Egypt. J. Chem. **Vol. 66**, No. 9 pp. 257 - 261 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Effect of Electrostatic Interactions on the Dye Removal Behavior of Different Hydrogel -Based Materials

Ibrahim M. Ibrahim[a*], Mostafa. A. Radwan[a], Mohammed. A. Sadek[a],
Sohair A. Darwish[a], Nasser Y. Mostafa[b]

[a] *Department of Chemical Engineering, the British University in Egypt, El-Shorouk City, Cairo, Egypt.*
[b] *Chemistry Department, Faculty of Science, Suez Canal University, Ismailia 41522, Egypt.*

Abstract

Dye removal from industrial wastewater is still a major challenge to this day. It is urged to find an efficient and economically feasible approach to remove dyes from wastewater before discharge. The use of hydrogels for dye removal has been proposed because of its high absorbing capacity and relatively low price. This work studies the dye removal behaviour of different hydrogels towards cationic and anionic dyes, by measuring the dye removal obtained through spectrophotometer techniques. The hydrogels investigated are Poly(2 -Acrylamido - 2 - Methylpropane Sulphonic Acid) (PAMPS) hydrogels, commercial sodium polyacrylate (Na - PA), chitosan (CH), and different mixtures such as CH/PAMPS and CH/Na -PA, along with a semi -IPN P(AMPS/Na -PA). It was found that the negatively charged PAMPS hydrogel showed greater cationic dye removal, opposed to the positively charged CH which removed more anionic dye. Regarding the CH/PAMPS hydrogels, it had an impressive dye removal of for both cationic and anionic dyes, reaching 90% and 85%, respectively. It is concluded that the electrostatic interaction greatly influences the dye removal capacity. Hence, the design of hydrogel materials for dye removal purposes should take into consideration the electrostatic interaction of the dye with the hydrogel surface.

Keywords: Hydrogel, Dye Removal, Wastewater, Absorption, 2-Acrylamido-2-Methylpropane Sulphonic Acid, Sodium Polyacrylate, Chitosan

1. Introduction

Hydrogels are a type of cross -linked polymeric networks that have the ability to absorb up to 1000 times its weight of water [1]. This high absorbing capacity is mainly due to the hydrophilic functional groups in the polymeric network, such as sulfonic acid ($–SO_3H$), carboxylic acid (–COOH), amide (–CONH), amine ($–NH_2$), and hydroxyl (–OH) functional groups [2]. Hydrogels have gained a lot of attention in recent years, not only because of its ability to absorb large amounts of water, but also because they can selectively diffuse solutes into its pores [3]. And the cherry on top of the cake is that hydrogels are eco -friendly, cheap, and do not require sophisticated production methods [4]. This has given hydrogels a very promising potential to be used in separation technologies, particularly those concerned with treating wastewater [5]. In fact, several researchers have innovated new hydrogel materials with the aim of removing dyes [6], heavy metal ions [7], pathogenic microorganisms [8], and even radionuclides [9]. The dye industry is a large industry worldwide. It is estimated that more than 10,000 different types of dyes and pigments are used globally for different purposes, including plastics, textile, dyeing, cosmetics, food industry, and many more. The worldwide production of synthetic dyes

---

*Corresponding author e-mail: Ibrahim.hamad@bue.edu.eg.; (Ibrahim M. Ibrahim).
Received date 23 November 2022; revised date 08 December 2022; accepted date 18 December 2022
DOI: 10.21608/EJCHEM.2022.176630.7228

