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Preparation and use of alginate-based composites with the addition of graphene oxide for the removal of dyes

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ABSTRACT

Industrial wastewater containing dyes is a significant burden to the environment. Many physicochemical methods have been used to remove these compounds. An interesting solution is the use of sorbents of natural origin. This paper describes a method for obtaining sorbents in the form of composite granules formed from a 2% alginate solution with the addition of 2.81% solution of graphene oxide (GO). The possibility of using the obtained granules for removing cationic dyes (methylene blue, rhodamine B, toluidine blue, Victoria blue B) and anionic dyes (orange II, Congo red, methyl blue) was investigated. As a result of the research it was demonstrated that the chemical and structural composition of the dye has a decisive influence on its sorption on composite granules. In cationic dyes, the number and order of amino groups are responsible for the rejection. In anionic dyes, on the other hand, the rejection factor increases with the number of sulfone groups. The granules obtained in the experiment can be successfully used to remove cationic dyes, achieving high rejection values (~100%), most quickly and efficiently removing dyes containing one such group (toluidine blue). In the case of anionic dyes, the highest rejection values (~80%) were obtained for methyl blue, which has three sulfone groups.

Keywords: alginate, graphene oxide, sorbent, cationic dyes, anionic dyes.

INTRODUCTION

Dyes are widely used by textile, tanning, paper, plastic, construction, cosmetics, pharmaceutical, food and many other industries [Ye et al., 2017; Zhu et al., 2015. Chemically, they are organic compounds of natural or synthetic origin that selectively absorb visible light in the range of 400 to 700 nm and have the ability to dye materials [Gürses et al., 2016]. One of the major industries in the world is the textile industry, which is highly water-intensive (2–180 L of water per 1 kg of textile products [Ong et al., 2014]) and produces huge amounts of wastewater containing waste textile dyes [Hayat et al., 2015], of which more than 80% of all dyes are the azo dyes [Tiwari et al., 2023]. In addition to dyes, they contain suspended solids, dispersants, bases, acids, detergents, salts, oxidants, surfactants, inhibitory compounds, grease and oil, toxicants, etc. [Hayat et al., 2015; Ong et al., 2014]. Wastewater with high content of dyes is rather dark in color [Raksaman et al., 2024]. A wide range of methods used to treat dye-polluted wastewater has been invented in recent years. These include biological methods (enzymes, microorganism), oxidation methods (chemical and advanced oxidation) and physical methods (filtration, flocculation, adsorption) [Holkar et al., 2016]. Since cost reduction is always a primary consideration, the most popular of these methods is adsorption, which can reduce organic and inorganic pollutants in wastewater [Wang et al., 2022].

Biopolymers, and more specifically alginic acid salts, provide the basis for adsorption composite materials [Li et al., 2024]. Sodium alginate is a non-toxic polymer which is found in the cell walls of brown seaweeds, for example of *Phaeophyceae* class. It is biodegradable [Such et al., 2023]. Chemically, it is a polysaccharide composed of mannuronic and guluronic acid units connected by a 1,4-β-glycosidic bond [Abka Khajouei et al., 2022]. This polymer has hydroxyl and carboxyl groups that form hydrogen bonds [Fernando et al., 2020]. In the presence of divalent and trivalent metal ions, alginate is cross-linked due to electrostatic attraction and a gel is formed [Mohammed et al., 2022]. Alginate-based composite materials with the addition of cellulose [Chen et al., 2024; Zha et al., 2024], biochar [Tao et al., 2024], montmorillonite [Fernández-Sainz et al., 2024], chitosane [Li et al., 2023], inorganic nanomaterials [Obireddy et al., 2023], and graphene-based materials [Ahmed et al., 2024; Li et al., 2024].

Graphene oxide (GO) is an oxidized derivative of graphene. It has the form of a two-dimensional layer in which oxygen functional groups (hydroxyl, epoxy, carboxyl, carbonyl, and phenol) are located on both sides of the plane and on its edges [Singh et al., 2016]. The presence of functional groups impacts the GO's ability to form stable aqueous dispersions. Moreover, reacting with these groups to functionalize the GO surface is possible, which broadens the scope of its application [Smith et al., 2019; Zhao et al., 2022]. Due to its good dispersibility in polymer matrices, GO can be used as an additive to composites in the form of membranes, fibers and granules [Smith et al., 2019]. Graphene oxide has also strong antibacterial properties [Chen et al., 2024].

The diversity of oxygen functional groups arranged on the GO surface makes it easy to be dispersed in polymer with functional groups [Hwang et al., 2016]. One such polymer is alginate, from which a composite membrane with the addition of GO was obtained and used to remove Congo red [Zhao et al., 2022] and other dyes, such as: Coomassie brilliant blue, Direct black 38, Amaranth red [Zhao et al., 2022]. The literature also reports about the possibility of using three-component composite membranes (sodium alginate/GO/chitosan) for the removal of methylene blue and Congolese red [Li et al., 2023]. Azo dyes: reactive blue 4, indigo carmine and acid blue 158, on the other hand, were removed using an alginate-based composite with hydroxyapatite-modified GO [Sirajudheen et al., 2021]. Ma et al. analyzed the possibility of removing cationic dyes using alginate-based granules with the addition of chitosan and magnetite-modified GO [Ma et al., 2021]. The literature provides examples of obtaining alginate-based granules with the addition of GO for the removal of drugs [Fei et al., 2016; Tang et al., 2024] and dyes, such as: methylene blue [Platero et al., 2017], acid blue 113 dye [Tiwari et al., 2023].

