

REMOVAL OF DYES FROM AQUEOUS SOLUTIONS BY GLAUCONITE IMMOBILISED ON CHITOSAN HYDROGEL BEADS

**Tomasz Józwiak^{1*}, Urszula Filipkowska¹, Paula Szymczyk¹,
Małgorzata Kuczajowska-Zadrożna², Artur Mielcarek¹**

¹*Department of Environmental Engineering, University of Warmia and Mazury
in Olsztyn ul. Warszawska 117, 10–720 Olsztyn, Poland
e-mail: tomasz.jozwiak@uwm.edu.pl*

²*Department of Department of Biotechnology in Environmental Protection,
University of Warmia and Mazury in Olsztyn ul. Słoneczna 45g, 10–702 Olsztyn, Poland*

Abstract

The sorption capacity of glauconite, glauconite immobilised on chitosan hydrogel beads and unmodified chitosan hydrogel beads against Reactive Black 5 and Basic Violet 10 was compared in this article. The effect of pH on the sorption effectiveness of dyes on the tested sorbents was investigated and the sorption capacity of sorbents after 24 and 72 h was determined. Langmuir sorption, double Langmuir and Freundlich isotherms were used to describe the experimental data.

The adsorption efficiency of the dyes on sorbents containing chitosan was highest at pH 4. In the case of glauconite, Reactive Black 5 removal efficiency was the highest at pH 3, and Basic Violet 10 removal efficiency was highest at pH 2.

The sorption capacity of glauconite immobilised on chitosan hydrogel spheres obtained after 72 h was -656.73 mg/g and -32.77 mg/g for Reactive Black 5 and Basic Violet 10, respectively.

Key words: *chitosan, hydrogel beads, glauconite, immobilisation, sorption, Reactive Black 5, Basic Violet 10*

Received: 18.03.2017

Accepted: 11.05.2017

1. Introduction

Coloured wastewater from the textile, leather or paper industries are particularly onerous. The discolouration of post-production water by conventional biological treatment systems is not effective because of the low susceptibility of dyes to biodegradation. Efficient methods for removing dyes from wastewater include precipitation methods (coagulation [1], electrocoagulation [2]), advanced oxidation methods (ozonation [3], the Fenton reaction [4], the reaction of NaOCl [5]) and membrane processes (ultrafiltration [6], nanofiltration, reverse osmosis) [7]. The disadvantage of precipitated methods is the salination of wastewater and the formation of significant amounts of sediment [1], whereas the imperfection of the oxidation method is a high risk of formation of toxic by-products such as aromatic amino groups [8]. The weaknesses of membrane methods are the considerable loss of water during the process, the high cost of membranes and the problem of their disposal after use [9].

Sorption is a promising wastewater discolouration method. Technologies based on the adsorption of dyes from wastewater are considered safe for the environment. In addition, the cost of sorption is mainly related to the price of the sorbent.

In recent years, chitosan has been gaining popularity as a sorbent. Chitosan is a polysaccharide, which is a deacylated form of chitin. It may take the form of a powder, flakes or granules of hydrogel. The advantage of the chitosan hydrogel is its efficient use of active sites during sorption [10, 11]. In addition, the chitosan hydrogel has the ability to immobilise other materials, which could assist the process of sorption [12, 13].

Absorbents in the form of chitosan hydrogel pellets may have a very high affinity for anionic dyes, where the sorption capacity can be more than 1000 mg/g [11, 14, 15]. These sorbents have low sorption capacity of cationic dyes, due to the basic nature of chitosan [12]. The solution to this problem could be to incorporate into the structure of the hydrogel a material that has strong affinity for cationic dyes.

Glauconite is a cheap and widely available material, exhibiting high affinity for cationic dyes. It is a mineral from the group of aluminosilicates characterised by high porosity and permeability. It is a common ion exchange material used for softening water. Due to the high content of silicate anions, glauconite is able to sorb most of the substances with a positive charge [16].

The present study has examined the effectiveness of the sorption of the anionic dye Reactive Black 5 and the cationic dye Basic Violet 10 on glauconite immobilised on chitosan hydrogel granules.

2. Materials and Methods

2.1. Materials

Chitosan used in the study was purchased from the company Heppe Medical Chitosan GmbH (Halle, Germany). Specifications provided by the manufacturer of chitosan is presented in Table 1.

Glauconite came from a quartz-glauconite sand mine in Nowogród (Poland). Glauconite with a grain fraction of 0.125–0.500 mm has been applied in the study.

