostov, Milenko Ljubojev

Publisher: Mining and Metallurgy Institute Bor

Printed in: "GRAFOMED-TRADE" Bor

Text printing preparation: Vesna Simić

Disclaimer: Authors are responsible for the content, translation and accuracy.

Circulation: 100 copies

CIP – Каталогизација у публикацији
Народна библиотека Србије, Београд

622(082)
669(082)

INTERNATIONAL October Conference on Mining and Metallurgy (53 ; 2022 ; Bor)
Proceedings / 53rd International October Conference on Mining and Metallurgy - IOC 2022, 3 % 5 October 2022, Bor ; [organizer] Mining and Metallurgy Bor and Technical Faculty in Bor, University of Belgrade ; editors Ana Kostov, Milenko Ljubojev. - Bor : Mining and Metallurgy Institute, 2022 (Bor : Grafomed-trade). - XV, 251 str. : ilustr. ; 25 cm

Tiraž 100. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-7827-052-9

a) Рударство - Зборници b) Металургија - Зборници

COBISS.SR-ID 74763529

Bor, October 2022

Conference is financially supported by the
Ministry of Education, Science and Technological
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IMMOBILIZED BENTONITE IN THE ALGINATE MATRIX – EFFICIENT SORBENT OF BRILLIANT GREEN

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Abstract

The environmental pollution by dyes has become an important concern due to the harmful effects on human health and entire ecosystem. In this study, bentonite immobilized in calcium-alginate (ImB) was studied as a sorbent for the Brilliant Green (BG) removal from aqueous solutions. The prepared composite sorbent was characterized by pH_{pzc}, SEM and EDX. The sorption kinetic was best fitted by the pseudo-second-order model and simultaneously followed the film diffusion and intra-particle diffusion model during the sorption. This study proved that ImB might be an efficient sorbent for removing dyes from aqueous solutions.

***Keywords**: bentonite, immobilization, adsorption, brilliant green, water purification*

1 INTRODUCTION

Dyes are widely used in industry, including textiles, paper, food, cosmetics and printing. Most dyes are toxic and not biodegradable, which is essential to remove them from the contaminated water before being discharged into the mainstream [1,2]. The toxic, mutagenic and carcinogenic Brilliant green (BG) is one of the typical cationic dyes, vastly used as a dermatological agent, biological marker, veterinary medicament, additive to poultry feed to inhibit expansion of vermin and to dye textiles. [3]. It is also hazardous in case of skin contact, eye contact and ingestion, and may cause the respiratory diseases. Additionally, the decomposition of BG may produce carbon monoxide, carbon dioxide, nitrogen oxide and sulfur dioxide which contribute to the greenhouse effect [4]. Therefore, similarly to the other dyes, it is necessary to remove it before being disposed of in the environment. Because the adsorption process is a simple and effective method, it is the most commonly employed in the BG removal, among all other processes including ion exchange, membrane filtering, coagulation-flocculation, flotation, electrochemical processes, and reverse osmosis.

Bentonite is a low-cost sorbent with lamellar and microporous structures, low hydraulic conductivity, and strong swelling capacity, and is one of the most abundant natural clay minerals [5]. However, raw bentonite powder generally has a low adsorption capacity and is difficult to separate from wastewater, which is considered due to its immobilization. Calcium alginate is a non-toxic, biodegradable material which is widely used for immobilization [6]. In this way, the capacity of bentonite for dye sorption, separation efficiency and feasibility in the contaminated water treatment process is improved.

Therefore, the main objectives of this study were to characterize and investigate the adsorption behavior of bentonite powder trapped in Ca-alginate for the BG removal from wastewater.

2 EXPERIMENTAL

Bentonite was taken from the deposit "Bijelo Polje" from Bar. The sample was milled (particle size < 37 µm) and further immobilized in sodium alginate using a method described by Zdujić et al., [7]. The immobilization led to the creation of spherical particles (Figure 1(b)), easily removable from water solution, which might be used in packed flow system.

A stock solution of BG concentration of 1000 mg/L was obtained dissolving 1.0 g of dye in 1.0 L of distilled water. Solutions of desired concentration were prepared by dilution of stock solution with distilled water.

The ImB's point of zero charge (pH_{pzc}) was determined by the method described elsewhere [8].

The morphology of ImB was analyzed by the Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX) after coating of samples with gold. The SEM-EDX analysis was performed using a JEOL JSM-6610 LV SEM model (JEOL Ltd., Japan).

In order to evaluate the kinetic mechanism that describes the sorption, the three reaction-based models were evaluated: the pseudo-first order, pseudo-second order and Weber-Morris intra-particle diffusion model. Kinetic parameters for the sorption process were studied adding 0.1 g of ImB to 50 mL solution with the initial BG concentration of 50 mg/L, at different time intervals from 2 to 420 minutes, at pH 6.8 and at room temperature. Following that, the amount of BG removed was calculated.

