Removal of Textile Dyes from Aqueous Solutions and Wastewaters using Biobased Interpenetrating Networks of Alginate, Collagen, and Polyurethane

Sara L. Carrillo-Cortés¹, Jesús A. Claudio-Rizo¹, Nidia G. Burciaga-Montemayor¹ & Martín Caldera-Villalobos¹∗

¹Universidad Autónoma de Coahuila, Blvd. Venustiano Carranza 935, República, 25280 Saltillo, Coahuila, México. Email: mcalderafcq@uadec.edu.mx∗

DOI: http://doi.org/10.38177/ajast.2022.6119

Copyright: © 2022 Sara L. Carrillo-Cortés et al. This is an open access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Article Received: 25 December 2021 Article Accepted: 17 March 2022 Article Published: 24 March 2022

ABSTRACT

The aim of this work was to study the adsorption properties of interpenetrating polymeric networks (IPNs) based on alginate, collagen, and two different polyurethanes (ACP(HDI), ACP(IPDI)) for the removal of textile dyes from aqueous solutions and wastewaters. The interaction of ACP(HDI) and ACP(IPDI) with methylene blue (BB9), malachite green (BG4), indigo carmine (AB74), and Congo red (DR28) was studied by adsorption kinetics and adsorption isotherms. Concentration profiles revealed a fast removal of dyes from aqueous solutions reaching the equilibrium after 4 h of contact. ACP(IPDI) removed up to 87 ± 0.5% of BG4 and the removal efficiency for the other dyes was lower. Experimental data fit the pseudo-second-order model showing that the removal process is controlled by diffusion. Adsorption isotherms were described by the Freundlich’s model observing concave up isotherms. Results showed that IPNs obtained from the polyurethane containing P(IPDI) cyclic moieties are better for dye removal than those obtained from the P(HDI) acyclic polyurethane.

Keywords: Alginate, Collagen, Polyurethane, Hydrogel, Removal, Textile dye.

1. Introduction

Algicin acid is a natural occurring anionic polyelectrolyte extracted from brown algae, mainly Laminaria hyperborea, Macrocystis pyrifera, Laminaria digitata, Ascophyllum nodosum, Laminaria japonica, Ecklonia maxima, Lessonia nigrescens, and Durvillaea antártica [1]. Algicin acid is comprised of D-manuronic acid and L-guluronic acid, the ratio of both monosaccharides in the polysaccharide and the sequence of union depends on the extraction source. Algicin acid is found in nature as a mixture of calcium, magnesium, and sodium salts. The most important uses of algicin acid are as stabilizing agents, viscosity modifiers, gelificants, and water retention [2].

Due to polyelectrolyte properties, biodegradability, and jellifying capacity of algicinate, this polysaccharide has been proposed for the removal of several water pollutants [3]. Particularly, algicin-based hydrogels have been studied for the removal of cationic dyes. A common approach to obtain algicin-base hydrogels is the free radical polymerization. For example, styrene and maleic anhydride were grafted on sodium algicinate yielding hydrogels useful for the removal of methyl violet 6B [4]. Also, alginc/polyacrylamide hydrogels were synthesized by free radical polymerization and applied for the removal of methylene blue [5]. Similarly, a highly efficient hydrogel for the removal of methylene blue was obtained grafting 2-acrylamide-2-methylpropanesulfonic acid onto algicinate [6].

