

DYESTUFFS REMOVAL FROM SYNTHETIC WASTEWATER WITH CHITOSAN, CROSS-LINKED CHITOSAN AND CHITOSAN-POLY (ACRYLIC ACID) CONJUGATE

SENTETİK ATIK SULARDAN BOYAR MADDELERİN KİTOSAN, ÇAPRAZ BAĞLI KİTOSAN VE KİTOSAN-POLİ (AKRİLİK ASİT) KONJUGATI İLE GİDERİLMESİ

Mithat CELEBI^{1*}, Zafer Omer OZDEMİR²

¹ Department of Polymer Engineering, Faculty of Engineering, Yalova University, 77100, Yalova, Turkey

² Department of Energy Systems Engineering, Faculty of Technology, Kırklareli University, 39100, Kırklareli, Turkey

Received: 25.02.2016

Accepted: 29.03. 2017

ABSTRACT

Remazol Brilliant Blue R (RBBR) and Naphthol Blue Black (NBB) dyestuffs are commonly utilized in the textile industry. In this study, RBBR and NBB dyestuffs were removed with chitosan, cross-linked chitosan and chitosan-poly(acrylic acid) (PAA) conjugate. Cross-linked chitosan and chitosan-poly(acrylic acid) conjugate were synthesized at 15 and 30 minutes respectively by using microwave energy. RBBR dyestuff was removed 70.23 % and 80.78 % at pH: 4.0 and pH: 5.0 respectively by chitosan-poly(acrylic acid) conjugate. NBB and RBBR were removed higher percent with crosslinked chitosan than chitosan-poly(acrylic acid) conjugate at acidic pHs. NBB and RBBR were removed successfully with approximately 100 % dye removal percentage using both chitosan and cross-linked chitosan.

Keywords: Chitosan, Conjugate, Dyestuffs, Microwave, Poly (acrylic acid), Removal

ÖZET

Remazol Brilliant Blue R (RBBR) ve Naphtol Blue Black (NBB) boyar maddeleri tekstil endüstrisinde yaygın olarak kullanılmaktadır. Bu çalışmada, RBBR ve NBB boyar maddeleri kitosan, çapraz bağlı kitosan ve kitosan-poli(akrilik asit) (PAA) konjugatı ile giderildi. Çapraz bağlı kitosan ve kitosan-poli(akrilik asit) konjugatı mikrodalga enerjisi kullanılarak sırasıyla 15 ve 30 dakikada sentezlendi. RBBR boyar maddesi kitosan-poli(akrilik asit) konjugatı ile pH: 4.0 ve pH: 5.0'te sırasıyla % 70.23 ve % 80.78 giderildi. NBB ve RBBR çapraz bağlı kitosan ile kitosan-poli(akrilik asit) konjugatına göre daha yüksek bir yüzde ile giderildi. NBB ve RBBR boyar maddeleri kitosan ve çapraz bağlı kitosan kullanılarak yaklaşık olarak % 100 boya giderme yüzdesi ile başarılı bir şekilde giderildi.

Anahtar Kelimeler: Boyar madde, Giderme, Kitosan, Konjugat, Mikrodalga, Poli (akrilik asit)

Corresponding Author: Mithat Çelebi, mithat.celebi@yalova.edu.tr

INTRODUCTION

Large volumes of wastewater coming out of the textile industries have a strong color with fluctuating pH and high chemical oxygen demand. Dyehouse wastewater may contain toxic and carcinogenic chemicals harmful to all species living in water (1–3). Photosynthetic interaction in an aquatic ecosystem is affected because of a decreased penetration of light and presents toxins which are waste from unbound textile dyestuffs (4).

