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Effect of Chitin Modification on the Sorption Efficiency of Reactive Black 5 Dye

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1. Introduction

Wastewater treatment from various industries is now a big challenge for scientists. The regulations, which limit the amount of pollution discharged to receivers, are becoming stricter each year and definitely do not make this task easier. Industrial wastewater contains many organic and inorganic compounds that are by-products or residues of technological processes.

Colored wastewater from the textile industry are particularly problematic. Dyes are chemical compounds with a complex structure that significantly hampers the process of removing them from industrial wastewater. Around $7 \cdot 10^5$ tons of dyes are produced annually for the world's textile, paper and tanning industry (Robinson et al. 2001). Due to the low susceptibility to staining of some materials, only about 60-90% of the dye contained in the dyeing bath binds to the fiber, and what is more, the process consumes 80-250 dm^3 of water for 1 kg of the colored product (Janeczko & Ay 2007). Due to the different susceptibility of materials to dyeing and high solubility of dyes, 10-50% of them get into sewage after dyeing process (Burkinshaw & Kabambe 2011). Conventional wastewater treatment systems are characterized by low efficiency of removal of this type of compounds, therefore 10-15% of dyes get to the natural environment (Robinson et al. 2001). Thus, large amounts of dyes with insufficiently purified waste water leak into the environment.

The penetration of dyes into the aquatic environment not only worsens the visual values, but above all disturbs the biological balance of the ecosystem, by limiting the light transmission and inhibiting photosynthesis in plants. Dyes are not biodegradable, and many of them have a toxic effect on living organisms (Machado et al. 2011). Therefore, it is very important to look for innovative methods that allow for the effective removal of these hazardous substances from wastewater.

Physical, chemical and biological methods of sewage discoloration have been proposed over the last few decades. Among these methods, adsorption is one of the most commonly used and provides satisfactory efficiency.

Until now, activated carbon was the most commonly used adsorbent. The use of this adsorbent on a technical scale is, however, unprofitable, as the production and regeneration costs are high (Filipkowska & Jóźwiak 2013). For this reason, many scientists conduct research in search of cheaper, widely available unconventional substitutes. Recently, chitin is becoming more and more popular among sorbents. Chitin is one of the most widespread biopolymers in nature (Filipkowska 2005). According to literature data, the annual global production of chitin by living organisms reaches even 10^{11} tons (Je & Kim 2006). However, all kinds of waste from various industry sectors are not always characterized by a high sorption capacity for dyes. Therefore, various methods of modifying potential sorbents are sought to improve this ability.

In this article, research was undertaken in order to increase the adsorptive capacity of chitin in relation to the Reactive Black 5 dye. For this purpose, the effects of microwaves, magnetic field, ultrasound and ozone was used to modify the sorbent.

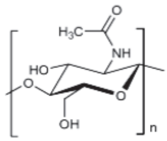
2. Materials and methods

2.1. Characteristics and sorbent preparation

2.1.1. Chitin

Chitin in the form of flakes were purchased from BioLog company. Characteristics of adsorbents were presented in Table 1.

Table 1. Characteristics of chitin
Tabela 1. Chatakterstyka chityny

Chitin	
Structural formula	
Deacetylation degree	< 15%
Origin of the material	Shrimp shells

2.1.2. Chitin modified with ultrasound

Two 200 ml beakers were filled with 5 g of unmodified chitin each and then 50 ml of distilled water was added to each of them. The beakers were then placed in the ultrasound generator for 15 minutes, setting the device's power to 350 W (beaker No. 1) and 700 W (beaker No. 2). Is-1K washer by InterSonic, which generates ultrasound at the frequency of 35 kHz, was used as the ultrasound source. After the process, the chitin was drained and dried.

2.1.3. Chitin modified with microwaves

The Amica microwave with a maximum power of 700 W was used for microwave emission. 5 g of chitin and 50 g of distilled water were weighed into beaker No. 3 and 4 in order to cause modification. The beakers were placed in the microwave for 5 minutes, setting its power to 50%, i.e. about 350 W, in the case of beaker 3 and 100%, i.e. about 700 W, in the case of beaker 4. After modification, the sorbent was drained and left to dry.