Further, superabsorbent hydrogels comprised of a ternary mixture of sodium algicinate, polyacrylic acid, and sodium humate showed a high efficiency for removal of methylene blue and crystal violet [7]. In other work, pH responsive hydrogels were obtained grafting poly(acrylic acid) on algicinate [8]. Further, algicin-based hydrogels can be prepared in a simple way using polyvalent ions as crosslinkers [9]. This approach was used to prepare algicinate/poly(vinyl alcohol) hydrogels with application in dye removal [10]. Also, algicin has been chemically modified to improve their adsorption performance. The functionalization with amino groups provides adsorption sites suitable for removing anionic dyes such as methyl blue [11].
Another strategy to modify the physicochemical properties of alginate-based hydrogels is the incorporation of composing materials to yield composite hydrogels. Among these materials, we can find inorganic and organic nanostructured materials, and raw materials such as natural clays or vegetal wastes. Composite hydrogels comprised of alginate/polyacrylamide networks and La(OH)$_3$ nanoparticles showed a high adsorption capacity for cationic dyes such as methylene blue, malachite green, and crystal violet. Also, these materials exhibit photocatalytic activity [12]. In other work, it was reported that the adsorption capacity of oxidized alginate hydrogels can be improved by decorating with silver nanoparticles [13]. Composite hydrogels containing graphene oxide showed being efficient for the removal of a wide library of dyes such as methylene blue, rhodamine B, vat green 1, and methyl orange [14]. Further, composite aerogels comprised of sodium alginate, montmorillonite, and graphene oxide were prepared using Ca$^{2+}$ as crosslinker ion followed by freeze drying. These aerogels were tested for the removal of methylene blue and rhodamine B observing a high adsorption capacity [15]. Cellulose nanofibers have been incorporated in alginate based hydrogels yielding efficient porous matrices for the removal of anionic and cationic dyes [16],[17].

Calcium alginate hydrogels reinforced with kaolin were used for preparing membranes with different thickness for removing Coomassie brilliant blue, crystal violet, and neutral red dyes [18]. Also, the mechanical strength and adsorption performance of alginate-based hydrogel can be improved by composing with natural materials such as rice husk [19]. Another composing raw materials used to improved the adsorption capacity of alginate-based hydrogels include apatite, attapulgite [20], bentonite [21], zinc oxide [22], hectorite [23], and tetraaminecopper (II) sulfate [24], observing a noticeable enhancement for the removal of dyes.

Recently, our research group reported the preparation of interpenetrating networks of collagen, polyurethane, and alginate as highly biocompatible hydrogels for tissue engineering [25]. These materials exhibit a high swelling capacity and the ability for the controlled release of cholecalciferol. Considering the potential multifunctional character of this IPNs they could be suitable for the removal of textile dyes from wastewaters. Thus, the aim of this work was to study the removal of textile dyes from aqueous solutions and wastewaters using two IPNs comprised of alginate, collagen, and two different polyurethanes containing cyclic and acyclic moieties.

2. Materials and Methods

2.1. Chemicals

Alginic acid sodium salt from brown algae, glycerol ethoxylate, hexamethylene diisocyanate (HDI), isophorone, diisocyanate (IPDI), methylene blue, malachite green, indigo carmine, and Congo red are commercially available from Sigma Aldrich Co. Collagen from bovine tendon was extracted by enzymatic hydrolysis following the procedure reported elsewhere [26]. Polyurethane crosslinkers based on HDI and IPDI were prepared as reported in [27].

2.2. Synthesis of IPNs

Interpenetrating polymeric networks of collagen, alginate, and polyurethane were synthesized as reported previously our research group [25]. For this, 10 mL of collagen solution (6 mg mL$^{-1}$), 5 mL de alginate solution (1
wt. %), 5 mL of polyurethane crosslinker (P(HDI) or P(IPDI)), and 30 mL of phosphate buffer saline (PBS-10X) were mixed in a beaker with magnetic stirring. The mixture was heated at 80 °C for 60 min with continuous stirring, and then 5 mL of magnesium chloride hexahydrate solution (1 wt. %) was added. The mixture was cooled at room temperature and the resulting precipitate was filtered, rinsed with water, and dried at room temperature.

2.3. Dyes

Figure 1 presents the structure of selected dyes. Methylene blue (BB9) and malachite green (BG4) are cationic dyes because they contain quaternary amine groups in their structures. Conversely, Congo red (DR28) and indigo carmine (AB74) are anionic due to the presence of sulfonate groups. The quantification of dyes in aqueous solutions was performed by UV-Vis spectrophotometry using a ThermoScientific MultiskanSky spectrophotometer. For this, calibration curves were constructed measuring the absorbance of aqueous solutions of dyes with concentration ranging between 0 and 100 mg dm$^{-3}$. For those solutions with high absorbance (A > 1.0 a.u.) an appropriate dilution factor was applied. The maximum absorbance wavelength of each dye ($\lambda_{\text{max}}$) was selected as the wavelength for detection. Calibration curves and some characteristics of the selected dyes are presented in Table 1.

