

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

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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 $87 \pm 0.5\%$ 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: Alginic acid, Collagen, Polyurethane, Hydrogel, Removal, Textile dye.

1. Introduction

Alginic 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 antarctica* [1]. Alginic 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. Alginic acid is found in nature as a mixture of calcium, magnesium, and sodium salts. The most important uses of alginic acid are as stabilizing agents, viscosity modifiers, gelificants, and water retention [2].

Due to polyelectrolyte properties, biodegradability, and jellifying capacity of alginate, this polysaccharide has been proposed for the removal of several water pollutants [3]. Particularly, alginate-based hydrogels have been studied for the removal of cationic dyes. A common approach to obtain alginate-based hydrogels is the free radical polymerization. For example, styrene and maleic anhydride were grafted on sodium alginate yielding hydrogels useful for the removal of methyl violet 6B [4]. Also, alginate/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 alginate [6]. Further, superabsorbent hydrogels comprised of a ternary mixture of sodium alginate, 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 alginate [8]. Further, alginate-based hydrogels can be prepared in a simple way using polyvalent ions as crosslinkers [9]. This approach was used to prepare alginate/poly(vinyl alcohol) hydrogels with application in dye removal [10]. Also, alginate 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 $\text{La}(\text{OH})_3$ 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 content 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.) a appropriate dilution factor was applied. The maximum absorbance wavelength of each dye ($\lambda_{\max}$) was selected as the wavelength for detection. Calibration curves and some characteristics of the selected dyes are presented in Table 1.

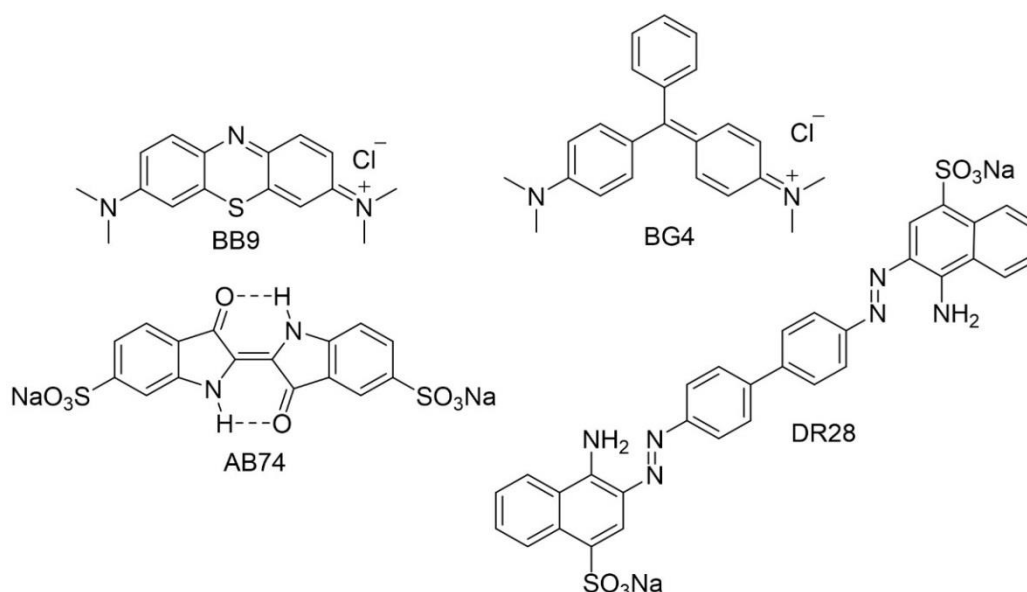


Fig.1. Chemical Structure of Selected Dyes

Table 1. Selected Dyes and Some Selected Characteristics

Dye (Colour Index)	Key	Character	$\lambda_{\max}$	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 cm³ 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 (dm³), 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:

$$\ln(a_e - a_t) = \ln a_e - k_1 t \quad (2)$$

$$\frac{t}{a_t} = \frac{1}{K_2 a_e^2} + \frac{t}{a_e} \quad (3)$$

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):

$$a = \frac{a_m K_L C_{eq}}{1 + K_L C_{eq}} \quad (4)$$

$$a = K_F C^{1/n} \quad (5)$$

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 (dm³ 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 determined by spectrophotometry and applying Equation 6:

$$\text{Removal of dye (\%)} = \frac{C_i - C_{eq}}{C_i} * 100 \quad (6)$$

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:

$$\text{Removal of dye (\%)} = \left(1 - \frac{A_{wwt}}{A_{wwt}}\right) * 100 \quad (7)$$

Where, A_{ww} is the absorbance of wastewater and A_{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 λ_{max} was used as the wavelength for detection (Table 2).

Table 2. Wavelengths for the Analysis of Wastewaters

Wastewater	λ_{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.