Dyes used in the study came from the Production Plant Dyes "Boruta" SA. The characteristics specified by the manufacturer of dyes has been compiled in Table 2.

Table 1. Specification of chitosan used in the study


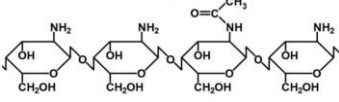
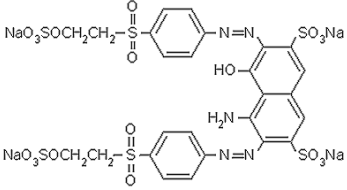
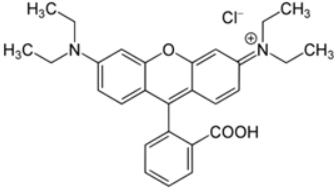
Appearance and form of chitosan		Deacetylation degree	85%
		Viscosity	100 mPas
		Ash content	<1%
		Dry mass content	86.8%
Structural formula		Heavy metals content	<40 ppm
		The source of raw material	Crab shells

Table 2. Characteristics of dyes used in the study

	Reactive Black 5 (RB5)	Basic Violet 10 (BV10)
Chemical structure		
Molar mass	991 g/mol	479 g/mol
λ_{max}	600 [nm]	554 [nm]
Type	anionic/reactive	cationic/basic
Application	dyeing of cotton, viscose, wool, polyamide fibers	dyeing of cotton, paper, leather preparation of printing/painting inks
Other commercial names	Begazol Black B, Celmazol Black B, Diamira Black B, Primazin Black BN, Remazol Black B	Rhodamine B, Futramine D, Peltol D, Basic Red RB, Basazol Red 71 L, Violet B

2.2. Methodology

2.2.1. Preparation of hydrogel beads of chitosan (CHs)

Chitosan in the form of flakes (25 g s.m.) was dissolved in 975 g of 5% acetic acid solution. The resulting chitosan solution (2.5%) was added dropwise through a needle of 0.9 mm to 2 M NaOH in order to form hydrogel beads. After 24 h, the gelated hydrogel beads formed were filtered and washed with distilled water to remove the hydroxide from the sorbent. Chitosan hydrogel beads prepared for research (CHs) (Fig. 1.A) were kept in distilled water at 4°C.

2.2.2. Preparation of glauconite immobilised on chitosan hydrogel beads (CHs-GLAU)

A quantity of 25 g of chitosan in the form of flakes was dissolved in 950 g of 5% solution of CH₃COOH. To this solution, 25 g of d.m. glauconite (GLAU) was added, then the solution was mixed. The resulting heterogeneous mixture containing 2.5% chitosan and 2.5% glauconite was added dropwise through a needle of 0.9 mm to 2 M sodium hydroxide solution. The formed beads containing immobilised glauconite were kept in a solution of NaOH for 24 h. The sorbent was filtered off and washed with

distilled water. The obtained glauconite immobilised on hydrogel beads (CHs-GLAU) had a glauconite:chitosan mass ratio of 1:1 (Fig. 1.C). The sorbent was kept in distilled water at 4°C.

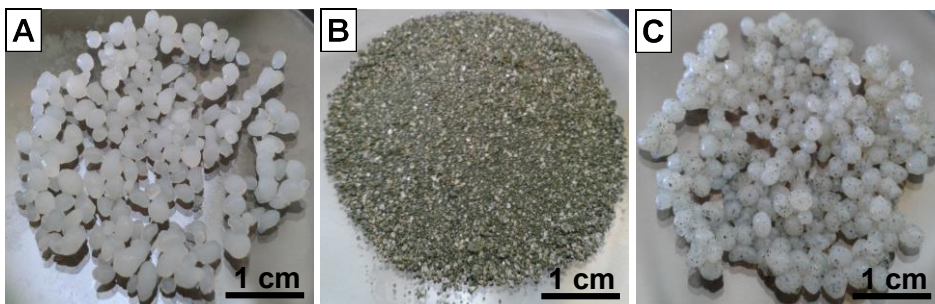


Figure 1. Sorbents used in the study: A) CHs, B) GLAU, C) CHs-GLAU

2.2.3. Determination of the pH effect on the sorption efficiency of dye

The sorbent (1 g d.m.) was weighed to conical flasks (250 mL) after which the dye solutions at pH 2–11 were added. The flasks were then placed on a shaker. Samples were taken after sorption of the solution (10 mL) in order to analyse the concentration of the dye remaining in solution. The test parameters are summarised in Table 3.