reached over 700,000 tonnes/year. Unfortunately, up to 200,000 tonnes/year of these dyes end up in effluent wastewater, considering only the textile industry [10]. In fact, textile industries are considered the most polluting industry relative to any other production sector, regarding both the volume of wastewater and its composition [11], [12]. Despite the many strict environmental regulations and legislations obliging textile industries to remove dyes from their disposed water effluent [13], most of these dyes do not get properly treated and eventually escape to the receiving water body. Treating effluent wastewater rich in dyes is still a challenge to this day due to dye's needed high stability. Dyes are designed to be stable and non -degradable, particularly against cleaning detergents. This explains the inefficiency of using conventional light, thermal, chemical, and biochemical wastewater treatment methods [14]. Additionally, the effluent wastewater from textile plants not only contains mostly non - degradable dyes, but also contains toxic chemical additives, high suspended solids content, high Chemical and Biological Oxygen Demands (COD and BOD, respectively), high levels of metals and salts content. Aside from that, wastewater in the textile industry varies greatly from one plant to another, the type of process employed, the equipment used, type of chemicals and additives used, the weight and type of fabric/textile manufactured, and even the time of year. All these complex factors and considerations increase the challenge of finding an effective and efficient wastewater treatment process for such heavily contaminated effluent water [15]. The common dye removal methods from wastewater [16] including physical [17], chemical [18] , and biochemical [19] treatment are not yet employed for industrial dye removal due to economic and efficiency drawbacks [20]. Such drawbacks include high capital investment, low dye removal efficiency, inefficiency towards some dyes, instability or short life time, the production of large amounts of sludge, or the complexity of the process [21]. For this reason, this research study proposes the use of hydrogels as an adsorbent material for wastewater treatment, especially for textile industries and other heavenly contaminating and polluting industry sectors such as steel. It is already proven that hydrogels have the ability to purify water from complex dyes [22], metal ions [23], and heavy metals [24]. The proposal is based on using the same process for removing several contaminates, in this case, dyes and heavy metal ions. However, it is important to design a hydrogel material that can selectively absorb dyes with high capacity and in a short time to improve the separation efficiency and meet industrial requirements. The novelty of this work is to scan the influence of electrostatic interaction on the dye adsorption mechanism of hydrogels. To do so, the dye removal capacity of different hydrogels is investigated towards both cationic and anionic dyes. Different hydrogel mixtures based on sodium polyacrylate (Na -PA), poly(2 -acrylamido-2-methylpropane sulphonic acid) (PAMPS) and chitosan (CH) were prepared and compared based on the dye removal capacity towards Methylene blue (MB), the cationic dye, and Methyl orange as the anionic dye.

2.Experimental

2.1 Materials

2-Acrylamido-2 -methylpropane sulfonic acid (AMPS) monomer was purchased as reagent grade from Alfa Aesar. The crosslinking agent is analytical grade N,N ' -methylene -bis - Acrylamide (MBA) purchased from Sigma Aldrich, while the initiator is reagent grade Ammonium persulfate (APS) from Sisco Research Laboratories (SRL). Sodium Polyacrylate (Na -PA) hydrogel was extracted from Molfix diapers. Chitosan (CH) was used as purchased from Alfa Chemicals without further preparation. The dyes used were cationic Methylene Blue (MB) from Carlo Erba and anionic Methyl orange (MO) from Alfa Chemicals .

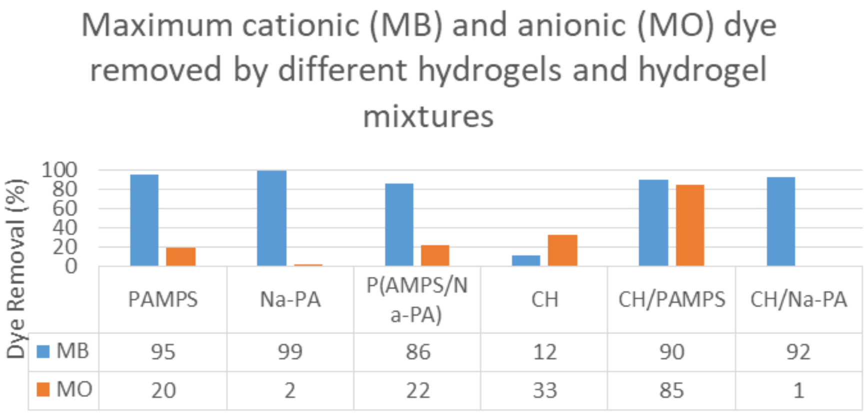
2.2 Preparation of PAMPS Hydrogel

PAMPS hydrogel was prepared through solution polymerisation. In 8 mL of distilled water, 3.0 grams of AMPS was added along with 0.1 g of the MBA crosslinker. An inert blanket is created by bubbling nitrogen gas through the mixture, then 0.1 g of the APS initiator is added carefully. The polymerisation reaction occurred at around 60 -70 °C for 3 hours. The formed PAMPS hydrogel were left to dry at 50 °C for 3 days before use [25].