Remazol Brilliant Blue R (RBBR) is a reactive dyestuff, extensively used in dyeing processes, which is soluble in water. It is easily hydrolyzed into insoluble forms, where 5–

10 % of the dyestuffs stay in the effluent. Therefore, useful and economical technique in order to remove dyes from the textile wastewater is a necessity (4–7). RBBR is a reactive dyestuff which is contain anthraquinone chemical structure and used in the textile manufacturing (Fig. 1) (8, 9). Naphthol Blue Black (NBB) involves azo, anthracene, naphthalene and sulfonated groups (Fig. 2). NBB has a high degree of light fastness and commercial grades. Therefore, NBB is also commonly used to dyeing wool, nylon, silk and textile printing. These dyestuffs have been used other industries such as include coloring soaps, anodizing aluminum, and casein, staining wood and preparing the ink (6, 10).

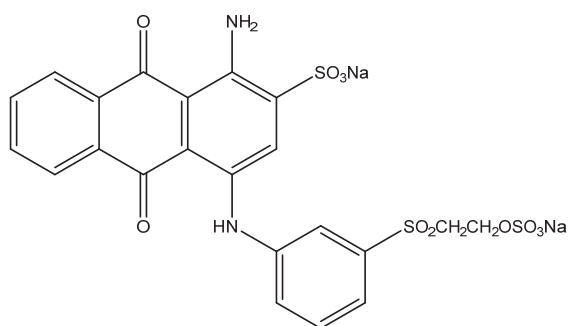


Figure 1. Remazol Brilliant Blue R (C.I: Reactive Blue 19, Mw: 616.50 g/mol)

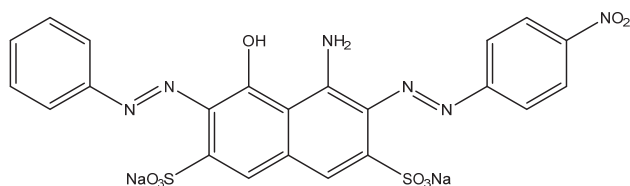


Figure 2. Naphthol Blue Black (C.I: Acid Black 1, Mw: 626.54 g/mol)

Polymeric coagulants can be applied to the treatment of wastewater. Natural polymers have been used due to their non-toxic, biodegradable, renewable, and efficient nature in wastewater treatment. High weight molecular weight and high charged polymers such as chitosan can be used as a coagulant. Chitosan is an amino polymer which is formed by deacetylation of chitin (in Figure 3; deacetylation degree: 100%). Chitosan is the most abundant natural polymer containing amino group. This amino polysaccharide has been paid attention for the past several decades in water treatment processes to eliminate particulate and dissolved wastes. Moreover, chitosan-based materials are extensively utilized as coagulants in wastewater treatment (9–15).

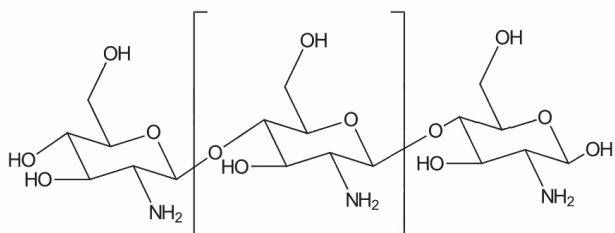


Figure 3. Chemical structure of Chitosan

Chitosan and derivatives are also known to be active to bind metal cations in almost neutral pHs owing to amine functional groups in glucosamine unit of chitosan. Furthermore, chitosan interacts with anionic organic chemicals in especially acidic solutions (10, 11). There are many studies in the literature about chitosan and derivatives to remove dyestuffs (9,12). However, there is not any work about removal of dyestuffs with chitosan-PAA conjugate. This study aims to remove the textile dyestuffs (NBB and RBBR) using chitosan, chitosan-poly(acrylic acid) and cross-linked chitosan. Dyestuff removal experiments were performed at different pHs and adsorbent dosages.