In this paper, the possibility of using alginate-based composite granules with the addition of GO for the removal of acidic and basic dyes was investigated. Initially, alginate-based granules containing 0.18; 0.33; 0.66; 1.33; 2.84; 5.62% of GO (dried substance) were obtained. The granule coagulation time was shortened to 5 minutes, whereas other authors carried out this process for 3 hours [Arshad et al., 2020], 24 hours [Ahmed et al., 2024; Zhang et al., 2022], and even 2–3 days [Fei et al., 2016]. Both cationic dyes (methylene blue, Rhodamine B, toluidine blue, Victoria blue B) and anionic dyes (orange II, Congo red, methyl blue) were selected for the study of sorption properties. It was demonstrated that the granules obtained in the experiment can be successfully used to remove cationic dyes, and the sorption rate and high rejection values depend on the number of amine groups and their ordering. Furthermore, it has been shown that anionic dyes can be removed on alginate granules, and that the more sulfonic groups there are in the dye, the greater the degree of its rejection.

MATERIALS AND METHODS

Reagents

Sodium alginate (ALG) Congo red, methylene blue, methyl blue, orange II, rhodamine B, toluidine blue, Victoria blue B were purchased from Sigma-Aldrich. Anhydrous calcium chloride was purchased from PPH ”STANLAB” Sp. J.

Graphene oxide (GO) was obtained using a modified Hummers method as described in our previous publication [Fryczkowska, 2018]. GO synthesis was performed at the University of Bielsko-Biala. Thus obtained GO was dispersed in water using an ultrasonic cleaner, and a dispersion with a GO/H_2O concentration of 2.81% was obtained.

Preparation of granules

A 2% aqueous solution of sodium alginate (ALG) was prepared. For this purpose, into an appropriate amount of distilled water an appropriate amount of ALG was introduced, and mixed using a laboratory overhead stirrer OS20-Pro from Chemland at a speed of 800 [rpm] for 24 hours, and then was left to deaerate.

Subsequently, the alginate solutions containing the GO additive were prepared. To do this, appropriate amounts of 2.81% GO solution were added to appropriate amounts of 2% ALG solution to obtain solutions with subsequent GO/ALG concentrations (Table 1), which were mixed on a DLAB MS-H-S10 multi-point magnetic stirrer for approximately 72 hours. A 2.5% aqueous $CaCl_2$ solution was also prepared.

Granules were formed using a syringe with a capacity of 100 cm^3 and an internal diameter of 5.25 mm. Subsequent alginate solutions were added dropwise to beakers containing a 2.5% $CaCl_2$ solution using a syringe (Table 1). The granules were coagulated for 5 minutes, after which they were filtered, washed multiple times with water and drained again.

Two batches of granules were prepared. The first batch was stored in sealed vessels containing deionized water (Figure 1a). The second series of granules was air-dried to constant weight (Figure 1b).

Testing of physicochemical properties

In order to determine the physicochemical properties, the granule size, their bulk density, as well as water content and absorbance were studied. The granule size was measured using a POWERFIX digital caliper. 40 measurements were performed for dry granules. The wet granules, on the other hand, were dried using filter paper and the measurements were performed on 40 granules from each batch. The bulk density of the granules was determined by placing the granules in a tared graduated cylinder with a capacity of 10 cm^3 (for dry granules) and 50 cm^3 (for wet granules), and weighing them to an accuracy of 0.0001 g on an OHAUS analytical balance, model: Adventurer Pro model, TYPE AV264CM. Then, the bulk density for each type of granules was calculated using formula (1).

$$d = \frac{m}{V} \tag{1}$$

where: d – bulk density [g/cm^3]; m – sample mass [g]; V – sample volume [cm^3].

The water content tests in wet granules were performed by pre-drying the wet granules on filter paper and then weighing 8 g of samples using an analytical balance. The granule samples were air-dried to constant weight and then weighed again. The water content in the wet granule batch was calculated using formula (2).

$$W_c = \frac{M_w - M_d}{M_d} \times 100\% \tag{2}$$

where: W_c – water content [%]; M_w – wet sample mass [g]; M_d – dry sample mass [g].

Water absorption tests were also performed for a series of dry granules. For this purpose,

Table 1. Composition of composite granules forming solutions and their quantitative composition

Sample	Mass of a 2.81% GO/H_2O dispersion [g]	Mass of a 2% ALG solution [g]	GO content in the dry substance of GO/ALG granules [%]
A0	-	100	-
A1	0.1273	100.20	0.18
A2	0.2339	99.37	0.33
A3	0.4007	98.86	0.66
A4	0.9344	98.85	1.33
A5	1.9990	98.10	2.84
A6	4.0040	97.24	5.62

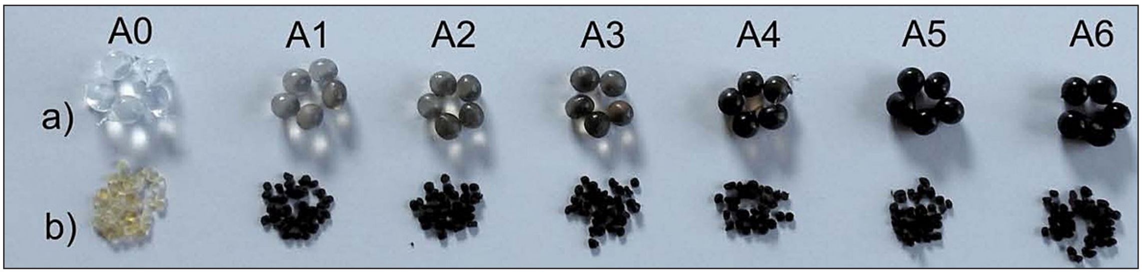


Figure 1. Pictures of a) wet and b) dry granules

1 g of samples from each batch (A0–A6) were weighed using an analytical balance. Then, samples of granules were placed in beakers and 10 cm^3 of distilled water was introduced into each of them. The samples were tightly sealed with Parafilm and left for 24 hours. After this time, the samples were filtered, dried on filter paper and weighed again. The tests have shown that the water absorption of dry granules was approximately 1%, which excluded them from further testing.

Study of the sorption properties

First, dye solutions (Table 2) with a concentration of 50 ppm were prepared. Then, measurements were performed using a Thermo-Scientific Evolution 220 series UV-Vis spectrophotometer by reading the wavelengths at which the absorbance maxima ($\lambda_{max.}$) occurred for the individual dyes. The obtained results are presented in Table 2. From the measurements performed, standard curves were prepared for the relationship between absorption and dye concentration.