![Chemical Structure of Selected Dyes](image)

**Table 1.** Selected Dyes and Some Selected Characteristics

| Dye (Colour Index)       | Key  | Character | $\lambda_{\text{max}}$ | Calibration curve | $R^2$ |
|--------------------------|------|-----------|------------------------|-------------------|-------|
| Methylene blue (Basic blue 9) | BB9  | Cationic  | 664                    | $c = A/0.0849$    | 0.9918|
| Malachite green (Basic green 4) | BG4  | Cationic  | 618                    | $c = A/0.1414$    | 0.9936|
| Congo red (Direct red 28)  | DR28 | Anionic   | 611                    | $c = A/0.0536$    | 0.9832|
| Indigo carmine (Acid blue 74) | AB74 | Anionic   | 497                    | $c = A/0.0304$    | 0.9904|
2.4. Characterization of IPNS

The chemical structure of IPNs was analysed by FT-IR spectroscopy using a Perkin Elmer Frontier spectrophotometer using an ATR accessory. The interaction of IPNs and dyes was studied by adsorption kinetics and adsorption isotherms.

Adsorption experiments were performed in polyethylene bottles placing 25 mg of ACP(HDI) or ACP(IPDI) in contact with 20 cm$^3$ of dye solution yielding a mass/volume ratio of 1.25 g dm$^3$. The adsorption kinetics was studied at 303.15 K with aqueous dye solutions with a starting concentration of 100 mg dm$^3$. Samples were placed in an orbital stirrer and aliquots of the medium were taken at different time intervals. The concentration of dye was measured by spectrophotometry. The amount of adsorbed dye was calculated applying Equation 1:

$$a = \frac{(C_0 - C_{eq})V}{m} \quad (1)$$

Where $a$ is the amount of adsorbed dye (mg g$^{-1}$), $C_0$ is the starting concentration of dye (mg dm$^3$), $C_{eq}$ is the concentration of dye at the adsorption equilibrium (mg dm$^3$), $V$ is the volume of dye solution (dm$^3$), and $m$ is the mass of adsorbent (g). After that, experimental data were analysed applying the pseudo-first-order (Equation 2) and pseudo-second-order (Equation 3) models:

$$\ln(a_e - a_t) = \ln a_e - k_1t \quad (2)$$
$$\frac{t}{a_t} = \frac{1}{k_2a_e} + \frac{t}{a_e} \quad (3)$$

Where $a_e$ is the amount of adsorbed dye in the equilibrium (mg g$^{-1}$), $a_t$ is the amount of adsorbed dye at the time $t$, $t$ is the time of contact (h), $k_1$ is the pseudo-first-order velocity constant (h$^{-1}$), and $k_2$ is the pseudo-second-order velocity constant (g mg$^{-1}$ h$^{-1}$).

For adsorption isotherms, dye solutions were prepared with a starting concentration ranging from 0-100 mg dm$^3$. The adsorption was carried out as described afore and at after 24 h of contact aliquots were taken from the medium and the concentration of dye was measured by spectrophotometry. Experimental data were analysed applying the Langmuir’s and Freundlich’s models (Equations 4 and 5, respectively):

$$a = \frac{a_mK_LC_{eq}}{1+K_LC_{eq}} \quad (4)$$
$$a = K_FC^{1/n} \quad (5)$$

Where, $a$ is the amount of adsorbed dye (mg g$^{-1}$), $a_m$ is the monolayer capacity (mg g$^{-1}$), $K_L$ is the Langmuir’s constant (dm$^3$ mg$^{-1}$). $K_F$ is the Freundlich’s constant (mg g$^{-1}$), and $n$ is a non-dimensional constant known as parameter of heterogeneity.