2.1.4. Chitin modifies with magnetic field

In order to perform modification of the magnetic field, 5 g of chitin was weighed and placed on watch glasses. The glasses were then placed for one hour in a magnetic field at the intensity of: 15 mT (glass nr 1) and 30 mT (glass nr 2).

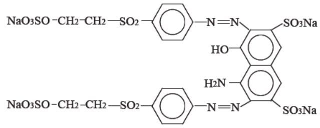
2.1.5. Ozone modified chitin

To each of two 200 ml beakers 5 g of chitin was weighted on an analytical balance and then 100 ml of distilled water was added to each of them. Both of the solutions were then transferred to the two separate reaction vessels of the ozonation plant. First sample was then subjected to ozone for 5 minutes, which gives 1 g of O_3, whereas the second sample was subjected to ozone for 10 minutes, which results in the dose of 2 g of O_3. After the ozonation process the chitin was filtered and dried at temperature of 100°C. The instalation used for the process of ozonation in the research consisted of two oxygen generators, ozone concentration meter, rotameter, reaction vessel with a capacity of 200 ml and post-reaction ozone destructor.

2.2. Dye characteristics and preparation

The study was conducted with anionic dye Reactive Black 5 (RB5), the structure and properties of which were presented in Table 2.

Table 2. Characteristics of RB5 dye
Tabela 2. Chatakterstyka barwnika RB5

Name	Reactive Black – RB 5
Chemical structure	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Structural formula	
Molecular weight	991,82 [g/mol]
λ_{max}	600 nm
Character of dye	Acidic (anionic - reactive)
Type of chromophore group	azo
Type of active groups	vinylsulfone

In order to prepare a working solution, 1 g of pure RB5 dye powder was weighed and transferred quantitatively into a 1 dm^3 measuring flask. The flask was then filled up with distilled water. Dye concentration in the resultant solution reached 1000 mg/dm^3.

2.3. Determination of the maximum sorption capacity

Unmodified and modified with each of the presented methods chitin was added to each of the five 100 ml Erlenmeyer flasks at a concentration of 1 g of dry mass/dm^3 and then solutions of the dye with concentrations: 10, 20, 30, 50, 75, 100, 150, 200 and 300 mgRB5/dm^3 were added at the pH of 4. Corrections of the reactions were carried out using aqueous solutions of NaOH and HCl. The flasks were then placed on a laboratory shaker whose rotational speed was set to 130 rpm.

2.4. Calculation methodology

The dependence was used to calculate the amount of sorbed dye:

$$Q_s = \frac{C_0 - C_s}{m} \tag{1}$$

Q_s – mass of the dye removed from the solution (mg/g d.m.),
m – concentration of chitin (g d.m./dm^3),
C_0 – initial concentration of dye in the sample ($mg/dm^{3)}$,
C_s – concentration of the dye after the sorption process (mg/dm^3).

The Langmuir adsorption isotherm (2) were used to determine the maximum sorption capacity of the sorbents tested.

$$Q = \frac{q_{max} \cdot K_c \cdot C}{1 + K_c \cdot C} \tag{2}$$

Q – amount of dye adsorbed by 1 g d.m. of the sorbent (mg/g d.m.),
C – removed substance concentration in a steady state (mg/dm^3),
K_c – constant (dm^3/g d.m.),
q_{max} – maximum sorption capacity (mg/g d.m.).

3. Overview and discussion on results

3.1. Maximum chitin sorption capacity

In the studies to describe the adsorption of RB 5 dye to chitin, the Langmiur model was used. Table 3 shows the constants determined with its application. Considering the values of the matching factor R^2, it can be concluded that the Langmuir isotherm describes the results very well.