Table 3. Parameters of analyses of pH value effect on the effectiveness of dye sorption on tested sorbents

Sorbent	Sorbent conc. [g/L]	Type of dye	Conc. of dyes [mg/L]	Sorption pH [pH]	Sorption time [min]	Stirring speed [r.p.m.]	Temp. [°C]
CHs, GLAU	5	RB5	100	2, 3, 4, 5, 6, 7, 8, 9, 10, 11	60	150	22
CHs-GLAU		BV10	10				

2.2.4. Determination of sorption capacity relative to dyes

Sorbent (1 g d.m.) was weighed into Erlenmeyer flasks (250 mL); the dyes solution at a concentration of 10–2000 mg/L (RB5) or 1–200 mg/L (BV10), with optimum pH (obtained in section 2.2.3), were added to the flask. The flasks were placed on a shaker. After 24 and 72 h, flask samples were taken to determine quantity of the dye remaining in solution. The most important parameters of this study are summarised in Table 4.

Table 4. Parameters of determination of sorption capacity of tested sorbents against dyes

Sorbent	Sorbent conc. [g/L]	Type of dyes	Conc. of dyes [mg/L]	Sorption pH [pH]	Sorption time [min]	Stirring speed [r.p.m.]	Temp [°C]
CHs, GLAU, CHs-GLAU	1	RB5	10, 25, 50, 100, 200, 300, 500, 750, 1000, 1500, 2000	Optimal, determined in point 2.2.3	1440, 4320	150	22
		BV10	1, 2, 5, 10, 25, 50, 75, 100, 150, 200		(24 and 72 h)		

2.2.5. Calculation methods

The amount of dye adsorbed on chitosan sorbent calculated from equation (1):

$$Q_s = \frac{(C_0 - C_s) \cdot V}{m} \quad (1)$$

where:

- Q_s – mass of sorbed dye (static conditions) [mg/g d.m.]
- C_0 – initial dye concentration [mg/L]
- C_s – dye concentration after sorption [mg/L]
- V – solution volume [L]
- m – sorbent mass [g d.m.]

Three popular adsorption isotherms – Langmuir (2), Langmuir 2 (double Langmuir isotherm) (3) and Freundlich (4) – have been used to determine the sorption capacity of the tested sorbents:

$$Q_s = \frac{q_{\max} \cdot K_c \cdot C}{1 + K_c \cdot C} \quad (2)$$

$$Q_s = \frac{b_1 \cdot k_1 \cdot C}{1 + k_1 \cdot C} + \frac{b_2 \cdot k_2 \cdot C}{1 + k_2 \cdot C} \quad (3)$$

$$Q_s = K \cdot C^n \quad (4)$$

where:

- Q_s – mass of sorbent dye (static conditions) [mg/g d.m.]
- C – the concentration of the dye remaining in solution [mg/L]
- q_{\max} – maximum sorption capacity in the Langmuir equation [mg/g d.m.],
- K_c – constants in Langmuir 2 equation [L/mg]
- b_1 – the maximum sorption capacity of the sorbent (active sites of the first type) [mg/g s.m]
- b_2 – the maximum sorption capacity of the sorbent (active sites of the second type) [mg/g s.m]
- $k_1; k_2$ – constant in Langmuir 2 equation [L/mg]
- K – sorption equilibrium constant in the Freundlich model
- n – Freundlich equation constant

3. Results and Discussion

3.1. Effect of pH on the efficiency of dye sorption

Hydrogel chitosan sorbents underwent dissolution at pH <4 and lost their sorption properties. Therefore, the dye sorption efficiencies on CHs and CHs-GLAU at pH 2 and 3 are not shown on Figure 2.

The RB5 sorption effectiveness on CHs and CHs-GLAU was the highest at pH 4, and decreased with increasing initial pH in the range of 4–7 and 9–11. Sorption of RB5 on GLAU occurred most intensively at a pH of 3. As in the case of CHs and CHs-GLAU, the effectiveness of RB5 sorption on GLAU decreased with increasing initial pH

in the range of pH 3–8 and 9–11. In every case, an increase in the intensity of RB5 sorption at pH 9 (Fig. 2.A) was observed.

The higher efficiency of RB5 sorption on chitosan sorbents at low pH was due to the protonation of the amine functional groups of chitosan. The positively charged chitosan chains are electrostatically attracted to an anionic dye and significantly assisted sorption. The positive impact of low pH on the sorption of anionic dyes has also been observed in studies of discolouration of aqueous solutions with the use of crosslinked chitosan [14, 17] and chitosan in the form of flakes [11].