2.3 Preparation of P(AMPS/Na -PA)

A Semi -Interpenetrating Polymer Network (Semi -IPN) hydrogel based on AMPS and Na -PA polymer was prepared trough polymerising the AMPS monomer in the presence of the Na -PA hydrogel.

The procedure of preparing P(AMPS/Na-PA) involves dissolving 4.0 grams of AMPS in 20 mL of distilled water, along with 0.1 g of the MBA crosslinker and 0.2 g of Na - PA. An inert blanket is created before adding 0.1 g of the APS initiator. The polymerisation of AMPS now occurs inside the Na - PA network, at around 60 -70 °C for 3 hours. The formed P(AMPS/Na -PA) hydrogel were left to dry at 50 °C for 3 days before use.



	PAMPS	Na-PA	P(AMPS/Na-PA)	CH	CH/PAMPS	CH/Na-PA
🟦 MB	95	99	86	12	90	92
🟧 MO	20	2	22	33	85	1

Figure 1, Maximum cationic (MB)and anionic (MO) dye removed by PAMPS, Na-PA, P(AMPS/Na-PA), CH, CH/PAMPS, and CH/Na-Pa hydrogels after 120 minutes.

2.4 Preparation of CH/PAMPS and CH/Na-PA

After drying the polymerised PAMPS hydrogel, a 1:1 mixture of PAMPS and CH was prepared by simply mixing 0.25 g of each hydrogel. Similarly, the CH/Na-Pa hydrogel mixture was also prepared by mixing 0.25 g of each hydrogel, yielding a 1:1 mixture.

2.5 Dye Removal

A small sample of each hydrogel (0.05 g) is left in contact with 250 mL of the dye solution (25 ppm) at room temperature and under shaking (150 rpm) until it reaches equilibrium, which is decided when the dye concentration no longer changes with time. The dye removal percent of each hydrogel was calculated using the following formula:

Equation 1 Percent dye removal

$$Dye\ Removal\% = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the initial concentration of the dye, and C_t is the concentration of the dye after contact time t.

The concentration of the dye was calculated after finding its absorbance using spectrophotometry techniques (METASH UV-5100 Spectrophotometer with MetaSpec Program V.2.2). The calibration line equations relating the concentration of MB and MO dyes and their absorbance at their maximum wavelengths were found experimentally to be as follows:

Equation 1 *Relationship between the concentration and absorbance of MB at 664 nm*

$$C_{MB}\ (ppm) = A/0.1124$$

Equation 2 *Relationship between the concentration and absorbance of MO at 464 nm*

$$C_{MO}\ (ppm) = A/0.0735$$

3. Results and Discussion

The dye removal capacity of each hydrogel considered in this work was examined with both a cationic and an anionic dye. Figure 1 shows the maximum cationic and anionic dye removal by PAMPS hydrogel, Na-PA hydrogel, the Semi-IPN hydrogel based on PAMPS and Na-PA, chitosan, and the hydrogel mixtures CH/PAMPS and CH/Na-PA.

It is clear that hydrogels including PAMPS can remove cationic dyes by greater extends compared to anionic dyes. This change in behaviour implies the presence of electrostatic interactions between the dyes and the hydrogel network. In fact, the PAMPS hydrogel is negatively charged due to the sulphonic functional groups. Thus, the chains can readily attract positively charged cationic dyes such as MB. On the other hand, CH is positively charged due to the protonation of amino groups [26], which explains its ability to remove more anionic dyes compared to cationic dyes. Upon using an adsorbent based on a cationic and an anionic hydrogel such as CH and PAMPS, respectively, it is expected to obtain the best results for removing both anionic and cationic dyes. This was proved by testing this mixture for MB and MO dye removal, and the results matched the expected outcome. The CH/PAMPS hydrogel mixture could remove up to 85% of MO and 90% of MB in only two hours.