Table 3. Constants determined with the use of Langmuir adsorption model
Tabela 3. Stałe wyznaczone z zastosowaniem modelu adsorpcji Langmuira

Sorbent		Constant		
		q_{max} [mg/g d.m.]	K_c [dm^3/g d.m.]	R^2
Unmodified chitin		30,37	0,80	0,9856
Chitin modified with ultrasound	150 W	29,55	1,29	0,9825
	300 W	27,29	0,92	0,9948
Chitin modified with microwaves	350 W	27,32	1,17	0,9980
	700 W	27,79	1,05	0,9970
Chitin modified with magnetic field	15 mT	38,40	0,38	0,9611
	30 mT	33,66	0,70	0,9673
Ozone modified chitin	1 g O_2	18,36	0,41	0,9800
	2 g O_2	13,37	0,11	0,9783

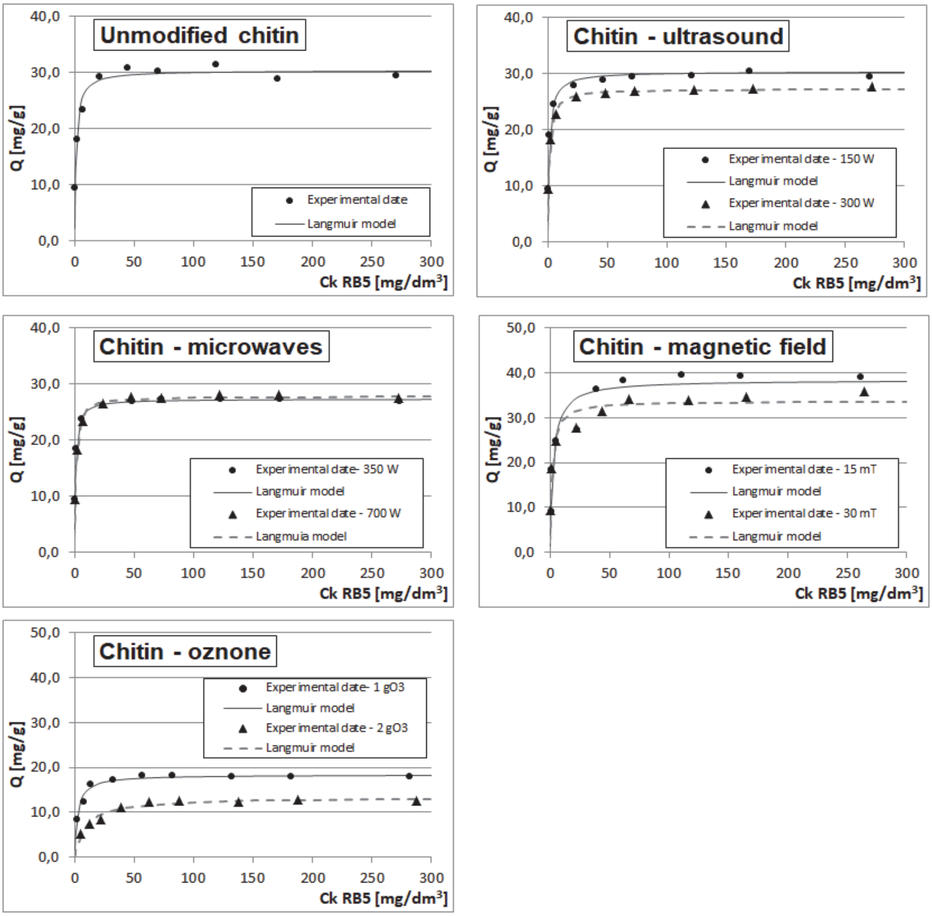


Fig. 1. Sorption capacities of unmodified and modified – RB5 dye
Rys. 1. Pojemności sorpcyjne chityny niemodyfikowanej i modyfikowanej – barwnik RB5