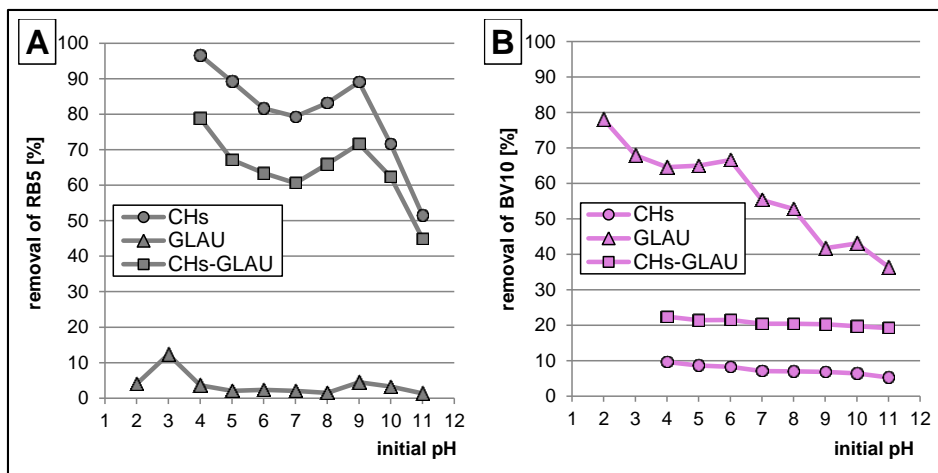


Figure 2. Effect of pH on the efficiency of dye sorption A) RB5, B) BV10 of the tested sorbents

Increasing the efficiency of RB5 sorption at pH 9 was most likely due to amino group possession by the dye. Presumably, all the absorbents tested at pH >8 gained a negative charge, while the amino group of RB5 at pH 9 still had a positive charge, which assisted the sorption of the dye. At pH >9, the amino group of RB5 lost its positive charge. Consequently, at a pH of 10–11, the electrostatic repulsion between the negatively charged sorbent and anionic dye resulted in low efficiency of RB5 sorption. Low effectiveness of binding RB5 at pH >10 could also result from the competition with OH⁻ ions of the active sites of sorbents.

The relatively low RB5 sorption efficiency on glaucanite was most likely caused by a high content of silicates. Silicates, having a negative charge, electrostatically repel anionic dyes, thus preventing its sorption.

BV10 sorption efficiency on the sorbents tested, despite the cationic character of the dye decreased with increasing initial pH of the solution (Fig. 2.B). The obtained results could be a result of BV10 having a carboxyl group. The local negative charge generated by a carboxyl group ($-\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+$) may be supported by sorption of BV10 at a low pH. At high pH, both dye and sorbents could gain a negative charge, resulting in electrostatic repulsion and limiting the effectiveness of BV10 sorption.

A significant decrease in the efficiency of BV10 sorption with increasing pH was also observed in studies on the purification of wastewater from colourful synthetic zeolites [18], as well as in the study of sorption of dyes on BiFeO₃ (ceramics) [19].

Higher efficiency of BV10 sorption on GLAU than CHs and CHs-GLAU resulted from an excess of negative charge in the crystal lattice of glaucanite (aluminosilicate).

The negative charge generated by silicates guarantee a good exchange capacity for cations and other compounds with a positive charge. In the case of CH-GLAU, the exchange capacity of glauconite immobilised in the hydrogel was limited by the content of chitosan. Chitosan, having a basic character, electrostatically repelled the cationic BV10, which inhibited its sorption.

The tested sorbents affected the dye to induce a change in the pH of the solution (Fig. 3). In the case of chitosan sorbents at the initial pH range of 4–9, the pH after 60 min sorption was in the range 7.2–8.2.

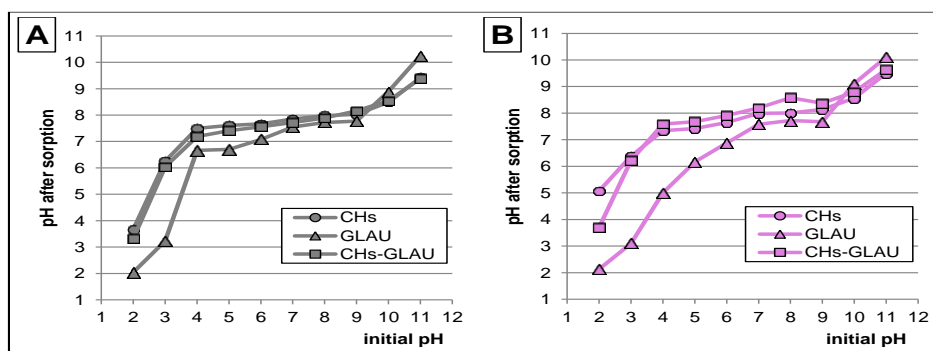


Figure 3. Effect of the sorbents on the change of pH after dye sorption: A) RB5, B) BV10

The change of pH during the sorption on glauconite depended to some extent on the type of sorbed dye. The reason for the observed differences in the change in pH of the solution during the sorption of the dye on GLAU (Fig. 3.A, B) can vary relative to the ion-exchange capacity of RB5 and BV10.