The sorption properties of pure calcium alginate granules (A0) and GO/ALG composite granules (A1–A6) were studied in the following way. First, the granules (A0–A6) were filtered on filter paper and then samples of 4 g were weighed into beakers with a capacity of 20 cm^3. Then, 10 cm^3 of solution of the tested dye was added to each beaker, tightly closed with Parafilm and stirred for 24 hours using a magnetic stirrer. Test samples were collected at intervals of 5, 10, 30, 60 minutes and 24 hours. Measurements were performed for subsequent samples at appropriate wavelengths using an Evolution 220 series UV-Vis spectrophotometer (Table 2). The concentrations of the tested dyes were read from the previously prepared standard curves and the results are summarized in Table 3 and Table 4.

The degree of removal for from the aqueous solutions each dye was calculated using formula (3) [Platero et al., 2017].

$$R = \frac{(C_0 - C_1)}{C_0} \times 100\% \tag{3}$$

where: R – degree of removal [%]; C_0 – component concentration in solution before testing [ppm]; C_1 – component concentration in solution after testing [ppm].

RESULTS AND DISCUSSION

This paper describes a method for producing alginate-based granules with the addition of GO, which resulted in obtaining wet and dry granules. Physicochemical properties such as size (diameter), bulk density and water content in wet granules were determined. First, the diameter of the granules was measured and the results are summarized in Figure 2.

Pure alginate granules (A0) are slightly larger than the composite granules (A1–A6), both wet and dry (Figure 2). In the case of wet granules, the larger size of the A0 granules is visible even to the naked eye. The rapid coagulation process (5 minutes) of sodium alginate, during which crosslinking with $CaCl_2$ takes place, leads to the formation of A0 granules with a diameter of 7.4 mm. By analyzing the results obtained for wet composite granules, a clear impact of the GO addition on their size can be observed. Wet A0 granules have a diameter 20% (A6) to 30% (A1) larger than GO/ALG granules. The slightly smaller sizes of A1–A6 granules may be the result of the formation of hydrogen bonds between the carboxyl groups of alginate and the oxygen functional groups located on the GO surface [Ahmed et al., 2024]. The diameter of wet GO/ALG granules obtained in our experiment was very similar and ranged from 5.1 mm to 5.9 mm, which is comparable to the results obtained by Ahmed et al. [2024].

Drying the entire batch of wet granules resulted in an approximately 4.5 times reduction in their diameter (Figure 2). A0 granules are larger than GO/ALG granules and their diameter is 1.65 mm. The smallest amount of GO addition (0.18%) in A1 granules results in a diameter reduction of about 5.5%, as expected. The diameters of the remaining composite granules ranged from 1.21 mm (for sample A2) to 1.35 mm (for samples A3, A4, A5).

The bulk density of the granules was then studied and the results are summarized in Figure 3. Analyzing Figure 3 it can be observed that the bulk densities for wet and dry granules are similar and range from 0.56 g/gm^3 to 0.6 g/cm^3. For both granule batches, the bulk density values increase slightly from A0 to A6. These results are closely related to their diameter, which decreases with the amount of GO addition. Granules with a smaller diameter are, therefore, better packed in the same volume and therefore the bulk density values are higher. It is also important to remember that wet granules are larger and therefore more difficult to

Table 2. Dyes used in the experiment

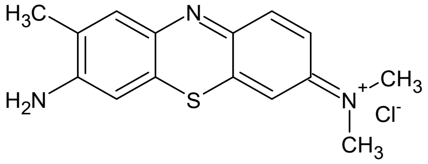
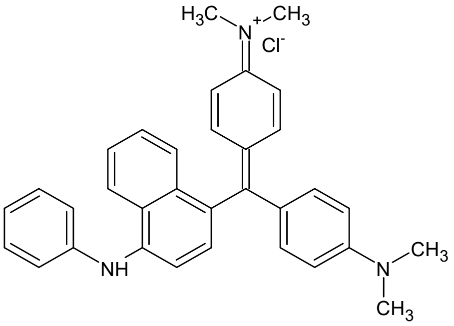
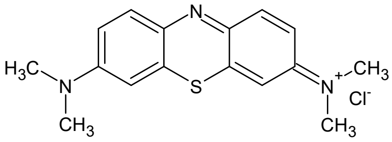
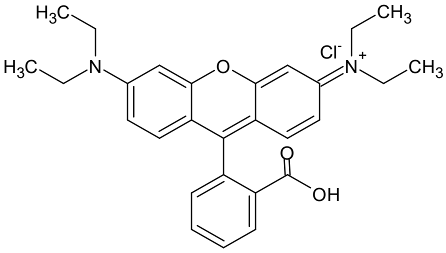
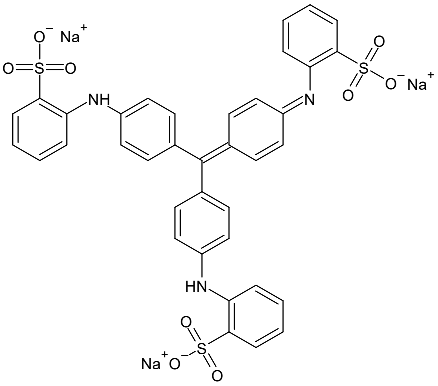
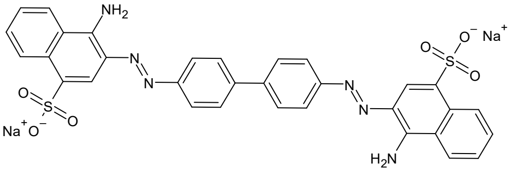
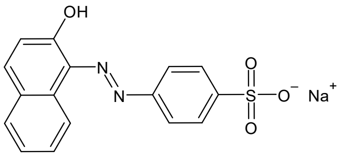
Type of dye	Name	Structural formula	$\lambda_{max.}$[nm]
Cationic dye (basic)	Toluidine blue		626
	Victoria blue B		619
	Methylene blue		598
	Rhodamine B		527
Anionic dye (acidic)	Methyl blue		598
	Congo red		499
	Orange II		481