2.5. Removal of Dye from Aqueous Solutions and Wastewaters

The removal of dye was analysed in aqueous solutions with a starting concentration of 100 mg dm$^3$. Adsorption was performed as described afore and aliquots from the supernatant were taken after 24 h of contact and the concentration of dye was determinate by spectrophotometry and applying Equation 6:
The removal of dyes from wastewaters was performed applying the same procedure used for removing dyes from aqueous solutions. Samples of wastewaters containing dyes were treated with ACP(HDI) and ACP(IPDI) and their absorbance was measured by UV-Vis spectrophotometry. Because the nature of the dyes occurring in wastewaters is unknown the removal of dye was calculated applying Equation 7:

\[
\text{Removal of dye (\%)} = \left(1 - \frac{A_{\text{wwt}}}{A_{\text{ww}}}\right) \times 100
\]  

Where, \(A_{\text{ww}}\) is the absorbance of wastewater and \(A_{\text{wwt}}\) is the absorbance of wastewater after being in contact with ACP(IPDI) or ACP(HDI). The absorption spectrum of each wastewater was recorded previously and \(\lambda_{\text{max}}\) was used as the wavelength for detection (Table 2).

| Wastewater     | \(\lambda_{\text{max}}\) (nm) |
|----------------|-------------------------------|
| Direct red     | 490                           |
| Direct black   | 475                           |
| Mordant yellow| 467                           |
| Basic green    | 624                           |

3. Results and Discussion

3.1. Adsorption Kinetics

Figure 2 shows the concentration profiles for the adsorption of textile dyes using the ACP(HDI) and ACP(IPDI) IPNs. The adsorption of dye occurs rapidly during the first 30 min of contact, and after that, the process becomes slower. After 2 h of contact, the concentration of dye in the solutions did not change significantly observing the equilibrium of the system after 4 h.

![Fig.2. Concentration Profiles for the Adsorption of Textile Dyes on a) ACP(HDI) and b) ACP(IPDI)](image)

Experimental data did not fit the pseudo-first-order model (\(R^2 \ll 1\)) but, they fit to the pseudo-second-order model (\(R^2 \approx 1\)) which establishes a process controlled by diffusion in three steps. First, dye molecules diffuse through a
fluid layer surrounding the adsorbent. Then, dye molecules diffuse into the pores of the material. Finally, dye molecules are adsorbed on an active site. This model describes well the observations made during the experimentation. In the beginning, the ACP(HDI) and ACP(IPDI) adsorbents are powders, and the adsorption takes place on the surface particle. As time goes by, ACP(HDI) and ACP(IPDI) swell forming hydrogels allowing the diffusion of dye molecules inland each particle. Thus, removal of dyes occurs by adsorption and absorption and both processes are dominant in different stages of the removal process.

Table 3. Kinetic Parameters for the Removal of Textiles Dyes

| Dye  | Adsorbent | $k_2$ (g·mg$^{-1}$·h$^{-1}$) | $a_e$ (mg g$^{-1}$) | R$^2$ |
|------|-----------|-----------------------------|---------------------|-------|
| BB9  | ACP(HDI)  | 0.3594                      | 39.1                | 0.9998|
| BG4  | ACP(HDI)  | 0.1012                      | 59.5                | 0.9986|
| AB74 | ACP(HDI)  | 0.8253                      | 43.7                | 0.9986|
| DR28 | ACP(HDI)  | 0.1422                      | 45.9                | 0.9961|
| BB9  | ACP(IPDI) | 0.6405                      | 41.3                | 0.9990|
| BG4  | ACP(IPDI) | 0.1643                      | 71.4                | 0.9955|
| AB74 | ACP(IPDI) | 0.4458                      | 30.1                | 0.9813|
| DR28 | ACP(IPDI) | 0.2670                      | 45.2                | 0.9956|

Table 3 shows calculated values for the pseudo-second-order velocity constant ($k_2$) and the amount of adsorbed dye in the equilibrium ($a_e$). According with the values of $a_e$, ACP(IPDI) have higher adsorption capacity than ACP(HDI) for the removal of BB9 and BG4 cationic dyes. ACP(HDI) was better for the removal of AB74 and for the adsorption of DR28 there was not observed significant differences between both materials. Finally, ACP(HDI) and ACP(IPDI) showed higher affinity for BG4 reaching up to 71.4 mg g$^{-1}$ of dye adsorbed.

3.2. Adsorption Isotherms

Figure 3 shows the adsorption isotherms of textile dyes on ACP(HDI) and ACP(IPDI). Experimental data did not fit the Langmuir’s model ($R^2 << 1$), but they fit to the Freundlich’s model ($R^2 \approx 1$). Points represent the experimental data and dashed lines represents the behavior predicted by Freundlich’s Equation. As mentioned afore, BG4 and DR28 were adsorbed better than BB9 and AB74. Electrostatic forces presence is responsible for the removal of dyes with anionic or cationic character.