The pH of the solution during sorption always endeavored to obtain a similar pH_{ZPC} of the tested sorbent (ZPC – point of zero charge). Figure 4 shows the method of determining the point of pH_{ZPC} . The point values of pH_{ZPC} obtained for CHs, GLAU and the CH-GLAU were 7.98; 7.67 and 7.87, respectively. The highest value of pH_{ZPC} for CHs resulted from the largest number of functional groups ($-NH_2$) of a basic nature.

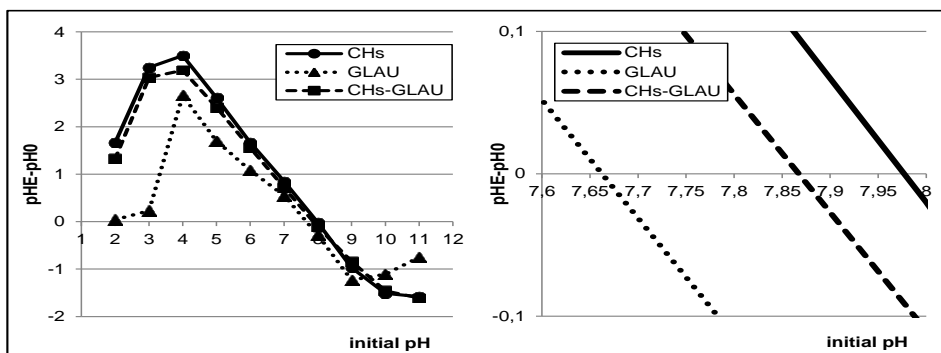


Figure 4. Difference between solution pH at the beginning and at the end of sorption as affected by the initial pH of the solution (determination of pH_{ZPC} of sorbents)

Due to the scope of the pH of the effluent colour, which is usually pH 4–7 [20, 21], experiments on the sorption capacity of the tested sorbent were performed at pH 4.

3.2. Sorption capacity in relation to dyes

The obtained research results were described by three isotherms of sorption (Langmuir, Langmuir 2 and Freundlich) (Fig. 5, Tables 5 and 6). In each case, the best fit to experimental data was shown by the double Langmuir isotherm. This might indicate the existence of at least two sorption centres in the structure of tested sorbents.

The sorption capacity of CHs obtained after 72 h in relation to RB5 was 875.66 mg/g and was multiple times higher than the capacity of GLAU (10.21 mg RB5/g) (Table 5, Fig. 5). In case of CHs-GLAU, the capacity of 656.73 mg RB5/g was reached (Table 5).