The highest sorption capacity was obtained during adsorption on chitin modified with magnetic field (Table 1, Figure 1). In the case of a field of 15 mT, it was 38.40 mg RB5/g d.m. and was over 25% higher than the maximum sorption capacity of unmodified chitin, whereas for modification with 30 mT field the result was 33.66 mg RB5/g d.m., which was higher by approx. 11% relative to the sorbent without modification. Slightly weaker results were noted in the case of dye removal using ultrasound-modified chitin and using microwaves (Table 1, Figure 1). In the first case, a better effect was obtained for the ultrasound modified sorbent when setting the device power at 350 W. It was only less than 3% lower than the result obtained for unmodified chitin and was 29.55 mg RB5/g d.m. The sorption capacities obtained during the removal of RB5 on a sorbent modified with microwaves of 150 and 300 W were similar: 27.32 and 27.79 mg RB5/g d.m. Significantly lower sorption capacities were noted for ozone-modified chitin, the lowest of which was obtained with 2 g of O_3 (Table 1, Figure 1). It was only 13.17 mg RB5/g d.m. and it was 56.6% lower than the unmodified chitin capacity. Little more was detected during the sorption chitin treated with 1 g O_3 – 18.36 RB5 mg/g d.m.

3.2. Sorption using unmodified chitin

As an unconventional sorbent, chitin gives satisfactory results. The initial concentration of the solution had a major influence on the process efficiency, which was noticed by Yagub et al. (2014). Only at low concentrations of the dye in the solution more than 90% removal efficiency can be obtained. An increase in the initial concentration from 10 mg/dm^3 to 300 mg/dm^3 resulted in a decrease in dye removal from approx. 95% to 10%. Relatively to anionic dyes, chitin has good adsorptive properties. The structure of chitin contains mostly acetamide groups, whereas the amino groups are only about 15%. Both of those groups play an important role in dye adsorption. In acidic environment these groups rea protonated according to the reaction: R-NHCOCH3 + H+X- ↔ R-NH+2COCH3X- and the affinity of protone to amino groups is bigger than to acetamide groups. In turn, the anionic dye contains negatively charged functional groups, which causes electrostatic attraction of the adsorbent and adsorbate (Filipkowska & Rodziewicz 2012). A similar sorption capacity in relation to the RB 5 dyestuff obtained in the tests is demonstrated by cotton stalks. Tunç Ö in his research. and others (2009) received an adsorption capacity of 30.70 mg/g d.m. with a solution of 1 pH and 35°C. They also noted the relationship between the initial dye concentration in the solution and the removal efficiency. At higher concentrations, efficiency decreases due to the almost complete use of active sites on the adsorbent surface.

3.3. Sorption with the use of ultrasound modified chitin

Seeking a way to increase the RB5 dye removing efficiency in the adsorption process on chitin, 4 modifications of this sorbent were carried out in this study. One of them was a modification using ultrasounds. The results obtained indicate that ultrasound does not improve the chitin adsorptive capacity. Considering the final concentrations of dyes in solutions obtained after the adsorption process on 150 W ultrasound-modified chitin and during adsorption on unmodified chitin, it can be concluded that in the first case only at concentrations of 10-30 mg/dm^3 better results were obtained. For initial concentrations of 10, 20 and 30 mg/dm^3 efficiencies were obtained successively: 95, 95 and 82% of dye removal on chitin treated with ultrasound and 94, 91 and 76% on chitin without modification. Analyzing the remaining results, during the sorption on chitin modified with ultrasounds, both 150 W and 300 W, the process efficiency is lower than during adsorption on the non-modified chitin. According to the values presented in Table 1, the maximum sorption volumes of the ultrasound modified chitin are 29.55 mg RB5/g d.m. for ultrasounds with a capacity of 150 W and 27.29 mg RB5/g d.m., i.e. by about 10% less, for ultrasounds with a power of 300 W. Thus, the power of the sound waves generated affects the sorptive capacity of the sorbent used in the studies. This is also confirmed by Lach J. et al. (2013) who studied cadmium sorption on activated carbon subjected to ultrasound with different vibration amplitudes. According to the researchers, ultrasounds with a higher sound power level during 10, 15 and 20 minutes cause changes in activated carbon resulting in reduced adsorption of cadmium ions. They explain that the effect of very high energy waves causes destructive changes in the residues of oxygen on the surface of activated carbon. They also observed the destruction of coal grains (dust in solution), especially at higher intensities (Lach and others 2013). Ultrasounds evoke a series of fast compresses and expansions in solid bodies, which create microscopic channels in their structure (Fijałkowska et al. 2015). J Mason et al. (2011) noticed that cavitation bubbles forming and disintegrating during this process have a big influence on mechanical and chemical changes. In the case of chitin, this may lead to the breaking of hydrogen bonds or the disconnection of amide groups responsible for good sorption properties with respect to anionic dyes. The smaller the ultrasonic power, the less physicochemical changes occur in the structure of chitin, therefore the efficiency of dye removal using 150 W ultrasound-modified chitin is higher than in the case of 300 W power.