EXPERIMENTAL

Materials and Methods

Medium molecular weight chitosan (degree of deacetylation: 75-85%), poly(acrylic acid) (PAA) (35 %, Mw: 100000 g mol⁻¹) and Remazol Brilliant Blue R (C.I. Reactive Blue 19, Mw: 624.54 g mol⁻¹) were purchased from Sigma. Naphthol Blue Black (C.I. Acid Black 1, Mw: 616.50 g mol⁻¹) was obtained from Fluka. Glutaraldehyde solution (50 % aq) was acquired from Molekula. All chemicals were utilized without any purification in this work.

Removal of NBB and RBBR was observed spectrophotometrically with using Shimadzu UV-1800 Spectrophotometer. Percent removal values of colored solutions were determined according to our previous study by followed decreasing of the absorbance at the maximum wavelength (λ_{max} : 620 nm for NBB; λ_{max} : 594 nm for RBBR) in the visible spectrum of each dyestuff (6). The yield of removal was disclosed as the percentage ratio of the decolorized dyestuff concentration.

$$\% \text{ Removal} = \frac{C_i - C_a}{C_i} \times 100 \quad (1)$$

C_i and C_a represent initial dye concentration (nmol/L) and dye concentration after 60 min. settling time (nmol/L), respectively in equation 1.

Preparation of Synthetic Wastewater

Textile dyestuffs, Naphtol Blue Black and Remazol Brilliant Blue R were selected as model dyes to prepare synthetic textile dye wastewater. Synthetic textile dye wastewater was prepared using stock solutions of dyestuffs in distilled water. The concentration of NBB (10 mg L⁻¹) differs from RBBR (67 mg L⁻¹) concentration. However, the absorbance of these dye solutions was identical to their maximum absorbance wavelengths. Synthetic dye wastewater was prepared according to this same absorbance of NBB and RBBR. Moreover, the absorbance of dyestuffs was measured at different concentrations of NBB and RBBR with their maximum wavelengths. Calibration curves of NBB and RBBR were shown in Fig. 4 and Fig. 5. pHs of the dye solution were adjusted with 1M HCl and 1M NaOH.

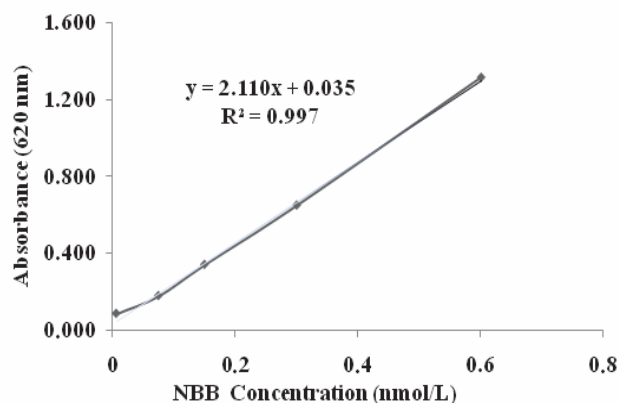


Figure 4. Calibration curve for NBB

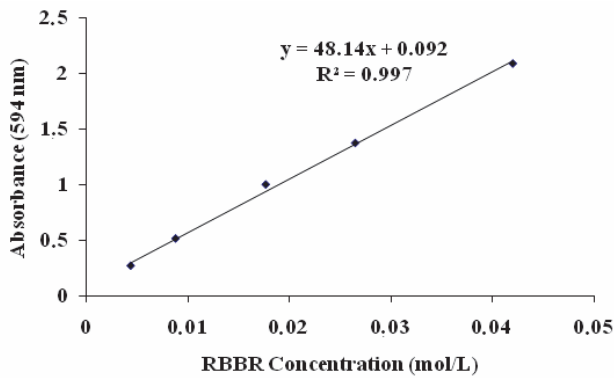


Figure 5. Calibration curve for RBBR

Adsorption Experiments

Various amounts of chitosan were added to synthetic textile dye wastewater. Coagulation experiments were carried out using Jar Test device. Synthetic dyestuff solution was mixed after adding chitosan under forceful agitation (400 rpm) for 5 min. After that synthetic dye solution was stirred slower than before with slow agitation (100 rpm) for 30 min. Bounding dyestuff molecules to chitosan molecules was collapsed at the bottom of beaker after 60 min. settling time. NBB removal was performed at different pHs (5.0, 6.0, 7.0, 8.0, 9.0, 10.0) with 100.0 mg/L, 200.0 mg/L and 400.0 mg/L chitosan amounts. RBBR removal was carried out with chitosan at different pHs (3.0, 4.0, 5.0, 6.0, 7.0). All experiments were performed at room temperature in triplicate.