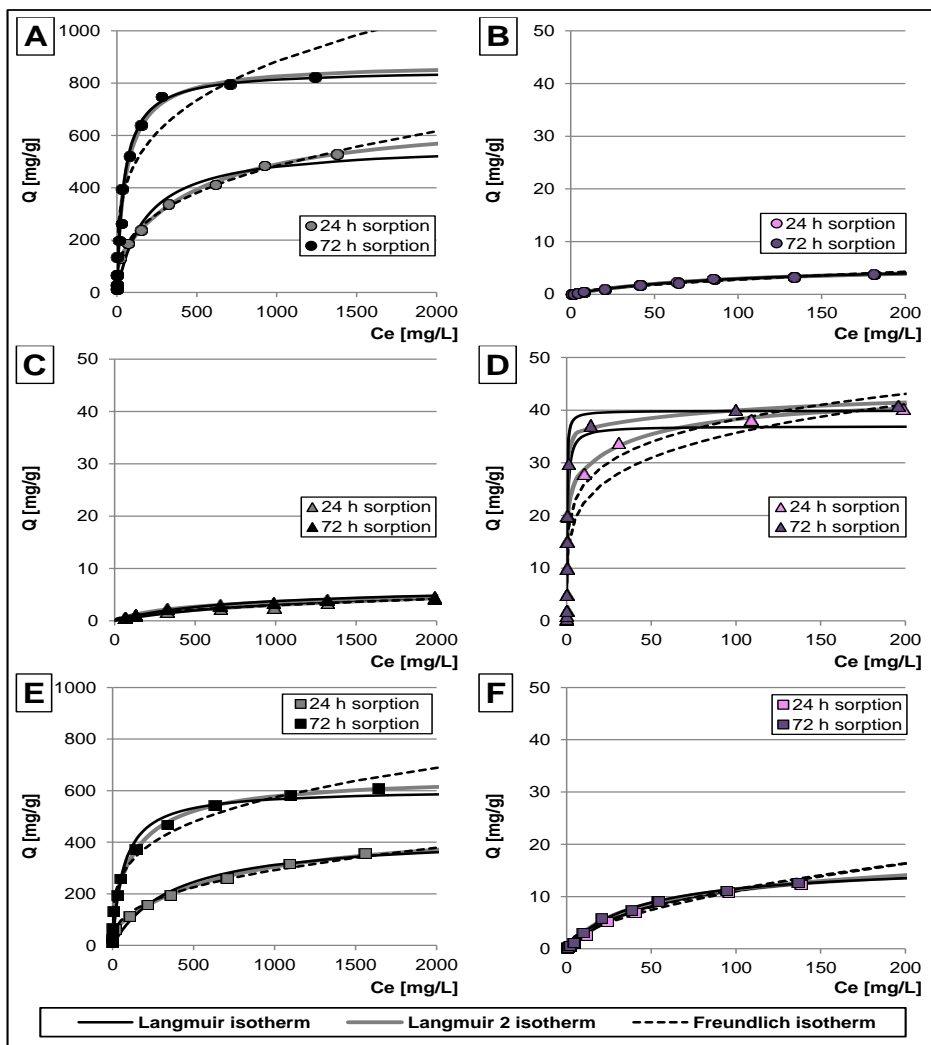


Figure 5. Dye sorption isotherms on the tested sorbents A) RB5 sorption on CHs, B) BV10 sorption on CHs, C) RB5 sorption on GLAU, D) BV10 sorption on GLAU, E) RB5 sorption on CHs-GLAU, F) BV10 sorption on CHs-GLAU

High values of k_1 constants, determined from the double Langmuir isotherm for the RB5 sorption on CHs as well as CHs-GLAU indicate that there is a high degree of affinity of first kind of the sorption centre to the dye. Much lower values of k_2 constants indicate a lower affinity of second kind of the active sites to RB5 (Table 5). Presumably, the described sorption centres are amino chitosan groups (b_1, k_1) as well as acetamide chitosan groups (b_2, k_2).

The sorption capacity of CHs in relation to BV10 was small and after 72 h of sorption, it was 5.95 mg/g. A much higher sorption capability of BV10 was demonstrated by GLAU (44.79 mg/g). The sorption capacity of CHs-GLAU was 26.8% lower and was 32.77 mg/g.

In the case of BV10 sorption on sorbents including glauconite (GLAU, CHs-GLAU), the main sorption centres are presumably silane groups from silicates ($-\text{Si-O}^-$). They are located in the tetrahedral layer of glauconite (1. type active sites) and in the octahedral layer (2. type sorption centers).

Table 5. Constants determined from Langmuir 1 and Langmuir 2 isotherms

DYE	TIME OF SORPTION	SORBENT	Langmuir (constants)			Langmuir 2 (constants)					
			Q_{\max}	K_c	R^2	Q_{\max}	b_1	k_1	b_2	k_2	R^2
			[mg/g]	[L/mg]	-	[mg/g]	[mg/g]	[L/mg]	[mg/g]	[L/mg]	-
RB5	24 h	CHs	566.8	0.0056	0.962	688.6	574.17	1.0037	114.44	0.0019	0.999
		GLAU	7.6	0.0007	0.972	9.8	1.09	0.0158	8.75	0.0003	0.991
		CHs-GLAU	428.4	0.0027	0.975	483.9	425.95	1.8780	57.94	0.0014	0.998
	72 h	CHs	851.2	0.0216	0.978	875.7	771.19	2.4278	104.47	0.0145	0.991
		GLAU	6.6	0.0013	0.986	10.2	3.52	0.0034	6.69	0.0002	0.996
		CHs-GLAU	605.7	0.0145	0.964	656.7	521.09	2.2941	135.64	0.0057	0.998
BV10	24 h	CHs	5.8	0.0101	0.997	5.8	2.92	0.0101	2.87	0.0101	0.997
		GLAU	37.0	1.8896	0.928	43.3	25.53	3.9841	17.73	0.0260	0.962
		CHs-GLAU	16.34	0.0236	0.997	17.7	8.82	0.0172	8.87	0.0172	0.997
	72 h	CHs	6.0	0.0099	0.993	6.0	2.95	0.0099	3.00	0.0099	0.993
		GLAU	39.9	5.2951	0.949	44.8	36.06	6.2856	8.73	0.0082	0.956
		CHs-GLAU	17.7	0.0172	0.997	32.8	19.50	0.0008	13.27	0.0302	0.997