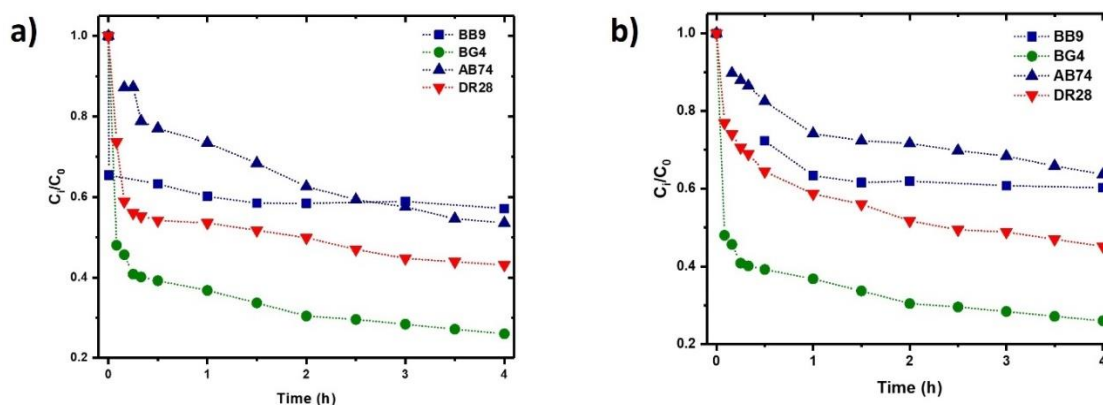


Fig.2. Concentration Profiles for the Adsorption of Textile Dyes on a) ACP(HDI) and b) ACP(IPDI)

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 ($R^2 \ll 1$), 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].

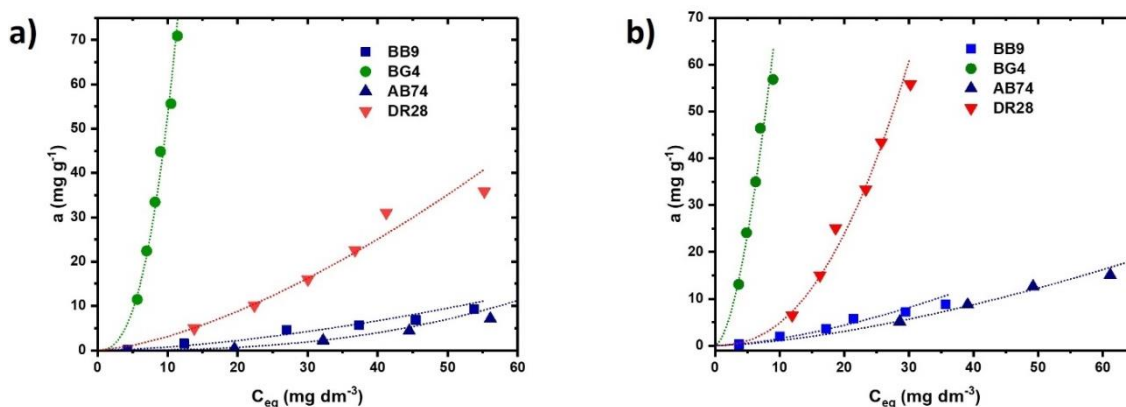


Fig.3. Adsorption Isotherms of Textile Dyes on a) ACP(HDI) and b) ACP(IPDI)

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

Dye	Adsorbent	$K_F (\text{mg g}^{-1})$	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 $87 \pm 0.5\%$ of dye.

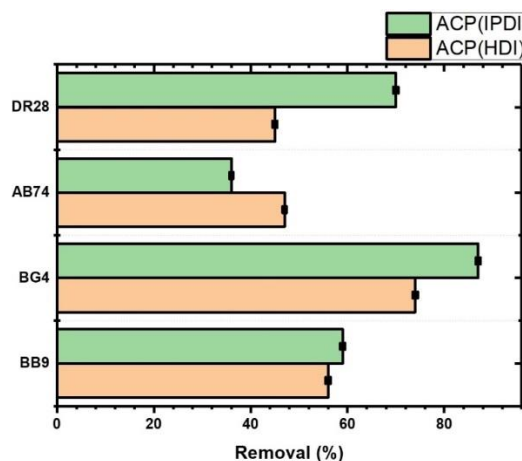


Fig.4. Removal Efficiency of Dyes from Aqueous Solutions

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.

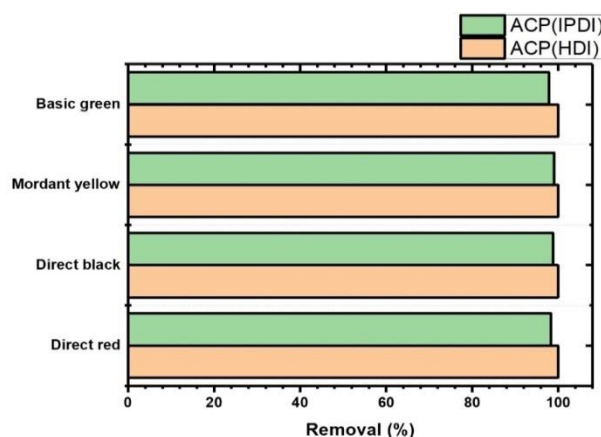


Fig.5. Removal Efficiency for the Removal of Dyes from Wastewaters

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

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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.

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