BG4 is a cationic dye which can interact electrostatically with carboxylate groups of alginate, and thus ACP(HDI) and ACP(IPDI) have a large adsorption capacity for this dye. However, both materials have low adsorption capacity for BB9, another cationic dye. In counterpart, ACP(HDI) and ACP(IPDI) showed high adsorption capacity for DR28, a dye with anionic character. Molecules of this dye should be repelled by the electrostatic field of alginate, both they could be retained in the polymer matrix by other interactions such as hydrogen bonding and hydrophobic interactions. Thus, electrostatic attraction is not the driven force for the adsorption of dye on alginate-based IPNs. Table 4 shows the Freundlich’s parameters for the adsorption of textiles dyes on alginate-based hydrogels. The values of $K_F$ are small for all dyes except BG4, showing that ACP(HDI) and
ACP(IPDI) have highest adsorption capacity for this dye. In all cases, it was observed that 1/n > 1, which corresponds to concave up isotherms where adsorption is not energetically favored [28].

![Figure 3. Adsorption Isotherms of Textile Dyes on a) ACP(HDI) and b) ACP(IPDI)](image)

**Table 4. Freundlich’s Parameters for the Adsorption of Textile Dyes on Alginate-Based IPNS**

| Dye   | Adsorbent | \(K_F\) (mg g\(^{-1}\)) | \(n\)  | \(R^2\)  |
|-------|-----------|--------------------------|-------|---------|
| BB9   | ACP(HDI)  | 0.0190                   | 0.6294| 0.9709  |
| BG4   | ACP(HDI)  | 0.1487                   | 0.3917| 0.9875  |
| DR28  | ACP(HDI)  | 0.0954                   | 0.6622| 0.9831  |
| AB74  | ACP(HDI)  | 0.0003                   | 0.3889| 0.9637  |
| BB9   | ACP(IPDI) | 0.0416                   | 0.6444| 0.9773  |
| BG4   | ACP(IPDI) | 1.5907                   | 0.5968| 0.9831  |
| DR28  | ACP(IPDI) | 0.0236                   | 0.4331| 0.9777  |
| AB74  | ACP(IPDI) | 0.0320                   | 0.6574| 0.9867  |

Figure 4 shows the removal efficiency of textiles dyes from aqueous solutions with a starting concentration of 100 mg dm\(^{-3}\). The ACP(IPDI) IPN showed better performance than ACP(HDI) for removing BB9, BG4, and DR28 dyes. The maximum efficiency was observed for BG4 removing up to 87 ± 0.5% of dye.

![Figure 4. Removal Efficiency of Dyes from Aqueous Solutions](image)
3.3. Wastewater Treatment

Wastewaters are mixtures with a very complex composition because they contain dyes, hydrolyzed dyes, salts, bases, acids, and surfactants which are employed for dyeing processes. For this, the removal efficiency of one material can vary significantly when is tested in aqueous solutions and wastewaters.

Figure 5 shows the efficiency of ACP(HDI) and ACP(IPDI) for the removal of several dyes occurring in wastewaters from dyeing. The removal efficiency was almost 100% for all experiments, showing the high absorption capacity of these IPNs against a wide variety of dyes.

These results were obtained without any previous treatment of the effluent such as neutralization, filtration, or coagulation-flocculation. Thus, alginate-collagen-polyurethane based IPNs could be applied for direct treatment of wastewaters.

![Figure 5. Removal Efficiency for the Removal of Dyes from Wastewaters](image)

4. Conclusion

Interpenetrating polymeric networks based on alginate, collagen and polyurethane showed the ability for removing textile dyes from aqueous solutions and wastewaters. Although the heterogeneity parameter ($n$) showed that adsorption is not energetically favored in these IPNs, they showed a high performance for the removal of some dyes such as BG4. The composition of the polyurethane used as crosslinker had a noticeable effect on the adsorption capacity of the resulting IPNs. The best results were obtained using ACP(IPDI).