To examine the effect of different amounts of chitosan and chitosan-PAA conjugates on adsorption of RBBR and NBB dyestuffs. Adsorption experiment was carried out in 2.0 L beaker. The effect of different initial pH on the adsorption of RBBR and NBB by chitosan and the conjugate at room temperature.

The adsorption capacities (q_e , mg/g) for dyestuffs, were calculated according to Equation (2) as Chen et al. (2014) (14).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

C_0 and C_e (mg/L) are the initial and equilibrium concentration, respectively. V (L) is the volume of dyestuff solution. In addition, m (g) represents the weight of the chitosan in Eq. 2.

Microwave assisted synthesis of cross-linked chitosan

Microwave assisted synthesis was carried out using with Milestone-Microsynth multi-mode microwave device. 0.2 g chitosan (1 % w/v) was dissolved in diluted acetic acid and reacted with different volumes of glutaraldehyde solution (50 % aq). Viscous gel formation was observed after the microwave reaction for 15 min. These gels were dried at 60.0 °C for overnight. Removal was carried out with cross-linked chitosan at pH: 3.0, 5.0 and 7.0. In this study, reaction media consists of water and DMF which are high dielectric solvents.

Chitosan amounts were kept constant at 0.2 g. However, glutaraldehyde concentration increased. After the removal of unbound chitosan and retained glutaraldehyde solution from the reaction media, crosslinked-chitosan amounts were dried. Synthesized crosslinked chitosan amounts were shown in Fig. 6.

Microwave-assisted synthesis of Chitosan-PAA conjugate

The poly(acrylic acid) powder was obtained from 35 % (w/w) PAA solution by using Telstar Cryodos lyophilizator. 1.0 g chitosan and 440.0 mg PAA were weighted and mixed in 0.5 M dimethyl formamide (DMF) media. DMF solution was prepared in 5.0 mL DMF, 5.0 mL activator o-benzotriazole-N, N, N', N'-tetramethyl-uronium-hexafluoro-phosphate (HBTU) and 5.0 mL N, N-diisopropylethylamine (DIEA) and N-methyl-2-pyrrolidone (NMP) as activator bases.

Table 1. Reaction conditions for microwave synthesis of cross-linked chitosan

	Time (min.)	Energy (W)	Maximum Temperature (°C)
Step 1	0-5	150	50
Step 2	5-10	150	50
Step 3	10-15	25	25

Table 2. Reaction conditions for microwave synthesis of Chitosan-PAA conjugate

	Time (min.)	Energy (W)	Maximum Temperature (°C)
Step 1	0-5	100	75
Step 2	5-25	100	75
Step 3	25-30	25	25

RESULTS and DISCUSSION

Microwave assisted reactions

The use of microwaves as an energy source for chemical reactions is extensively grown up since 1985 (16). Microwave energy is also called dielectric heating (17) and it is effectively used for homogeneous heating of reaction media. Also, chemical reactions are enhanced by using microwave energy, because of the fast heating of the polar solvents and tension effects (18-20).