3.4. Sorption on chitin modified with microwaves

Another modification carried out on the sorbent in the present studies was the microwave treatment of chitin. Only at lower initial concentrations of RB5 can there be a slight improvement in the efficiency of removal on modified chitin compared to normal chitin. At a concentration of 10 mg/dm^3 during sorption on chitin modified with microwaves, when the device was set to 700 W, the result was 0.02 mg/dm^3 lower. Higher efficiency was also obtained for a concentration of 20 mg/dm^3 for both 350 W and 700 W, which increased by 14.13% and 1.1% respectively as compared to the unmodified sorbent. Also, about 7% of dye more was adsorbed on chitin modified with microwaves of 350 W at an initial concentration of 30 mg/dm^3, where the result was 6.20 mg RB/dm^3 in the final solution. Analyzing the results presented in Table 1, it can be noticed that sorption on 350 W modified chitin, compared to the 700 W microwaved chitin, was only more effective at initial concentrations of 20 and 30 mg RB5/dm^3. At the remaining concentrations, better results were noted for higher power, which translates to a higher sorption capacity by 0.47 mg/g d.m. of the microwave-treated chitin with the device set to 700 W power. As noted by Połowiński (2001), the treated polymers undergo a degradation process, which may be accompanied by destruction processes. In this study, chitin was exposed to sonic degradation in the electromagnetic field and to thermal degradation associated with elevated temperature. The modified chitin was in an aqueous medium, which could cause the breaking of amide and hydrogen bonds during the operation of the microwave, responsible for good sorption properties. In addition, the elevated temperature may cause cracking of C-C bonds, which in turn leads to the formation of free radicals. The higher the temperature, the more intensive the process. Consequently, it is possible that free radicals improve the adsorptive capacity of chitin in relation to dyes. Perhaps this is why in our research during sorption on chitin modified with higher power microwaves, a slight increase in the efficiency of RB 5 removal in relation to sorption on chitin modified with 350 W microwaves was observed. Considering the fact that the sorption capacity of modified chitin in relation to the unmodified one has decreased slightly, it can be concluded that the degradation process, including its accompanying phenomena, did not occur to a small extent. Bathen (2003) in his article noted that distilled water may limit the ability of microwave penetration, which may also explain the above observation. The lack of electromagnetic influence of microwave radiation on the adsorptive capacity of activated carbons was noticed by Ania et al. (2005). They showed that the heat-treated sorbent using the 2450 MHz microwave method retains its porous structure, and the size of the micropores did not differ significantly from those that the sorbent had before the modification. Nair and others (2016) came to a different conclusion. Microwave-treated bisected basal protein (*Prosopis juliflora*) significantly increased its porosity. Thanks to this, the sorption capacity of biocarbon with respect to Remazol Brilliant Blue R has more than doubled, reaching 83.33 mg/g d.m. Thus, it can be concluded that microwaves have different effects, depending on the initial structure of the material being treated.