Declarations

Source of Funding

This research was funded by Consejo Nacional de Ciencia y Tecnología (CONACYT) (grant FORDECYT-PRONACES/6660/2020).

Competing Interests Statement

The authors declare no competing financial, professional and personal interests.

Consent for publication

Authors declare that they consented for the publication of this research work.
References

[1] De Jesus Raposo MF, De Morais AMB, De Morais RMSC (2015) Marine polysaccharides from algae with potential biomedical applications. Mar Drugs 13:2967-3028. https://doi.org/10.3390/md13052967.

[2] Xu SY, Huang X, Cheong KL (2017) Recent advances in marine algae polysaccharides: Isolation, structure, and activities. Mar Drugs 15:1-16. https://doi.org/10.3390/md15120388.

[3] Thakur S, Sharma B, Verma A, et al (2018) Recent progress in sodium alginate based sustainable hydrogels for environmental applications. J Clean Prod 198:143-159. https://doi.org/10.1016/j.jclepro.2018.06.259.

[4] Eskhan A, Banat F, Selvaraj M, Abu Haija M (2019) Enhanced removal of methyl violet 6B cationic dye from aqueous solutions using calcium alginate hydrogel grafted with poly (styrene-co-maleic anhydride). Polym Bull 76:175-203. https://doi.org/10.1007/s00289-018-2378-y.

[5] İsmail O, Gökçe Kocabay Ö (2021) Absorption and adsorption studies of polyacrylamide/sodium alginate hydrogels. Colloid Polym Sci 299:783-796. https://doi.org/10.1007/s00396-020-04796-0.

[6] Shao Z jian, Huang X lian, Yang F, et al (2018) Engineering sodium alginate-based cross-linked beads with high removal ability of toxic metal ions and cationic dyes. Carbohydr Polym 187:85-93. https://doi.org/10.1016/j.carbpol.2018.01.092.

[7] Agnihotri S, Singhal R (2019) Effect of Sodium Alginate Content in Acrylic Acid/Sodium Humate/Sodium Alginate Superabsorbent Hydrogel on Removal Capacity of MB and CV Dye by Adsorption. J Polym Environ 27:372-385. https://doi.org/10.1007/s10924-018-1349-6.

[8] Thakur S (2018) Synthesis, swelling and adsorption studies of a pH-responsive sodium alginate–poly (acrylic acid) superabsorbent hydrogel. Polym Bull 75:4587-4606. https://doi.org/10.1007/s00289-018-2287-0.

[9] Hu T, Liu Q, Gao T, et al (2018) Facile Preparation of Tannic Acid-Poly(vinyl alcohol)/Sodium Alginate Hydrogel Beads for Methylene Blue Removal from Simulated Solution. ACS Omega 3:7523-7531. https://doi.org/10.1021/acsomega.8b00577.

[10] Liu C, Liu H, Xiong T, et al (2018) Graphene oxide reinforced alginate/PVA double network hydrogels for efficient dye removal. Polymers (Basel) 10:1-14. https://doi.org/10.3390/polym10080835.

[11] Godiya CB, Xiao Y, Lu X (2020) Amine functionalized sodium alginate hydrogel for efficient and rapid removal of methyl blue in water. Int J Biol Macromol 144:671-681. https://doi.org/10.1016/j.ijbiomac.2019.12.139

[12] Qian D, Bai L, Wang YS, et al (2019) A Bifunctional Alginate-Based Composite Hydrogel with Synergistic Pollutant Adsorption and Photocatalytic Degradation Performance. Ind Eng Chem Res 58:13133-13144. https://doi.org/10.1021/acs.iecr.9b01709.

[13] Abou-Zeid RE, Awwad NS, Nabil S, et al (2019) Oxidized alginate/gelatin decorated silver nanoparticles as new nanocomposite for dye adsorption. Int J Biol Macromol 141:1280-1286. https://doi.org/10.1016/j.ijbiomac.2019.09.076.
[14] Gan L, Li H, Chen L, et al (2018) Graphene oxide incorporated alginate hydrogel beads for the removal of various organic dyes and bisphenol A in water. Colloid Polym Sci 296:607-615. https://doi.org/10.1007/s00396-018-4281-3.