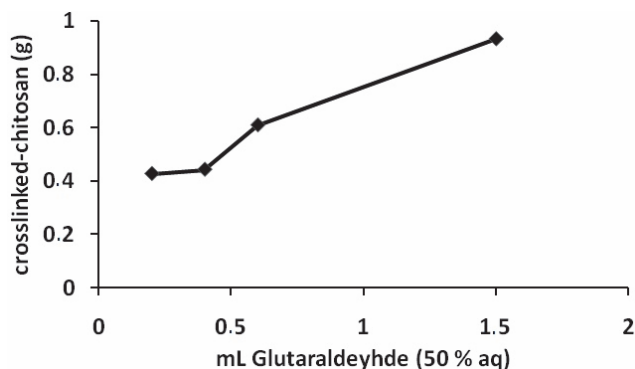


Figure 6. Crosslinked chitosan amounts from 0.2 g chitosan with different volumes of glutaraldehyde (50 % aq).

The conjugation reaction was carried out in the solid phase. Solid phase organic synthesis is suggested in conjugate synthesis because it is favorable for very mild purification of synthetic intermediates from soluble chemicals of the reaction solution by filtration technique (21, 22). Synthesized chitosan-PAA conjugate did not soluble in DMF. After the reaction occurred, unbounded PAA was removed by washing with DMF. Moreover, unbounded chitosan was also removed by acetate buffer washing. Chitosan-PAA conjugate was dried at 60 °C overnight and composed 1350.0 mg product. Reaction yield was calculated as 93 %. RBBR removal was carried out using Chitosan-PAA conjugate at pH: 4.0 and 5.0 in this study.

Removal of synthetic wastewater with chitosan and adsorption capacities

In this work, electrostatic interaction system is causing the strong attraction between chitosan and anionic dyestuffs which are Naphthol Blue Black and Remazol Brilliant Blue R. The best interaction of chitosan and dyestuffs were carried out at acidic pHs due to protonation of amine groups. Dye removal values percentages of NBB and RBBR with chitosan was shown in Fig. 7 and Fig. 8. at different pHs using different amounts of chitosan.

Effect of pH and adsorbent dosage

pH is the most important factor, affecting the capacity of adsorbent in wastewater treatment. Adsorption efficiency depends on pH of the solution. Once the pH of the solution is changed, the surface properties and ionic character of chitosan also change (4, 13).

In low pH, chitosan is charged with positive charge. Electrostatic interaction occurred between chitosan and dyestuff molecules, and dye removal efficiency increased.

At pH about neutr (pH: 7.0) chitosan pKa, chitosan dye removal efficiency was decreased, However, dye removal efficiency increased because of coordination covalent bond forming at pH: 8.0 and 9.0. Maximum NBB dyestuff removal was reached at pH: 5.0 for different chitosan dosages in Fig. 7.

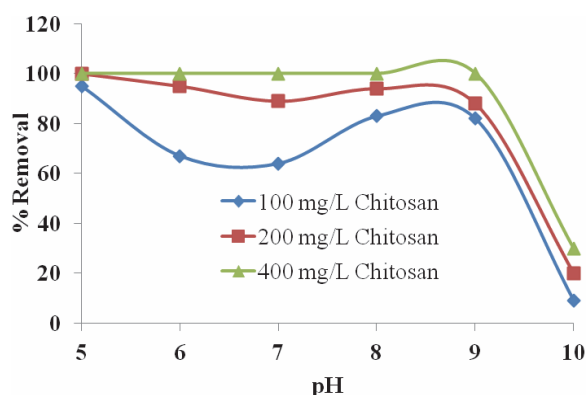


Figure 7. Removal of NBB at different Chitosan dosages and pHs.

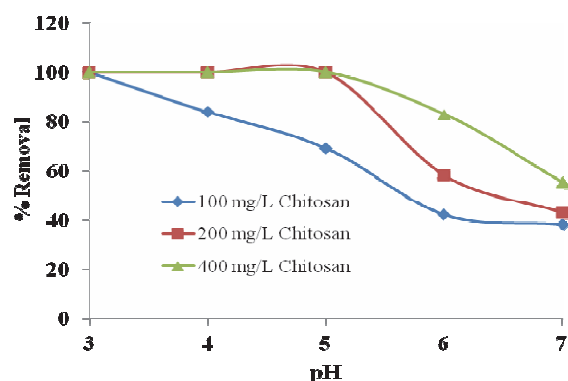


Figure 8. Removal of RBBR at different chitosan amounts and pHs.