3.5. Sorption on chitin modified with magnetic field

Adsorption of the dye on chitin modified with magnetic field gave the best results among all the methods used in this research. A little higher sorption efficiency on unmodified chitin in relation to chitin subjected to this modification was recorded only at the initial concentration of 10 and 50 mg RB5/dm^3. The efficiency was 95.2% and 58.6% for unmodified chitin, and respectively 91.3 and 93.4% as well as 54.4% and 55.5% for the chitin modified magnetic field with the intensity of 15 mT and 30 mT were obtained. removing the dye. In the case of other concentrations, higher efficiency during adsorption on chitin modified with magnetic field was noted. These results are reflected in the maximum sorption capacity determined using the Langmuir model. For chitin treated with a field of 15 mT, it is 38.02 mg/g d.m. and is higher by 13% than the volume of chitin modified with a field of 30 mT, of 33.66 mg/g d.m. The effectiveness of RB5 removal is influenced by both the initial concentration in the solution and the type of sorbent used. It can be noted that in the case of concentrations of 10-50 mg/dm^3, chitin modified with a magnetic field of higher intensity works better, whereas at concentrations of 75-300 mg/dm^3 chitin modified with a smaller magnetic field gives better results. Differences in the amount of adsorbed dye from solutions with lower concentrations are small – they differ a maximum of 0.53 mg/dm^3 with respect to both modifications by magnetic field. However, at higher concentrations these differences are more visible and range from 3 to 5.54 mg/dm^3. This is reflected in the maximum sorption capacity, where for the chitin modified with a magnetic field of lower intensity, the result was 13% higher than for the chitin subjected to the magnetic field of higher induction. Positive influence of the magnetic field on the sorbent is also confirmed by Samonin et al. (2012), who investigated the effectiveness of sorption of benzene vapors on active carbon subjected to modification with a magnetic field. According to the present research, the magnetic field caused a 14% increase in the sorption of benzene vapors by activated carbon.

3.6. Sorption on ozone-modified chitin

The least effective modification of chitin carried out in this study was ozonation. Removal of the dye by using ozone-modified chitin in 1 g O_3 and 2 g O_3 was much less efficient than removal by using unmodified chitin. Depending on the initial concentration, differences in efficiency were very high. The biggest difference was observed for the initial concentration of 20 mg RB5/dm^3. After adsorption on the unmodified chitin, less dye was left in the solution than after adsorption on chitin treated with 1 g and 2 g of O_3, respectively 5.74 and 10.82 mg/dm^3. The obtained maximum adsorptive capacities relative to RB5 amounted to: 18.36 mg/g d.m. in the case of modified chitin with 1 g ozone, and 13.17 mg/g d.m. in the case of modified chitin with 2 g ozone. Longer time of ozonization worsened the sorption capacity of chitin by almost 40% in relation to the shorter time. The highest removal efficiency, as with other modifications, was obtained at an initial concentration of 10 mg RB5/dm^3. For chitin treated with 1 g O_3 it was 82.9%, whereas for chitin treated with 2 g O_3 only 52.4%. In comparison, at the same initial concentration unmodified chitin adsorbed as much as 95.2% of the dye. The biggest difference in the amount of removed RB 5 was observed for samples with an initial concentration of 150 mg/dm^3. The ozone-modified chitin during 5 and 10 minutes removed respectively by 13.55 and 19.13 mg RB5/dm^3 less from the solution than chitin without modification. Significantly weaker results from among ozonated sorbents were obtained during sorption on chitin modified for 10 minutes. However, taking the performances obtained in both cases into account, there is a reduction in differences with the increase in the initial concentration of the dye in solution. For example, with an initial concentration of 10 mg RB5/dm^3, the difference was 30.5%, and at a concentration of 300 mg/dm^3 only 1,8%. As is well known, ozone is a very strong oxidant. Direct or indirect, through the generation of radicals, it reacts with most organic compounds (Lucas et al. 2010). In contrast to the other modifications used in this study, which were physical modifications, ozonation qualifies as chemical modification. During this process, some of the hydroxyl groups of the glucose units are oxidized, thereby carboxyl or carbonyl groups are formed. The formation of carboxylic groups may particularly adversely affect the sorption of the anionic RB5 dye, as they have a negative charge. Therefore, there may be electrostatic repulsion between the dye molecule and modified chitin (Jóźwiak et al. 2016). Furthermore, ozonation leads to partial depolymerization of chitin and to the loosening or cracking of some bonds, which may also cause deterioration of sorption properties (Ostrowska-Czubenko and others 2016). Most likely, the bonds responsible for the good sorptive properties of chitin, such as hydrogen bonds, were ruptured. The intensity of these processes, as noted earlier, increases with the prolongation of the ozonation time and increasing the dose of O_3. Alvarez et al. (2004) in their research used activated carbon activated treated with ozone as a sorbent for phenol. As in these studies, it turned out that the longer modification time, the lower sorption capacity. In the study they explained that during ozonation acidic groups are formed on the surface of activated carbons, which in the case of phenol sorption is an detrimental phenomenon.