Table 3. Concentrations of solutions of tested cationic dyes measured during sorption on granules

Parameter	Time [min]	Concentration of cationic dye in the sample [ppm]						
		A0	A1	A2	A3	A4	A5	A6
Toluidine blue	5	4.89±0.53	5.87±0.42	6.83±0.40	5.20±0.31	6.48±0.32	8.79±0.68	8.18±0.42
	10	3.49±0.11	2.88±0.25	2.86±0.23	2.60±0.25	3.44±0.45	2.95±0.25	2.68±0.25
	30	2.75±0.25	2.39±0.15	1.83±0.15	0.71±0.10	0.38±0.11	0.27±0.03	-
	60	2.19±0.24	1.50±0.01	0.27±0.15	-	0.4±0.05	-	-
	1440	0.15±0.02	0.52±0.03	-	-	-	-	-
Victoria blue B	5	12.52±0.44	13.70±0.47	11.27±0.48	14.02±0.24	16.27±0.02	23.37±1.56	20.08±0.53
	10	8.88±0.27	9.68±0.86	8.17±0.20	7.59±0.20	11.82±0.56	10.77±0.17	10.90±0.15
	30	4.74±0.27	4.42±0.56	3.92±0.18	3.77±0.21	4.95±0.57	4.24±0.41	4.10±0.18
	60	3.59±0.12	3.80±0.30	3.28±0.18	3.31±0.12	2.88±0.29	2.60±0.02	1.73±0.02
	1440	2.33±0.25	1.00±0.09	0.62±0.24	0.32±0.04	0.44±0.06	0.19±0.04	0.08±0.06
Methylene blue	5	18.03±2.19	16.89±1.54	18.44±1.46	18.93±0.49	25.75±2.60	19.09±0.65	32.90±0.41
	10	15.51±1.79	12.43±2.60	13.56±0.16	16.65±1.46	22.50±1.79	13.89±2.11	28.43±0.45
	30	12.59±1.60	11.37±0.11	16.08±0.24	11.04±0.14	18.03±0.73	10.23±0.08	27.46±0.28
	60	14.54±0.17	11.37±1.24	13.56±1.14	9.74±0.73	15.59±1.22	7.71±0.16	20.96±0.28
	1440	1.86±0.03	-	1.46±0.14	-	-	-	-
Rhodamine B	5	36.11±0.88	36.57±0.26	36.11±1.32	34.41±0.58	26.38±0.94	26.98±0.94	22.18±0.94
	10	35.29±0.26	34.71±0.24	34.27±0.48	27.82±1.78	20.92±0.28	20.42±0.86	15.56±0.56
	30	31.83±0.04	29.24±0.87	25.32±0.32	22.12±0.84	12.13±0.39	11.89±0.33	10.33±0.48
	60	30.85±0.42	25±0.16	19.76±0.20	18.72±0.80	8.05±0.16	5.65±0.24	2.73±0.08
	1440	27.82±0.02	25.04±0.28	15.74±0.58	19.02±0.54	4.05±0.56	-	-

Table 4. Concentrations of solutions of tested anionic dyes measured during sorption on granules

	Time [min]	Concentration of anionic dye in the sample [ppm]						
		A0	A1	A2	A3	A4	A5	A6
Methyl Blue	5	18.27±0.49	13.99±1.32	19.59±1.65	22.23±2.47	15.96±0.82	17.86±1.89	18.44±1.15
	10	10.69±1.65	12.75±1.89	15.55±0.91	9.04±0.01	10.20±0.66	15.39±0.41	17.53±0.74
	30	9.45±0.73	11.60±1.40	9.21±0.50	10.85±1.48	10.11±1.07	11.68±0.17	12.17±0.66
	60	8.22±0.99	12.09±0.41	10.94±1.71	9.95±1.06	4.92±0.17	10.85±0.66	11.35±0.13
	1440	9.21±0.50	13.49±0.13	14.73±1.06	9.45±1.07	5.17±0.57	11.02±0.82	5.58±0.16
Congo Red	5	39.57±0.06	32.36±1.76	37.35±0.14	39.12±0.03	38.67±1.46	38.29±1.77	43.63±0.80
	10	38.29±0.69	31.25±1.78	31.25±2.36	32.95±5.24	37.22±0.76	38.05±0.49	37.46±0.17
	30	35.10±0.72	28.23±0.55	28.23±0.24	30.35±1.04	30.00±3.28	30.21±0.62	38.95±0.56
	60	32.98±0.24	25.32±0.46	26.15±1.21	22.16±2.20	23.86±2.24	21.71±2.92	36.04±0.28
	1440	9.57±2.81	8.04±0.32	5.09±0.42	8.84±0.14	3.88±1.63	2.52±0.42	0.58±0.01
Orange II	5	43.55±1.96	43.83±1.89	44.17±0.04	43.07±2.23	45.61±0.38	38.03±1.65	38.55±0.10
	10	40.16±3.70	41.91±2.99	41.8±0.28	41.6±2.47	42.93±0.93	35.01±3.12	33.85±0.41
	30	38.55±2.58	37.93±1.06	40.5±1.65	37.41±2.27	39.57±0.86	27.3±2.97	23.8±0.03
	60	37.38±3.33	37.28±1.38	33.44±2.06	35.29±3.36	37.04±1.07	22.36±2.44	15.64±1.54
	1440	33.09±0.35	32.27±1.58	37.38±1.34	33.06±3.04	31.31±0.21	13.13±1.23	2.88±0.03

pack than dry granules. The paper also studies the water content in wet granules, and the results are presented in Figure 4.