In this stage, removal of NBB and RBBR by using the only chitosan have been examined at different pHs and various amounts of chitosan. It was investigated at pH: 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 for NBB removal and at pH: 3.0, 4.0, 5.0, 6.0 and 7.0 for RBBR removal. In Fig. 7, NBB removal was carried out efficiently by acidic and broad pH band (pH: 5.0-9.0). However, NBB removal values are high, especially at acidic pHs because of the lower initial dye concentration from RBBR (Fig. 8).

Yazdani et al. studied with feldspar/titanium/chitosan hybrid to remove NBB (C.I Acid Black 1) dyestuff. They reported that their the hybrid adsorbent 72 mg/g adsorption capacity and 86% removal values at 200 rpm and 25 °C temperature, and 50 mg/L initial dye concentration (initial pH: 4.0, final pH:9.0) (12). Jabli et al. (2013) studied with Acid Blue 25 by using cellulose-chitosan microspheres and Cu(II)/cellulose-chitosan at different pH ranges of 3.0 and 9.0. Optimum pH was found pH: 5.0 for adsorption of AB25 with q_e : 2 mg/g adsorption capacity with cellulose-chitosan microspheres. q_e : 6.8 mg/g adsorption capacity with Cu(II)/cellulose-chitosan dye removal from aqueous solution at initial dye concentration: 50 mg/L (13). Adsorption capacity (q_e) was determined as 870 mg/g at pH: 5.0 and at room temperature

for NBB dyestuff. In addition, Adsorption capacity (q_e) was determined as 26509 mg/g at pH: 3.0 and at room temperature for RBBR dyestuff in this study.

Chitosan is protonated in low pHs to neutral pHs with a charge density depending on the pH and of deacetylation degree of chitin (13). In this work, chitosan interacted with anionic dye solutes (NBB, RBBR) at acidic solutions. Dye removal from synthetic wastewater solutions was pH dependent. Few amounts of chitosan were required at acidic pHs. For both dyes, acidic pH was efficiently more suitable to remove dyes from synthetic dye solutions.

Adsorption for dyestuff removal was remarkably depended on the initial dyestuff concentration. Usually, the percentage of removal values decrease with an increasing in the initial dyestuff concentration, because of the saturation of adsorption functional residuals on the adsorbent surface. In addition to this, the increase in initial dyestuff concentration would lead to an increase in the capacity of the chitosan (4).

Removal of synthetic wastewater with cross-linked chitosan and chitosan-PAA conjugate

Removal of synthetic dye solutions of NBB and RBBR have been investigated by using cross-linked chitosan. UV-Vis. Spectra of initial dye absorbance were shown in Fig. 10 and Fig. 11. Removal of NBB values was higher than the removal of RBBR values. Removal values can be changed due to the chemistry of dye molecules, pK_a of dyes and dye concentration. Furthermore, dye removal results for both dyes (NBB, RBBR) increases especially at acidic pHs (Fig. 7 and Fig. 8). Removal values percentages of NBB and RBBR with 100.0 mg cross-linked chitosan was shown in Fig. 9. Chitosan-PAA conjugate was more effective than

chitosan in removing dyestuffs at pH: 5.0 in Fig. 11. In addition to these, any decreased in the density of free amine groups at the chitosan derivative, cross-linked chitosan with glutaraldehyde has also higher dye decolorization values than chitosan.