[15] E T, Ma D, Yang S, Hao X (2020) Graphene oxide-montmorillonite/sodium alginate aerogel beads for selective adsorption of methylene blue in wastewater. J Alloys Compd 832:154833. https://doi.org/10.1016/j.jallcom.2020.154833.

[16] Mokhtari A, Sabzi M, Azimi H (2021) 3D porous biosorbents based on chitosan/alginate/cellulose nanofibers as efficient and recyclable adsorbents of anionic dye. Carbohydr Polym 265:118075. https://doi.org/10.1016/j.carbpol.2021.118075.

[17] Liu H. et al (2021) Crucial roles of graphene oxide in preparing alginate/nanofibrillated cellulose double network composites hydrogels. Chemosphere 263:128240. https://doi.org/10.1016/j.chemosphere.2020.128240.

[18] Bai T, Zhao K, Gao Q, et al (2020) Kaolin/CaAlg Hydrogel Thin Membrane with Controlled Thickness, High Mechanical Strength, and Good Repetitive Adsorption Performance for Dyes. Ind Eng Chem Res 59:4958-4967. https://doi.org/10.1021/acs.iecr.9b06687.

[19] Alver E, Metin AÜ, Brouers F (2020) Methylene blue adsorption on magnetic alginate/rice husk bio-composite. Int J Biol Macromol 154:104-113. https://doi.org/10.1016/j.ijbiomac.2020.02.330.

[20] Li Y, Liu SJ, Chen FM, Zuo JE (2019) High-Strength Apatite/Attapulgite/Alginate Composite Hydrogel for Effective Adsorption of Methylene Blue from Aqueous Solution. J Chem Eng Data 64:5469-5477. https://doi.org/10.1021/acs.jced.9b00616.

[21] Subhan H, Alam S, Shah LA, et al (2021) Sodium alginate grafted poly(N-vinyl formamide-co-acrylic acid)-bentonite clay hybrid hydrogel for sorptive removal of methylene green from wastewater. Colloids Surfaces A Physicochem Eng Asp 611:125853. https://doi.org/10.1016/j.colsurfa.2020.125853.

[22] Makhado E, Pandey S, Modibane KD, et al (2020) Sequestration of methylene blue dye using sodium alginate poly(acrylic acid)@ZnO hydrogel nanocomposite: Kinetic, Isotherm, and Thermodynamic Investigations. Int J Biol Macromol 162:60-73. https://doi.org/10.1016/j.ijbiomac.2020.06.143.

[23] Pawar RR, Lalthiansiama, Gupta P, et al (2018) Porous synthetic hectorite clay-alginate composite beads for effective adsorption of methylene blue dye from aqueous solution. Int J Biol Macromol 114:1315-1324. https://doi.org/10.1016/j.ijbiomac.2018.04.008.

[24] Mozaffari T, Keshkar Vanashi A, Ghasemzadeh H (2021) Nanocomposite hydrogel based on sodium alginate, poly (acrylic acid), and tetraaminecopper (II) sulfate as an efficient dye adsorbent. Carbohydr Polym 267:. https://doi.org/10.1016/j.carbpol.2021.118182.

[25] Claudio-Rizo JA, Carrillo-Cortés SL, Becerra-Rodríguez JJ, et al (2022) Composite hydrogels comprised from interpenetrating networks of alginate-collagen-polyurethane for biomedicine. J Mater Res 37:636-649. https://doi.org/10.1557/s43578-021-00476-z.
[26] Claudio-Rizo JA, Rangel-Argote M, Castellano LE, et al (2017) Influence of residual composition on the structure and properties of extracellular matrix derived hydrogels. Mater Sci Eng C 79:793-801. https://doi.org/10.1016/j.msec.2017.05.118.

[27] Mendoza-Novelo B, Mata-Mata JL, Vega-González A, et al (2014) Synthesis and characterization of protected oligourethanes as crosslinkers of collagen-based scaffolds. J Mater Chem B 2:2874-2882. https://doi.org/10.1039/c3tb21832e.

[28] Tseng RL, Wu FC (2008) Inferring the favorable adsorption level and the concurrent multi-stage process with the Freundlich constant. J Hazard Mater 155:277-287. https://doi.org/10.1016/j.jhazmat.2007.11.061.