The conducted studies (Figure 4) show that the A0 granules, which are characterized by the largest diameter, contain the most water (over 1230%) (Figure 2). The results confirm the fact that during the coagulation of a pure sodium alginate solution in a $CaCl_2$ solution, a cross-linking reaction occurs and a three-dimensional network,

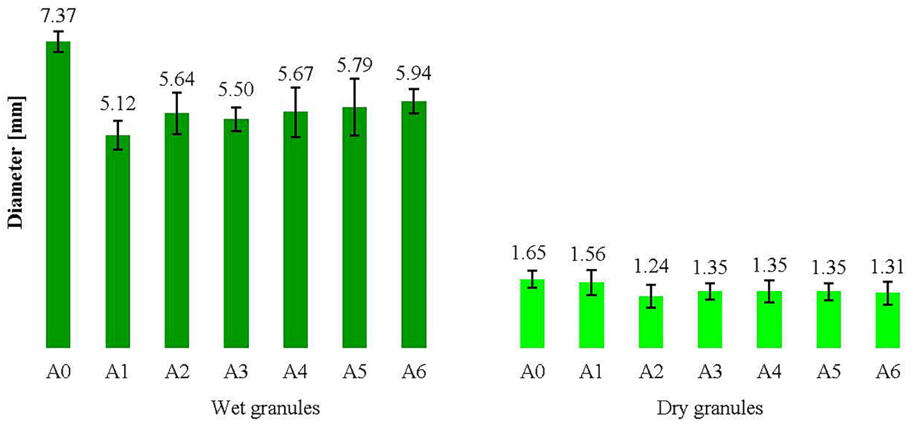


Figure 2. Diameter of wet and dry granules

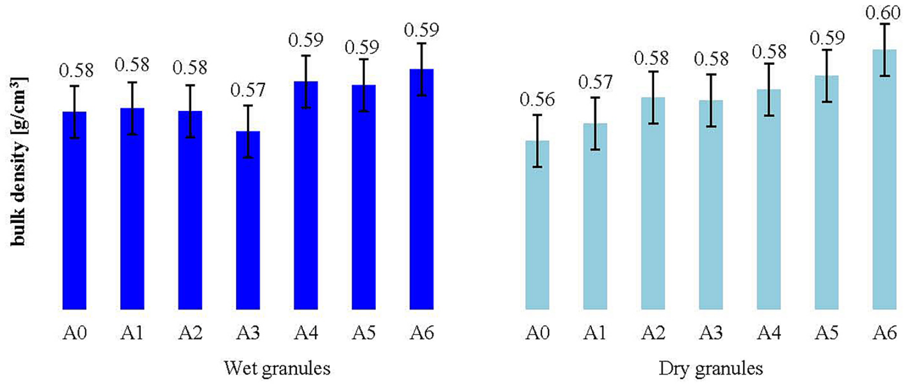


Figure 3. Bulk density of prepared granules

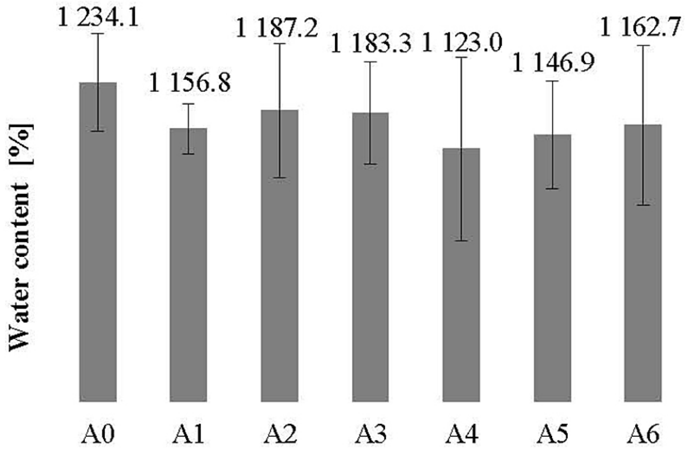


Figure 4. Water content in wet granules

referred to as an egg box, is formed [Kajouei et al., 2022]. This cross-linking occurs in stages. First, a membrane forms on the surface of the granules, after which Ca^{2+} ions penetrate into the granules. The short coagulation time caused the resulting A0 granules to be soft and therefore containing high amount of water. On the other hand, the water content in the A1–A6 composite granules is lower by 4% (A2 and A3 granules), 6% (A1 and A6 granules), 7% (A5 granules) and 9% (A4 granules). The obtained results allow to conclude that the amount of GO addition to the ALG matrix influences the formation of hydrogen bonds between the functional groups of GO and ALG. However, it is not significant enough to cause hydrophobization of the surface and inside of the granules, which could result in the removal of water from the interior of the resulting composite material.

The next area of the study was verifying the possibility of using granules as a sorbent for selected cationic dyes: toluidine blue, Victoria blue B, methylene blue and rhodamine B and the results are summarized in Figures 5–8. As can be seen in Figure 5, the sorption of toluidine blue on the tested granules occurs very quickly. Within the first 5 minutes the dye concentration is reduced by approximately 83–90%, and after 30 minutes the value reaches 85% to 100%. Pure alginate granules (A0) sorb the cationic dye approximately in 90–97%. It is observed that with the increase of GO concentration in GO/ALG granules, the degree of Toluidine Blue removal is lower than for A0 for the first 5 to 10 minutes, and increases to 100% after 30 minutes. Therefore, the granules obtained in the experiment are good sorbents of this cationic dye. Subsequently, Victoria blue B dye sorption tests were performed on pure alginate (A0) granules and composite granules, and the results are presented in Figure 6.