4. Conclusions

In this paper modifications of chitin were carried out using ultrasound, microwaves, magnetic field and ozone in order to investigate the possibility of increasing the adsorptive capacity of this sorbent in relation to the RB5 dye. As a result of proper modification, the maximum sorption capacity of chitin in relation to the RB5 anionic dye may change. Among all the modifications which were carried out, chitin modified with a magnetic field of 15 mT induction had the highest sorption capacity – 38.02 mg RB5/dm^3. It was 25% higher than the maximum sorption capacity of unmodified chitin. The lowest sorption capacity, 13.17 mg RB5/dm^3, was observed for the chitin which was treated with ozone for 10 minutes. Ozonation has a negative effect on the sorption capacity of chitin by its partial depolymerisation and bond disruption, such as hydrogen bonds, which are responsible for this ability. The effectiveness of the RB5 dye sorption on chitin was affected by the initial solution concentration and the intensity of the modifying agent.

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Wykorzystanie niekonwencjonalnych systemów do usuwania barwnika RB5

Streszczenie

Na potrzeby światowego przemysłu włókienniczego, garbarskiego i papierniczego wytwarzanych jest rocznie około $7 \cdot 10^5$ ton barwników. Z powodu niskiej podatności niektórych materiałów na barwienie i wysokiej rozpuszczalności barwników nawet do 50% z nich po procesie barwienia przedostaje się do ścieków, z czego koło 15% trafia do środowiska naturalnego. Substancje barwne w większości są trudno-biodegradowalne, więc dekoloryzacja ścieków za pomocą metod biologicznych stosowanych na konwencjonalnych oczyszczalniach ścieków nie jest skuteczna.

Jedną z efektywniejszych, tańszych i przyjaznych dla środowiska metod usuwania barwników ze ścieków jest proces adsorpcji. Pomimo tego jej praktyczne zastosowanie napotyka na szereg ograniczeń, głównie z uwagi na wysoki koszt komercyjnych sorbentów i trudności w ich regeneracji. W związku z tym wiele badań koncentruje się na poszukiwaniu sorbentów tanich a zarazem efektywnych.

W ostatnim czasie coraz większym zainteresowaniem wśród sorbentów cieszy się chityna, która jest jednym z najbardziej rozpowszechnionych biopolimerów w przyrodzie. Według danych literaturowych roczna światowa produkcja chityny przez organizmy żywe osiąga nawet 10^{11} ton, a z odpadów przetwórstwa bezkręgowców morskich rocznie na świecie pozyskuje się 120 000-200 000 ton chityny. Jednak wszelkiego rodzaju odpady z różnych sektorów przemysłu nie zawsze charakteryzują się wysoką pojemnością sorpcyjną względem barwników. W związku z tym poszukuje się różnych metod modyfikacji potencjalnych sorbentów w celu poprawienia tej zdolności.