CONCLUSION

Eventually, chitosan is protonated in acidic pHs with a charge density depends on degree of deacetylation value. Chitosan interacts with anionic dyestuffs (NBB, RBBR), especially in acidic solutions. Few amounts of chitosan were required at acidic pHs to remove textile dyestuff molecules. Acidic pHs are more suitable to remove dyestuffs for both dyestuffs. Dyestuff removal values of cross-linked chitosan are higher than chitosan-PAA conjugate. The density of positive charges may have decreased with cross-linking and PAA conjugation of chitosan. However, these synthesized polymers can be adsorb and/or penetrate the dyestuffs because of porous chemical structure. Hence, removal values of cross-linked chitosan and chitosan-PAA conjugate were higher than chitosan.

In this study, microwave energy was used to the synthesis of cross-linked chitosan and Chitosan-PAA conjugate. According to the results of synthesis, microwave energy was clear effective on these reactions. Microwave is heat the reaction media fastly. Because of this, microwave heating was applied step by step in a very short time. High adsorption capacities (q_e) were obtained as 870 mg/g (pH: 5.0) and 26509 mg/g (pH: 5.0) respectively, for NBB and RBBR dyestuffs.

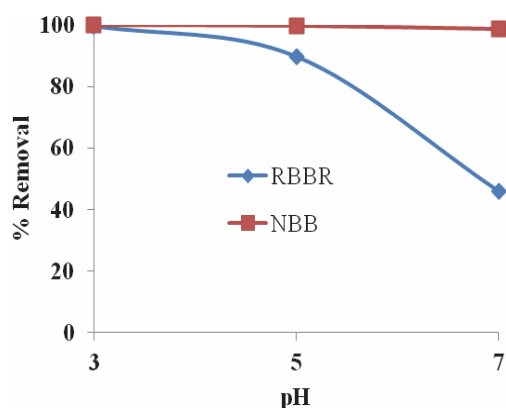


Figure 9. Removal of NBB and RBBR with 100.0 mg cross-linked chitosan at pH: 3.0, 5.0 and 7.0.

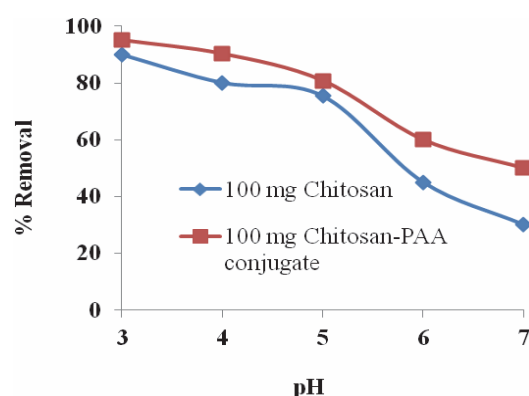


Figure 10. RBBR dye removal with 100.0 mg chitosan-PAA conjugate and 100.0 mg chitosan at pH: 3.0, 4.0, 5.0, 6.0 and 7.0.

REFERENCES

1. Yaman, Y.C., Gündüz, G., Kumbasar, E.P.A., 2010, "The treatment of waste water of dyeing by fenton oxidation in presence and absence of ultrasound", *Tekstil ve Konfeksiyon*. 20, pp. 348–358.
2. Eren H.A., Yıldız, D., Demir, C., Şahin, S., 2013, "Color removal of disperse blue dyes by ozonation", *Tekstil ve Konfeksiyon*. 23, pp. 267–272.
3. Karatas, M., Dursun, S., Argun, M.E., 2010, "The Decolorization of Azo Dye Reactive Black 5 in a Sequential Anaerobic-Aerobic System", *Ekoloji*. 19, pp. 15–23.

4. Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M., 2014, "Dye and its removal from aqueous solution by adsorption: A review", *Advanced Colloid Interface Science*, 209, pp. 172–184.
5. Deveci, T., Unyayar, A., Mazmanci, M.A., 2004, "Production of Remazol Brilliant Blue R decolourising oxygenase from the culture filtrate of *Funalia trogii* ATCC 200800", *Journal of Molecular Catalysis. B Enzyme*, 30, pp. 25–32.
6. Onder, S., Celebi, M., Altikatoglu, M., Hatipoglu, A., Kuzu, H., 2011, "Decolorization of naphthol blue black using the horseradish peroxidase", *Applied Biochemistry and Biotechnology*, 163, pp. 433–443.
7. Song, S., Yao, J., He, Z., Qiu, J., Chen, J., 2008, "Effect of operational parameters on the decolorization of C.I. Reactive Blue 19 in aqueous solution by ozone-enhanced electrocoagulation", *Journal of Hazardous Materials*, 152, pp. 204–210.
8. Celebi, M., Altikatoglu, M., Akdeste, Z.M., Yildirim, H., 2013, "Determination of decolorization properties of Reactive Blue 19 dye using Horseradish Peroxidase enzyme", *Turkish Journal of Biochemistry*, 38, pp. 200–206.
9. Vakili, M., Rafatullah, M., Salamatinia, B., Abdullah, A.Z., Ibrahim, M.H., Tan, K.B., Gholami, Z., Amouzgar, P., 2014, "Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review", *Carbohydrate Polymers*, 113, pp. 115–130.
10. Guibal, E., Roussy, J., 2007, "Coagulation and flocculation of dye-containing solutions using a biopolymer (Chitosan)", *Reactive and Functional Polymers*, 67, pp. 33–42.
11. Petzold, G., Schwarz, S., 2006, "Dye removal from solutions and sludges by using polyelectrolytes and polyelectrolyte-surfactant complexes", *Separation and Purification Technology*, 51, pp. 318–324.
12. Crini, G., Badot, P.M., 2008, "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature", *Progressive Polymer Science*, 33, pp. 399–447.
13. Yazdani, M., Bahrami, H., Arami, M., 2014, "Feldspar/titanium dioxide/chitosan as a biophotocatalyst hybrid for the removal of organic dyes from aquatic phases", *Journal of Applied Polymer Science*, 131, pp. 1–9.
14. Jabli, M., Aloui, F., Ben Hassine, B., 2013, "[Copper (II) / Cellulose-Chitosan] Microspheres Complex for Dye Immobilization : Isotherm , Kinetic and Thermodynamic Analysis", *Journal of Engineered. Fibers and Fabrics*, 8, pp. 19–34.
15. Chen, Y., He, F., Ren, Y., Peng, H., Huang, K., 2014, "Fabrication of chitosan/PAA multilayer onto magnetic microspheres by LbL method for removal of dyes", *Journal of Chemical Engineering*, 249, pp. 79–92.
16. Nüchter, M., Ondruschka, B., Bonrath, W., Gum, A., 2004, "Microwave assisted synthesis - a critical technology overview", *Green Chemistry*, 6, pp. 128–141.
17. Michael, D., Mingos, P., Baghurst, D.R., 1991, "Applications of Microwave Dielectric Heating Effects to Synthetic Problems in Chemistry", *Chemical Society Reviews*, 20, pp. 1–47.
18. Baig, R.B.N., Varma, R.S., 2012., "Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis", *Chemical Society Reviews*, 41, pp. 1559–1584.
19. Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., Rousell, J., 1986, "The use of microwave ovens for rapid organic synthesis", *Tetrahedron Letters*, 27, pp. 279–282.
20. Polshettiwar, V., Varma, R.S., 2008, "Microwave-Assisted Organic Synthesis and Transformations using Benign Reaction Media", *ACS, Accounts Chemical Resources*, 41, pp. 629–639.
21. Jiang, X., Cai, K., Zhang, J., Shen, Y., Wang, S., Tian, X., 2011, "Synthesis of a novel water-soluble chitosan derivative for flocculated decolorization", *Journal of Hazardous Materials*, 185, pp. 1482–1488.
22. Renault, F., Sancey, B., Badot, P.M., Crini, G., 2009, "Chitosan for coagulation/flocculation processes - An eco-friendly approach", *Journal of European Polymers*, 45, pp. 1337–1348.