Sorption of the Victoria Blue B dye occurs quickly and with relatively high efficiency. As can be seen in Figure 6, for the first 5 minutes the cationic dye removal rate was at 53% for sample A5 and at 75% for A0. As the sorption time increases, the R coefficient is observed to take increasingly higher values, to reach the value of 93% (for sample A0) and 97% (for sample A6) after 60 minutes. Moreover, the study demonstrated that with the increase of GO concentration in the A1–A6 composite granules, the degree of removal of Victoria Blue B for the first 5 to 10 minutes is lower than for A0. This phenomenon was also observed in Figure 5. Based on the study it can be concluded that the granules obtained in the experiment are good sorbents of this cationic dye. Then, sorption

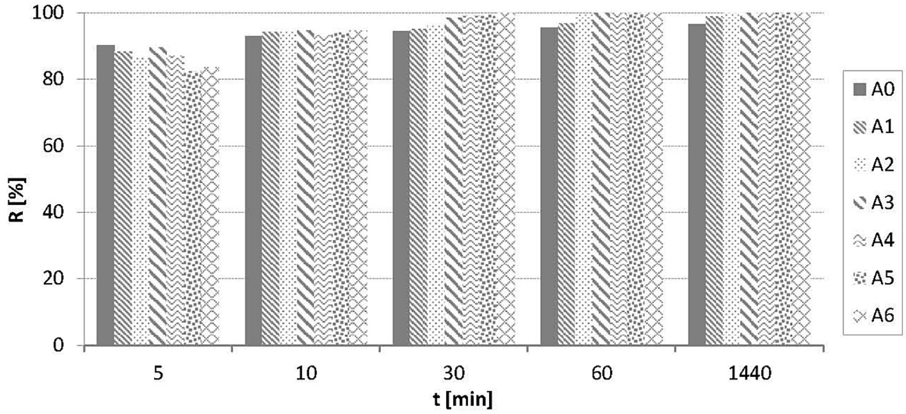


Figure 5. Degree of removal [R] of toluidine blue on pure alginate granules (A0) and on composite granules (A1–A6)

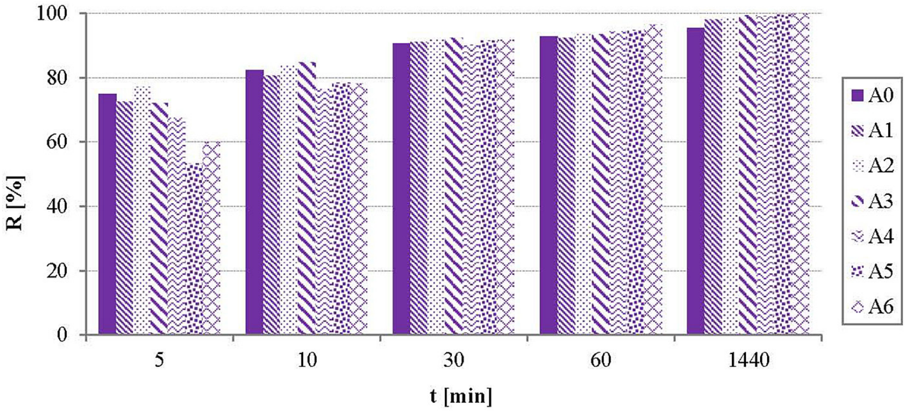


Figure 6. Degree of removal [R] of Victoria blue B on pure alginate granules (A0) and on composite granules (A1–A6)

tests of the cationic dye – methylene blue were performed and the obtained results are summarized in Figure 7. Sorption of methylene blue (Figure 7) on the granules within the first 5 minutes allows for 34% (sample A6) to 66% (sample A1) reduction of the dye concentration. In the subsequent minutes of the test the removal rate increases to reach 100% of removal after 24 hours. When analyzing the obtained results, it can also be noticed that the composite granules containing the largest amount of GO additive (A6) are characterized by the lowest degree of cationic dye removal within 60 minutes of the test.

Comparing the experimental results with the literature data, it can be concluded that the A0 and composite A1–A6 granules are characterized by higher removal values than those described by Platero et al. (Platero et al., 2017). The last studied cationic dye was rhodamine B. The degree of removal obtained in the experiment are summarized in Figure 8. Rhodamine B sorption studies (Figure 8) show that for all tested samples the removal values increase with the increase of GO concentration in the composite granules. In the first 5 minutes of the test, dye sorption for sample A0 is the lowest and the rejection factor is 28%, while for sample A6 it is 56%. Dye adsorption increases slowly over time and after 24 hours rodhamine B was removed in 100% (for samples A5 and A6). Therefore, the removal capacity for this cationic dye is the lowest as compared to those discussed earlier.

Analyzing the studies on the sorption of cationic dyes using pure alginate granules and composite granules, it can be concluded that the adsorption of this type of dyes is possible, but with varying efficiency. It seems that the causes of this phenomenon can be found in the chemical and structural composition of the dyes themselves. All cationic dyes discussed above (Table 2) in their molecule contain an amino group. The amino group in these dyes is present in the form

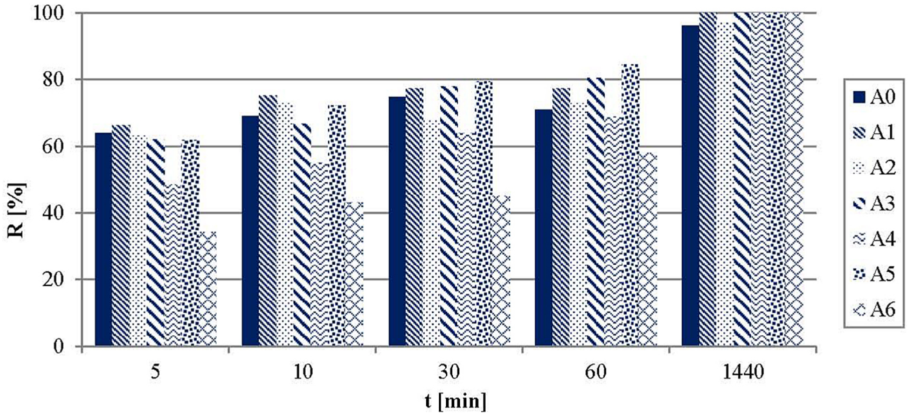


Figure 7. Degree of removal [R] of methylene blue on pure alginate granules (A0) and on composite granules (A1–A6)

