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Eco-Conscious Synthesis of a Starch-Magnetic Hydrogel for Effective Methylene Blue Decontamination in Wastewater Treatment

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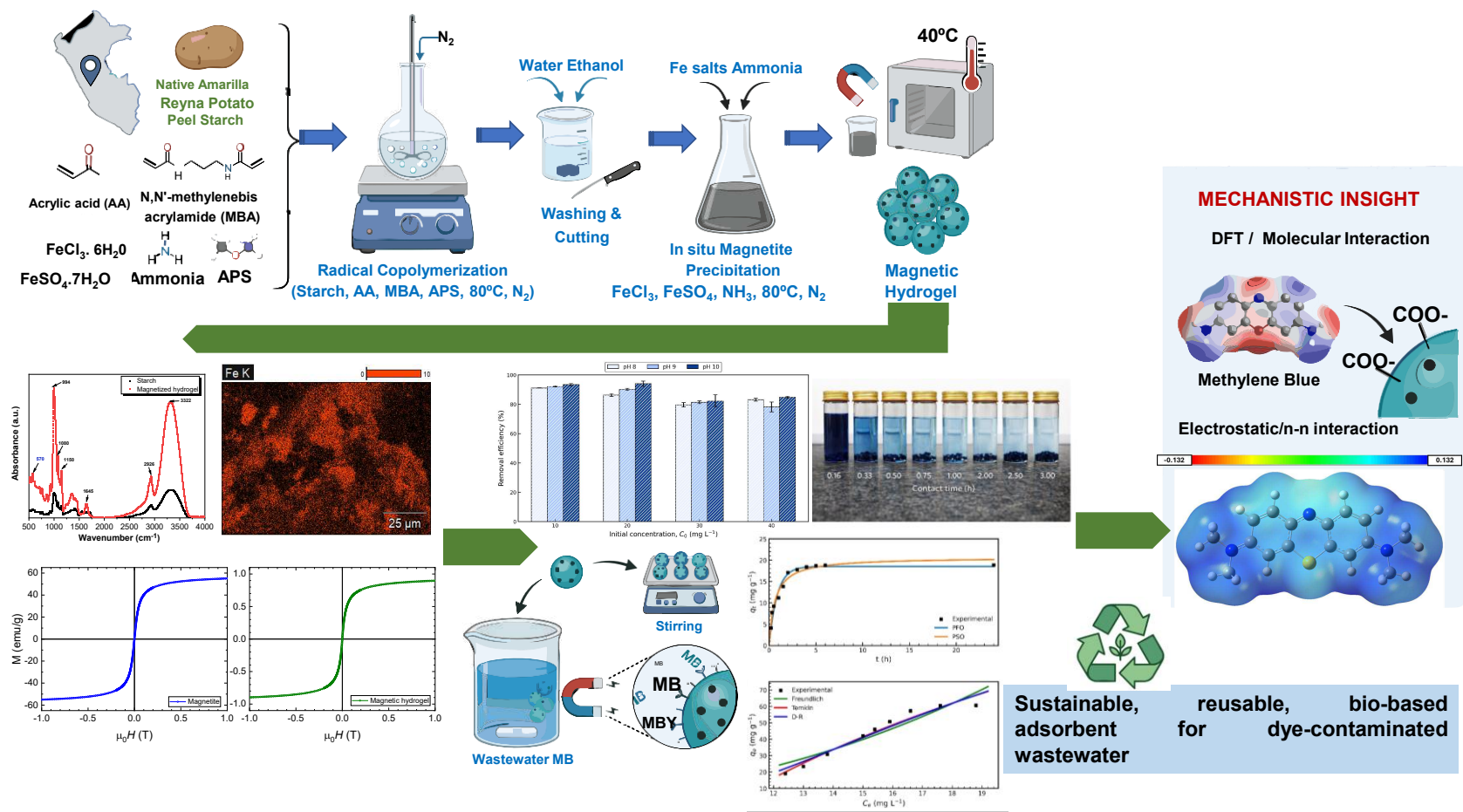
Abstract

Novel magnetic hydrogels based on native Peruvian *Amarilla Reyna* potato starch were synthesized via radical copolymerization, followed by *in situ* co-precipitation of magnetite, nanoparticles for Methylene Blue (MB) removal from aqueous matrices. The materials were characterized by FTIR, XRD, SEM-EDS, VSM, swelling measurements, and pH_{PZC} determination, confirming successful polymer grafting, a homogeneous Fe₃O₄ incorporation, magnetic recoverability, and a high swelling capacity (352.1 g/g). The magnetic hydrogel achieved a MB removal efficiency of 96% and an equilibrium adsorption capacity of 1148.3 mg/g at pH 10 and 30°C. Adsorption kinetics followed the pseudo-first-order (PFO) kinetic model, reaching the equilibrium within 3 h, while the good fitting to the Langmuir isotherm model confirmed a monolayer adsorption behaviour. Thermodynamic analysis revealed that the adsorption process was spontaneous and exothermic, while Density Functional Theory (DFT) calculations indicated a highly delocalized positive charge over the MB molecule, providing a molecular-level explanation for its weaker competition with small inorganic cations for negatively charged adsorption sites in complex aqueous matrices. Likewise, the hydrogel retained over 90% MB removal efficiency after five consecutive adsorption-desorption cycles, demonstrating an excellent reusability of the material. Tests in real water

matrices showed a decreasing in the MB removal efficiency, c.a. 30-38%, due to ionic competition for the active sites and organic matter interference. The synthesized magnetic hydrogel demonstrated environmental safety, with no significant toxicity after treatment of the real effluents. These findings highlighted the potential of the obtained magnetic hydrogel as a sustainable and reusable adsorbent for dyes removal from complex aqueous matrices.