W pracy zbadano możliwość zwiększenia zdolności adsorpcyjnej chityny względem barwnika RB5 poprzez wstępną modyfikację sorbentu. Jako czynnik modyfikujący chitynę przed sorpcją wykorzystano ultradźwięki, mikrofale, pole magnetyczne i ozonowanie W wyniku odpowiedniej modyfikacji maksymalna pojemność sorpcyjna chityny względem barwnika anionowego Reactive Black 5 uległa zmianie. Stwierdzono, iż na efektywność sorpcji barwnika RB 5 na chitynie miały wpływ początkowe stężenie roztworu oraz rodzaj czynnika modyfikującego. Spośród testowanych sorbentów największą pojem-

nością sorpcyjną wynoszącą 38,02 mg/dm^3 charakteryzowała się chityna modyfikowana polem magnetycznym o indukcji 15 mT. Efektywność usuwania barwnika anionowego na tym sorbencie była wyższa od maksymalnej pojemności sorpcyjnej chityny niemodyfikowanej o 25%. W celu określenia dokładnego wpływu pola magnetycznego na chitynę, należałoby przeprowadzić dodatkowe i bardziej szczegółowe badania. Natomiast najniższą pojemność sorpcyjną odnotowano dla chityny poddanej działaniu ozonu w ilości 2 g O_3, gdzie uzyskano wynik 13,17 mg/dm^3. Ozonowanie negatywnie wpłynęło na zdolność sorpcyjną chityny poprzez jej częściową depolimeryzację oraz rozrywanie wiązań, takich jak wiązania wodorowe, odpowiedzialnych za sorpcję zanieczyszczeń w formie anionów.

Abstract

Around $7 \cdot 10^5$ tons of dyes are produced annually to supply for the needs of the global textile, tanning and paper industry. Due to the low susceptibility of some materials to dyeing process and high solubility of dyes, up to 50% get into sewage, about 15% of which goes to the natural environment. Colored substances are mostly difficult to biodegrade, so decolorization of wastewater using biological methods used on conventional wastewater treatment plants is not effective. One of the most effective, cheap and environmentally friendly methods of removing dyes from wastewater is the adsorption process. However, the practical application of this process encounters a number of limitations, mainly due to the high cost of commercial sorbents and difficulties in their regeneration. Therefore, many studies focus on the search for cheap and effective sorbents. Recently, chitin, which is one of the most widespread biopolymers in nature, is becoming more and more popular among sorbents. According to literature data, the annual global production of chitin by living organisms reaches up to 10^{11} tons and 120,000-200,000 tons of chitin are obtained in the world from the waste of marine invertebrates processing annually. However, not all kinds of waste from various industry sectors are characterized by a high sorption capacity for dyes. That encourages seeking various methods of modifying potential sorbents to improve this ability. The study investigated the possibility of increasing the adsorption capacity of chitin in relation to the RB5 dye by initial modification of the sorbent. Modifying factors such as ultrasound, microwaves, magnetic field and ozone were used. Due to appropriate modification, the maximum sorption capacity of chitin in relation to the anionic dye Reactive Black 5 has changed. It was found that the effectiveness of the RB5 dye on chitin was influenced by the initial concentration of the solution and the type of modifying agent. Among the tested sorbents, the highest sorption capacity of 38.02 mg/dm^3 was obtained for chitin modified with magnetic field at an induc-

tion of 15 mT. The efficiency of removing the anionic dye on this sorbent was higher than the maximum sorption capacity of unmodified chitin by 25%. In order to determine the exact effect of the magnetic field on chitin, additional and more detailed studies would have to be carried out. The lowest sorption capacity was obtained for chitin treated with ozone in the amount of 2 g of O_3, where the result of 13.17 mg/dm^3 was obtained. Ozonation affected negatively the sorption capacity of chitin by its partial depolymerisation and disruption of bonds, such as hydrogen bonds, responsible for the sorption of impurities in the form of anions.

Słowa kluczowe:
sorpcja, barwnik, RB5, ultradźwięki, pole magnetyczne, mikrofale, ozon, chityn

Keywords:
sorption, dye, RB5, ultrasounds, magnetic field, microwaves, ozone, chitin