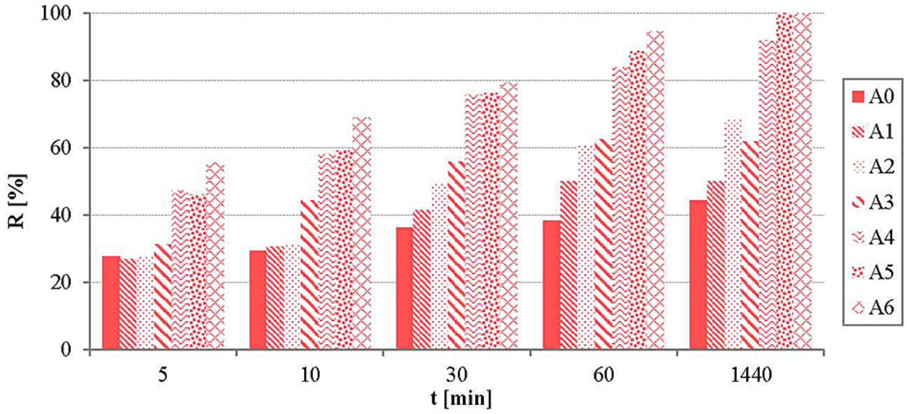


Figure 8. Degree of removal [R] of rhodamine B on pure alginate granules (A0) and on composite granules (A1–A6)

of water-soluble amine hydrochloride. It is also known that amino groups can form bonds with e.g. oxygen groups (hydroxyl, carboxyl, etc.), the tertiary amino groups being the most reactive [McMurry, 2017]. Therefore, the sorption intensity of individual dyes is influenced by their structure. Thus, toluidine blue, containing one tertiary amino group, reacts most easily with ALG and GO. Victoria blue B, methylene blue and rhodamine B each have two tertiary amino groups. In the case of rhodamine B, the longest sorption time and the lowest removal coefficient values may result from the presence of a carboxyl group in the molecule, which hinders the formation of hydrogen bonds with the ALG and GO functional groups.

The above conclusions are confirmed by the photos of granule samples after 24 hours of sorption of toluidine blue and rhodamine B (Figure 9). These photos show (especially for A0 granules) a clear difference in the color intensity of the samples. The granules that have absorbed toluidine blue have an intense blue color. In contrast, the granules in Figure 9b are light red.

The next group of dyes for which sorption studies were carried out were anionic dyes: Methyl blue, Congo red and orange II. First, the possibility of removing the methyl blue dye was tested and the results are summarized in Figure 10. In Figure 10 it can be seen that methyl blue dye is sorbed on all tested granules in a similar manner, i.e. regardless of the amount of GO added to the ALG matrix. After 5 minutes of testing, rejection rates of 63–72% can be observed. However, after 24 hours of sorption the rejection values for this dye ranged from 71% (A2) to 90% (A4). At the same time, it was noticed that methyl blue is intensively sorbed for 10 to 30 minutes, after which the rejection rate values continue to change, but insignificantly.

It was also observed that upon completion of the methyl blue test, the granules (Figure 11) and solution were light blue in color and a dark blue precipitate had formed at the bottom of the beaker.

Congo red sorption tests were performed next, and the results obtained are summarized in Figure 12. Sorption of Congo red dye molecules (Figure 12) on pure alginate granules (A0) and GO/ALG composite granules is slower than that observed for methyl blue. After 5 minutes of testing, rejection rates are only at 13–35%, and after 60 minutes they slowly increase to 28–56%. Leaving test granules in the dye solution for 24

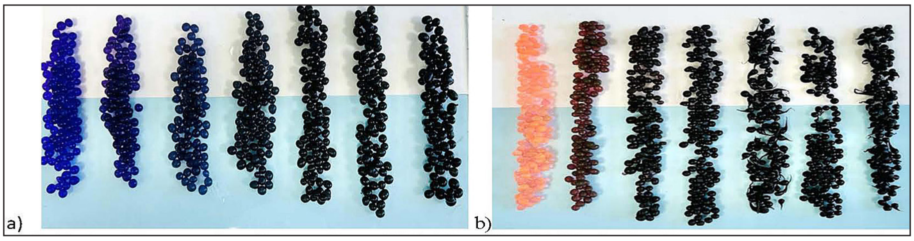


Figure 9. Photo of the granules after sorption: (a) toluidine blue; (b) Rrhodamine B on pure alginate granules (A0 – first on the left) and composite granules (A1–A6, second and subsequent from the left)

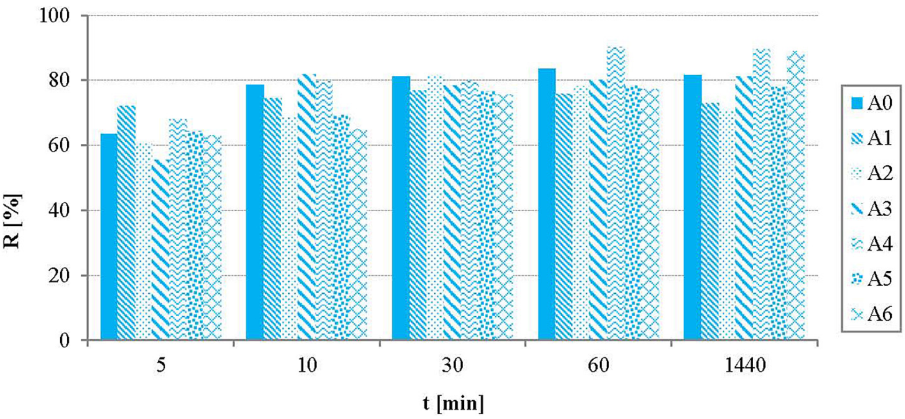


Figure 10. Degree of removal [R] of methyl blue on pure alginate granules (A0) and on composite granules (A1 – A6)

Figure 11. Photo of the granules after methyl blue sorption on pure alginate granules (A0 – first on the left) and composite granules (A1 – A6, second and subsequent from the left)