3. Conclusion

This paper investigates the dye removal capacity of different hydrogels and hydrogel mixtures towards both cationic and anionic dyes. The hydrogels considered in this study are PAMPS, Na-PA, CH, CH/PAMPS, CH/Na-PA, and a Semi-INP based on PAMPS and Na-PA. It was found that the PAMPS hydrogel and all the mixtures it was involved in resulted in impressive cationic dye removal. This is due to the anionic nature of the polymeric chains. On the other hand, CH showed better anionic dye removal due to its cationic nature. This paper also investigated the dye removal behaviour of a mixture based on both PAMPS and CH. This mixture showed the best dye removal capacity towards both anionic and cationic dyes, as expected. It is concluded that during the design of hydrogel materials for dye removal purposes, the electrostatic interaction of the dye with the hydrogel surface should be taken into consideration. The results also encourage the use of an ampholytic hydrogel (which has both positive and negative charges on the polymeric backbone) for enhanced removal of both cationic and anionic dyes.

References

[1] G. Kowalski, K. Kijowska, M. Witczak, L. Kuterasiński, and M. Lukasiewicz, “Synthesis and effect of structure on swelling properties of hydrogels based on high methylated pectin and acrylic polymers,” *Polymers (Basel).*, vol. 11, no. 1, pp. 1–16, 2019, doi: 10.3390/polym11010114.

[2] R. S. P. Teixeira, R. J. Correa, J. S. Bello Forero, M. G. S. Silva, R. C. S. Oliveira, and R. S. Souza, “Comparative study of PEO and PVA hydrogels for removal of methylene blue dye from wastewater,” *J. Appl. Polym. Sci.*, vol. 134, no. 28, p. 45043, Jul. 2017, doi: 10.1002/APP.45043.

[3] C. L. Bell and N. A. Peppas, “Measurement of the swelling force in ionic polymer networks. III. Swelling force of interpolymer complexes,” *J. Control. Release*, vol. 37, no. 3, pp. 277–280, 1995, doi: 10.1016/0168-3659(95)00085-2.

[4] H. Wang, X. Ji, M. Ahmed, F. Huang, and J. L. Sessler, “Hydrogels for anion removal from water,” *J. Mater. Chem. A*, vol. 7, no. 4, pp. 1394–1403, Jan. 2019, doi: 10.1039/C8TA10286D.

[5] V. Sinha and S. Chakma, “Advances in the preparation of hydrogel for wastewater treatment: A concise review,” *J. Environ. Chem. Eng.*, vol. 7, no. 5, p. 103295, Oct. 2019, doi: 10.1016/J.JECE.2019.103295.

[6] Y. Yang *et al.*, “Hydrogels for the removal of the methylene blue dye from wastewater: a review,” *Environ. Chem. Lett. 2022*, vol. 1, pp. 1–21, Apr. 2022, doi: 10.1007/S10311-022-01414-Z.

[7] B. Sonmez and A. N. Celikkol, “Pullulan based hydrogels for the removal of various metal ions from aqueous solutions,” *J. Environ. Chem. Eng.*, vol. 9, no. 5, p. 106188, Oct. 2021, doi: 10.1016/J.JECE.2021.106188.

[8] E. Caetano Nazzari *et al.*, “Hydrogel Applications to Microbiological Water Treatment,” *https://doi.org/10.1080/15422119.2022.2048394*, pp. 1–9, Mar. 2022, doi: 10.1080/15422119.2022.2048394.

[9] J. Ding *et al.*, “An innovative strategy for construction of pH-responsive supramolecular hydrogel from graphene quantum dots clusters toward integration of detection and removal of uranium,” *Appl. Surf. Sci.*, vol. 583, p. 152492, May 2022, doi: 10.1016/J.APSUSC.2022.152492.

[10] F. M. D. Chequer, G. A. R. de Oliveira, E. R. A. Ferraz, J. C. Cardoso, M. V. B. Zanoni, and D. P. de Oliveira, “Textile Dyes: Dyeing Process and Environmental Impact,” *Eco-Friendly Text. Dye. Finish.*, Jan. 2013, doi: 10.5772/53659.

[11] K. Manzoor, S. J. Khan, M. Yasmeen, Y. Jamal, and M. Arshad, “Assessment of anaerobic membrane distillation bioreactor hybrid system at mesophilic and thermophilic temperatures treating textile wastewater,” *J. Water Process Eng.*, vol. 46, p. 102603, Apr. 2022, doi: 10.1016/J.JWPE.2022.102603.

[12] K. Bailey, A. Basu, and S. Sharma, “The Environmental Impacts of Fast Fashion on Water Quality: A Systematic Review,” *Water*, vol. 14, no. 7, p. 1073, 2022, doi: 10.3390/w14071073.