3 RESULTS AND DISCUSSION

The point of zero charge (pH_{pzc}) is a pH value at which the total positive charge on an adsorbent surface equals the total negative charge on it, showing the pH value on which sorbent has surface zero charge. For ImB, the point of zero charge is determined to be 7.02. At higher pH values, the ImB surface is negatively charged, while at lower pH values, the ImB surface is positively charged. Due to the fact that BG is a cationic dye, the sorption is enhanced at pH values higher than pH_{pzc}. Based on the operating pH and the obtained pH_{pzc}, it can be concluded that the physical adsorption does not occur, which was confirmed by a kinetic study. According to Nandi et al. [9] study, which was focused on BG removal using the sorbent based on kaolin, similar value of the point of zero charge (pH_{pzc} =7.0) was obtained at the same operating pH.

The SEM micrograph of bentonite, immobilized in calcium-alginate, is presented in Figure 1 (a). The structure is assembled of crosslinked polymer networks with the ionic bonding of Ca^{2+} and carboxyl groups. The heterogeneous and rough surface, caused by numerous bulges on the ImB composite, was noticed. Elemental analysis of ImB by EDX (Fig. 1 (c)) confirmed the presence of Oxygen (O), silicon (Si), calcium (Ca), aluminum (Al), chlorine (Cl), magnesium (Mg) and traces of iron (Fe), sodium (Na) and potassium (K), which indicates a possible cation exchange.

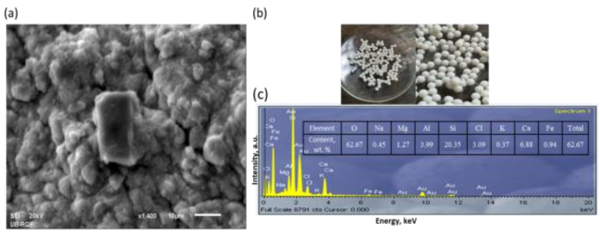

Figure 1 *SEM-EDX analysis of ImB sample (a) SEM micrograph; (b) imB particles; (c) EDX analysis results*

Since the kinetics study provides the information like adsorption rate, adsorbent performance, and mass transfer mechanisms, it is fundamental for the description of sorption systems. Sorption of BG onto Imb was investigated using the pseudo-first order, pseudo-second order and intraparticle diffusion model. Table 1 summarizes the obtained parameters.

Table 1 *Adsorption kinetic model parameters for sorption of BG on Imb*

Model	Parameter	Imb
Pseudo-first order	q_e (mg/g)	27.9494
	k_1 (min^{-1})	0.0139
	R^2	0.9793
	χ^2	2.2010
Pseudo-second order	q_e (mg/g)	35.9176
	k_2 (g/mg/min)	0.0004
	R^2	0.9852
	χ^2	1.5784
Intraparticle diffusion	K_d (mg/(min$^{1/2}$g))	2.0212*
		0.1486**
	C	0.5745*
		24.4360**
	R^2	0.9967*
		0.8337**

* - first slope, ** - second slope

From the parameters presented in Table 1, it can be seen that the pseudo-second order better fits the experimental data compared to the pseudo-first order model. The pseudo-second order showed a higher correlation coefficient (R^2=0.9852) and lower chi-squared value (χ^2=1.5784) than the pseudo first order (R^2=0.9793, χ^2=2.2010), which indicates that the sorption rate is controlled by the chemisorption. Mane et al. [10], also reported that the pseudo second order kinetic model could fit well to explain the BG sorption on fly ash.

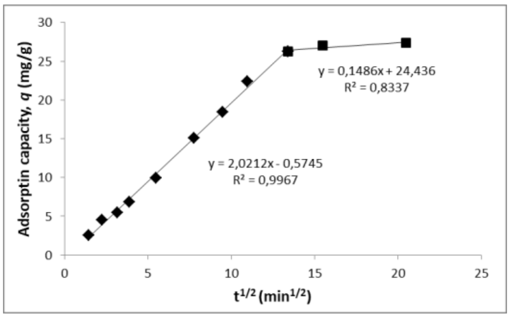

Figure 2 *Intra-particle diffusion model for the sorption of BG on Imb*

Figure 2 presents the intra-particle diffusion model for the BG sorption onto Imb, which takes place through two stages. In the first stage (straight line), which lasts for almost 200 minutes, the sharp rise of slope signifies that the BG molecules are transported to the external surface of the Imb through a film diffusion and its rate is very fast. This might be a consequence of numerous cations present on the ImB surface, which are firstly exchanged with BG. After the surface is saturated, the dye molecules slowly diffuse into the Imb by the intra-particle diffusion through the pore until equilibrium is reached, as shown by the second straight line in Figure 2. Since there is no equilibrium line, it can be concluded that the time necessary for sorbent surface saturation is much higher than 420 minutes, as we did in these experiments.

4 CONCLUSION

In this paper, the characterization and sorption kinetics of immobilized bentonite for BG removal were examined. The SEM micrographs showed that sorbent ImB has regular, spherical rough structure, suitable for binding of dye molecules. Sorption kinetics followed the pseudo second order model, suggesting that chemisorption is the rate-limiting step. The intra-particle diffusion study revealed that both film diffusion and intra-particle diffusion were employed during the sorption of BG on Imb. Evidently, the synergistic effects of low-cost bentonite and alginate, enabled obtaining an efficient sorbent for BG removal from the aquatic environments. Anyway, further research with this material should be conducted, in order to reach equilibrium time and improve overall sorption kinetics.

ACKNOWLEDGEMENTS

The results and discussions in this study are a part of research funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200023).

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