Table 6. Constants determined from the Freundlich isotherm

DYE	TIME OF SORPTION	SORBENT	Freundlich (constants)		
			k	n	R ²
			-	-	-
RB5	24 h	CHs	44.126	0.3468	0.996
		GLAU	0.099	0.4930	0.989
		CHs-GLAU	22.102	0.3737	0.993
	72 h	CHs	140.124	0.2665	0.935
		GLAU	0.198	0.4117	0.981
		CHs-GLAU	93.752	0.2624	0.984
BV10	24 h	CHs	0.165	0.6113	0.978
		GLAU	13.906	0.2046	0.885
		CHs-GLAU	0.810	0.5667	0.975
	72 h	CHs	0.170	0.6080	0.981
		GLAU	17.326	0.1719	0.812
		CHs-GLAU	1.043	0.5195	0.978

4. Summary

The immobilisation of glauconite on chitosan hydrogel provided beneficial results and these are outlined as follows. Chitosan and glauconite in the CHs-GLAU form (1:1) had higher bonding efficiency than CHs and GLAU used separately, calculated per unit of sorbent dry mass. Specifically, 2 g CHs-GLAU can bind more dye than 1 g CHs + 1 g GLAU.

The condition of obtaining satisfactory results of dye sorption on chitosan sorbents and glauconite is the correction of pH. The sorption of RB5 and BV10 on CHs and CHs-GLAU is the most effective at pH 4. In the case of GLAU, the effectiveness of RB5 sorption is the highest at pH 3 and BV10 at pH 2.

Glauconite may be used as a good filler for the production of hydrogel sorbents intended for anionic dye bonding. The main advantage of the use of CHs-GLAU for cationic dye removal in comparison with GLAU is the possibility of easy separation of the sorbent from the solution after the purification process.

CHs-GLAU is a good example of a universal sorbent, capable of effective removal of anionic as well as cationic dyes. For this reason, CHs-GLAU might be used for the decolourisation of mixed wastewater containing various dye types.

5. Acknowledgements

This study was financed under Project No. 18.610.008-300 of the University of Warmia and Mazury in Olsztyn, Poland.

6. References

- [1] Liang C Z, Sun S P, Li F Y, Ong Y K, Chung T S; (2014) Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration. *J Membrane Sci* 469, 306–315. DOI: 10.1016/j.memsci.2014.06.057.