[13] EPA, “Environmental Guidlines for the Textile Dyeing and Finishing Industry,” Environment Protection Authority, State Government of Victoria, 1998.

[14] S. Rodríguez Couto, “Dye removal by immobilised fungi,” *Biotechnol. Adv.*, vol. 27, no. 3, pp. 227–235, May 2009, doi: 10.1016/J.BIOTECHADV.2008.12.001.

[15] D. A. Yaseen and M. Scholz, “Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review,” *Int. J. Environ. Sci. Technol.*, vol. 16, no. 3, pp. 1193–1226, 2019, doi: 10.1007/s13762-018-

2130-z.

[16] G. Bal and A. Thakur, “Distinct approaches of removal of dyes from wastewater: A review,” *Mater. Today Proc.*, vol. 50, pp. 1575–1579, Jan. 2022, doi: 10.1016/J.MATPR.2021.09.119.

[17] M. Kaykhaii, M. Sasani, and S. Marghzari, “Removal of Dyes from the Environment by Adsorption Process,” *Chem. Mater. Eng.*, vol. 6, no. 2, pp. 31–35, Jul. 2018, doi: 10.13189/CME.2018.060201.

[18] B. T. Ergan and E. Gengec, “Dye degradation and kinetics of online Electro-Fenton system with thermally activated carbon fiber cathodes,” *J. Environ. Chem. Eng.*, vol. 8, no. 5, p. 104217, Oct. 2020, doi: 10.1016/J.JECE.2020.104217.

[19] L. Y. Jun *et al.*, “An overview of immobilized enzyme technologies for dye and phenolic removal from wastewater,” *J. Environ. Chem. Eng.*, vol. 7, no. 2, Apr. 2019, doi: 10.1016/J.JECE.2019.102961.

[20] G. Pei, F. Yu, and L. Zhang, “Comparative Analysis of dyeing wastewater treatment Technology,” no. Iccte, pp. 427–430, 2016, doi: 10.2991/iccte-16.2016.71.

[21] R. G. Saratale, G. D. Saratale, J. S. Chang, and S. P. Govindwar, “Bacterial decolorization and degradation of azo dyes: A review,” *J. Taiwan Inst. Chem. Eng.*, vol. 42, no. 1, pp. 138–157, 2011, doi: 10.1016/j.jtice.2010.06.006.

[22] P. Mohammadzadeh Pakdel, S. J. Peighambardoust, N. Arsalani, and H. Aghdasinia, “Safranin-O cationic dye removal from wastewater using carboxymethyl cellulose-grafted-poly(acrylic acid-co-itaconic acid) nanocomposite hydrogel,” *Environ. Res.*, vol. 212, p. 113201, Sep. 2022, doi: 10.1016/J.ENVRES.2022.113201.

[23] S. S. Li, Y. L. Song, H. R. Yang, Q. Da An, Z. Y. Xiao, and S. R. Zhai, “Modifying alginate beads using polycarboxyl component for enhanced metal ions removal,” *Int. J. Biol. Macromol.*, vol. 158, pp. 493–501, Sep. 2020, doi: 10.1016/j.ijbiomac.2020.05.038.

[24] Z. Zhao, Y. Huang, Y. Wu, S. Li, H. Yin, and J. Wang, “α-ketoglutaric acid modified chitosan/polyacrylamide semi-interpenetrating polymer network hydrogel for removal of heavy metal ions,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 628, p. 127262, Nov. 2021, doi: 10.1016/J.COLSURFA.2021.127262.

[25] S. A. Darwish, I. M. Ibrahim, N. Y. Mostafa, M. A. Radwan, M. A. Sadek, and H. A. Elazab, “Water Absorption Enhancement of Sodium Poly Acrylate and Poly(2-Acrylamido-2-Methylpropane Sulphonic Acid) Based Hydrogel Mixtures,” *Open Chem. Eng. J.*, vol. 15, no. 1, pp. 49–54, Dec. 2021, doi: 10.2174/1874123102115010049.

[26] A. C. Jayasuriya, “Production of micro- and nanoscale chitosan particles for biomedical applications,” *Chitosan Based Biomater.*, vol. 1, pp. 185–209, Jan. 2017, doi: 10.1016/B978-0-08-100230-8.00008-X.