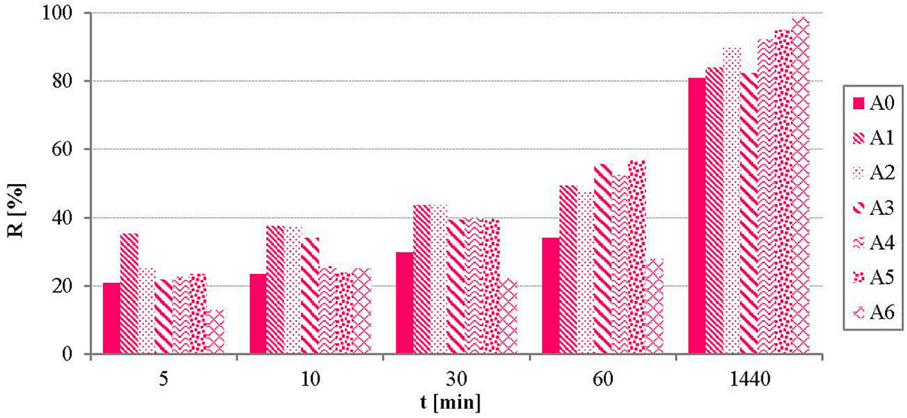


Figure 12. Degree of removal [R] of Congo Red on pure alginate granules (A0) and on composite granules (A1–A6)

hours results in a rejection rate of 81–99%. Additionally, after 24 hours of testing, the granules and solution were observed to be light red in color (Figure 13), and a dark red precipitate had formed at the bottom.

The last anionic dye tested was Orange II and the removal factor values for this are summarized in Figure 14.

Orange II is the dye with the lowest adsorption among all those tested in our experiment. Analyzing Figure 14 it can be observed that for samples A0–A4 the rejection values are similar and at 5, 10, 30, 60 minutes and 24 hours amount to ~12%; 16%; 22%; 29%; 33%, respectively. However, the composite granule samples containing 2.83% and 5.62% of GO additive were characterized by

Figure 13. Photo of the granules after Congo red sorption on pure alginate granules (A0 – first on the left) and composite granules (A1–A6, second and subsequent from the left)

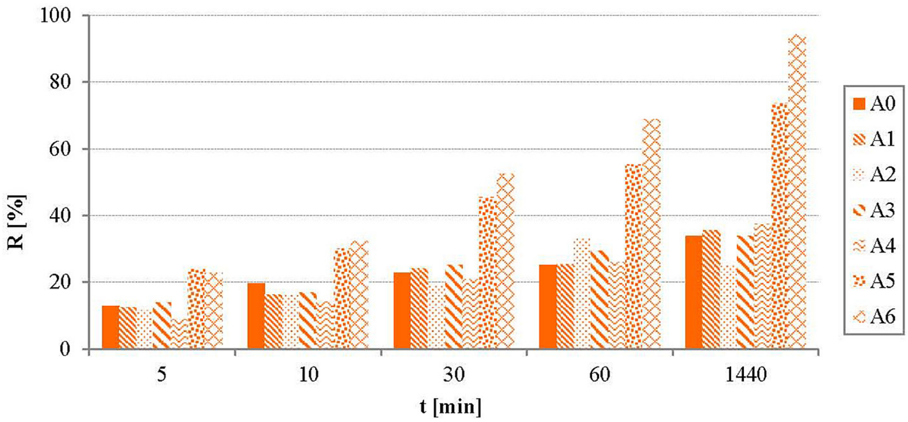


Figure 14. Degree of removal [R] of orange II on pure alginate granules (A0) and on composite granules (A1–A6)

Figure 15. Photo of the granules after orange II sorption on pure alginate granules (A0 – first on the left) and composite granules (A1–A6, second and subsequent from the left)

much higher rejection values of over 80% (A6) after 24 hours of testing. At the same time, no precipitation from the solution is observed.

Figure 15 shows a photo of the granules after the sorption process, where it is clearly visible that samples A0 and A1 are very weakly colored. It was also observed that the solution above granules A0–A4 is only slightly discolored, whereas in the case of samples A5 and A6 it became light red.

Analyzing the studies on the sorption of anionic dyes on pure alginate granules and composite granules, it can be concluded that the removal of this type of dyes from aqueous solutions is possible. During the studies, various phenomena, which may also be related to the chemical structure of the dyes themselves, were observed. All anionic dyes discussed above (Table 2) contain a strongly acidic sulfonic group in their molecule [McMurry, 2017]. Methyl Blue has 3 sulfone groups in its molecule, Congo red has 2 sulfone groups, and orange II - only one. The presence of these groups in the form of sodium salts makes the dyes soluble. At the same time, these groups can react with calcium alginate to form water-soluble sodium alginate. The number of sulfone groups present in the dye molecule also affects the rejection value. Methyl blue dye, containing 3 sulfonic acid groups, has the highest rejection values. Congo red is characterized by slightly lower rejection values. Orange II, on the other hand, which has only one sulfonate group and one hydroxyl group in its structure, is not well removed from the solution, except for samples A5 and A6, in which, due to the additive content, probably form links with GO oxygen groups.

CONCLUSIONS

A method for obtaining alginate-based pure alginate granules and composite granules with the addition of GO was developed, consisting in forming spheres in which the interior in the form of a gel is surrounded by a semi-permeable membrane.

Selected cationic and anionic dyes were tested in terms of their removal from aqueous solutions with a view to using the tested granules for the treatment of industrial wastewater.

It was demonstrated that the chemical and structural composition of the dye has a decisive influence on its sorption on composite granules.

It was also shown that ALG and GO/ALG granules can be successfully used to remove cationic dyes (methylene blue, rhodamine B, toluidine blue, Victoria blue B). The sorption rate and high rejection values are dependent on the chemical structure of the dye, including on the number of amino groups and their ordering. The more tertiary amino groups, the lower the degree of rejection. Dyes containing one such group (toluidine blue) are removed most quickly and effectively.

It was verified whether anionic dyes (Congo red, methyl blue, orange II) containing sulfonic groups in their structure could be removed on alginate granules. It was demonstrated that the more sulfonic groups there are in the dye, the greater its degree of rejection.

The granules obtained in the experiment can be regenerated by dissolving them in NaCl, separating the dyes and then coagulating them again.

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