- [2] Nandi B K, Patel S; (2013) Effects of operational parameters on the removal of brilliant green dye from aqueous solutions by electrocoagulation. *Arab J Chem*, (in print). **DOI:** 10.1016/j.arabjc.2013.11.032 .
- [3] Wijannarong S, Aroonsrimorakot S, Thavipoke P, Kumsopa C, Sangjan S; (2013) Removal of reactive dyes from textile dyeing industrial effluent by ozonation process. *APCBEE Procedia* 5, 279–282. **DOI:** 10.1016/j.apcbee.2013.05.048.
- [4] Sohrabi M R, Khavaran A, Shariati S, Shariati S; (2014) Removal of Carmoisine edible dye by Fenton and photo Fenton processes using Taguchi orthogonal array design. *Arab J Chem* (in print) **DOI:** 10.1016/j.arabjc.2014.02.019.
- [5] Omura T; (1994) Design of chlorine-fast reactive dyes: Part 4: Degradation of amino-containing azo dyes by sodium hypochlorite. *Dyes Pigm* 26, 33–50. **DOI:** 10.1016/0143-7208(94)80028-6.
- [6] Ramesh B B, Parande A K, Raghu S, Prem K T; (2007) Textile technology. Cotton textile processing: Waste generation and effluent treatment. *J Cotton Sci* 11, 141–153.
- [7] Yu S, Chen Z, Cheng Q, Lü Z, Liu M, Gao C; (2012) Application of thin-film composite hollow fiber membrane to submerged nanofiltration of anionic dye aqueous solutions. *Sep Purif Technol* 88, 121–129. **DOI:** 10.1016/j.seppur.2011.12.024.
- [8] Hamada K, Nishizawa M, Yoshida D, Mitsuishi M; (1998) Degradation of an azo dye by sodium hypochlorite in aqueous surfactant solutions. *Dyes Pigm* 36, 313–322. **DOI:** 10.1016/S0143-7208(97)00030-2.
- [9] Nataraj S K, Hosamani K M, Aminabhavi T M; (2009) Nanofiltration and reverse osmosis thin film composite membrane module for the removal of dye and salts from the simulated mixtures. *Desalination* 249, 12–17. **DOI:** 10.1016/j.desal.2009.06.008.
- [10] Józwiak T, Filipkowska U, Szymczyk P, Kuczajowska-Zadrożna M, Mielcarek A, Zyśk M; (2016) The influence of chitosan deacetylation degree on reactive black 5 sorption efficiency from aqueous solutions. *Prog Chem Appl Chitin Derivatives* 21, 83–92. **DOI:** 10.15259/PCACD.21.08.
- [11] Józwiak T, Filipkowska U, Szymczyk P, Zyśk M; (2017) Effect of the form and deacetylation degree of chitosan sorbents on sorption effectiveness of Reactive Black 5 from aqueous solutions. *Int J Biol Macromol* 95, 1169–1178. **DOI:** 10.1016/j.ijbiomac.2016.11.007
- [12] Józwiak T, Filipkowska U, Rodziewicz J, Grabowski P; (2013) Wykorzystanie niekonwencjonalnych sorbentów do usuwania barwników ze ścieków przemysłowych. *INSTAL* 341, 48–51.
- [13] Kuczajowska-Zadrożna M, Filipkowska U, Józwiak T, Szymczyk P; (2015) Biosorption/desorption of cadmium(II) and zinc (II) from aqueous solutions by activated sludge immobilized onto chitosan beads. *Prog Chem Appl Chitin Derivatives* 20, 142–155 **DOI:** 10.15259/PCACD.20.13.
- [14] Filipkowska U, Józwiak T; (2013) Application of chemically-cross-linked chitosan for the removal of Reactive Black 5 and Reactive Yellow 84 dyes from aqueous solutions. *J Polym Eng* 33, 735–748. **DOI:** 10.1515/polyeng-2013-0166.
- [15] Józwiak T, Filipkowska U, Szymczyk P, Kuczajowska-Zadrożna M; (2015) Application of chitosan ionically crosslinked with sodium edetate for reactive dyes

- removal from aqueous solutions. *Prog Chem Appl Chitin Derivatives* 20, 82–96. DOI: 10.15259/PCACD.20.08.
- [16] Selim K A, Youssef M A, Hassan M S, El-Rahiem F H Abd; (2013) Removal of dyes from aqueous solutions using surface modified bentonite and glauconite minerals. *J Ore Dress* 15, 21–32.
- [17] Józwiak T, Filipkowska U, Rodziewicz J, Nowosad E; (2013) Effect of cross-linking with glutaraldehyde on adsorption capacity of chitosan beads. *Prog Chem Appl Chitin Deriv* 18, 35–38.
- [18] Józwiak T, Filipkowska U, Szymczyk P, Mielcarek A; (2016) Zastosowanie niekonwencjonalnych sorbentów do usuwania Basic Violet 10 z roztworów wodnych. *Inż Ekolog* 47, 95–103. DOI: 10.12912/23920629/62853.
- [19] Zhang J, Gondal M A, Wei W, Zhang T, Xu Q, Shen K; (2012). Preparation of room temperature ferromagnetic BiFeO₃ and its application as an highly efficient magnetic separable adsorbent for removal of Rhodamine B from aqueous solution. *J Alloy Compd* 530, 107–110. DOI: 10.1016/j.jallcom.2012.03.104.
- [20] Mattioli D, De Florio L, Giordano A, Tarantini M, Scalbi S, Aguado M M, Bianchi R, Bergna G, Witters H, Genne I, Schiettecatte W, Spanjers H, Bisschops I, Hanke G, Loos R, Ligthart J, Osset P, Vayn C, De Vresse I; (2005) Efficient use of water in the textile finishing industry. *E-Water* (electronic publication of the European Water Association) p. 1–18.
- [21] Mihułka M, Sójka-Ledakowicz J, Gajdzicki B, Machnowski W, Żyła R, Lewartowska J, Grzywacz K, Ewa Strzelecka-Jastrząb E; (2003) Charakterystyka technologiczna przemysłu włókienniczego w Unii Europejskiej. Ministerstwo Środowiska, Warszawa.