Keywords: Adsorption; Magnetic hydrogel; Methylene Blue; Potato starch; Wastewater.

Graphical Abstract



Highlights

- A magnetic hydrogel used as MB adsorbent was successfully synthesized from starch.
- A removal efficiency of 96% and adsorption capacity of 1148.3 mg/g were obtained.
- Kinetics followed PFO model, while the monolayer isotherm well-fitted to Langmuir.
- Hydrogel retained >90% removal efficiency after five consecutive adsorption cycles.
- MB removal in real water matrices decreased due to competition for the active sites.

1. Introduction

The ongoing release of synthetic dyes into the aquatic ecosystems has emerged as a significant environmental issue owing to their toxicity, persistence, and resistance to biodegradation (Oladoye et al. 2022). The global textile, paper, leather, and pharmaceutical industries discharge an estimated 280,000 tonnes of synthetic dyes annually into the aquatic bodies. These compounds can be classified into several chemical families, e.g., azo, thiazine, anthraquinone, triarylmethane, and indigo, and include both cationic and anionic dyes. Among these pollutants, Methylene Blue (MB), a cationic thiazine dye, poses serious ecological and health risks: carcinogenic, mutagenic, and endocrine-disrupting effects even at trace concentrations (Oladoye et al. 2022, Banik et al. 2025). Therefore, the efficient removal of MB from aqueous solutions remains a pressing priority for sustainable wastewater management.

Several physic-chemical and biological strategies have been explored for dyes removal from wastewater, including coagulation–flocculation, photocatalytic degradation, electrochemical oxidation, membrane filtration, and biological treatments (Banik et al. 2025, Seida and Tokuyama, 2022). Although these methods can be effective, they often suffer from high operational costs, complex equipment requirements, or the generation of secondary pollutants, particularly at low dye concentrations (Seida and Tokuyama 2022, Naushad et al. 2019). In this context, carbon hydrogels have attracted increasing attention owing to their three-dimensional polymeric networks, high porosity, and strong capacity to retain and capture pollutants (Darban et al. 2022, Shalla et al. 2018, Hu et al. 2018, Resende et al. 2023). These materials can be synthesized from natural, semisynthetic, or synthetic polymers, allowing fine-tuning of their chemical functionalities and mechanical performance depending on the required application (Alves et al. 2020, Chen et al. 2021, Cui et al. 2022, Lapointe and Barbeau 2020).

In this sense, biopolymer-based hydrogels derived from starch, cellulose, chitin, or natural gums have demonstrated great promise as sustainable and biodegradable alternatives for the remediation of contaminated water environments (Arayaphan et al. 2021, Nguyen et al. 2022, Pinzón-Moreno et al. 2022, Zhu et al. 2023). Their copolymerization or blending with synthetic monomers, such as acrylic acid or acrylamide, has led to hybrid materials with enhanced structural stability, swelling capacity, and affinity towards a wide range of pollutants (Pakdel and Peighambaroust 2018, Dai et al. 2019, He et al. 2017, Lv et al. 2020, Zamani-Babgohari et al. 2024). The modification of biopolymers—with carboxymethyl cellulose, chitosan, and starch—allow to introduce functional groups, such as carboxyl, amino, and hydroxyl moieties in the hydrogel structure, promoting specific interactions with the target pollutants (Kamel et al. 2020, Makhado et al. 2018, Melo et al. 2018, Zhang et al. 2022). These developments align with the current trend towards the use of eco-friendly and sustainable adsorbents (Vara et al. 2024, Jumnonng et al. 2023).

The incorporation of magnetic iron oxide nanoparticles-magnetite- (Fe_3O_4) into polymeric matrices and nanocomposites (Huacalco-Aguilar et al. 2021) has led to the development of magnetic hydrogels, which offer additional advantages such as easy magnetic recovery and enhanced adsorptive performance (Ozay et al. 2009, Li et al. 2011, Filho et al. 2021, Hosseini et al. 2022, Ludeña Huaman et al. 2024). In this sense, these materials have been extensively investigated for the removal of cationic dyes, e.g., Methylene Blue, Crystal Violet, as well as heavy metals and metalloids (Beigi et al. 2023, Nguyen et al. 2023, Zeng et al. 2024). Thus, recent advances demonstrate substantial improvements in adsorption efficiency through surface functionalization and the design of hybrid matrices, such as pectin hydrogel@ Fe_3O_4 –bentonite (Beigi et al. 2023) and Fe_3O_4 /poly(HEMA-co-AMPS) magnetic hydrogels (Ludeña et al. 2024, Ccoyo Ore et al. 2024). These materials exhibited high adsorption capacity values and an excellent regeneration ability, reinforcing their potential for industrial wastewater

treatment (see Table 1, for comparison purposes) (Guo et al. 2018, Dutta et al. 2021, Andolsi et al. 2023).

Table 1. Studies about the synthesis of magnetic hydrogels-based adsorbents for the removal of hazardous dyes and metal ions.

Adsorbent	Contaminant	Adsorption capacity / Efficiency	Operating conditions	Ref.
Carboxymethyl cellulose hydrogel with modified magnetite	MB	96.1%, 222.2 mg/g	pH = 5.6, 50 mg/L, 0.1 g adsorbent, 25 °C, 30 min	(Kamel et al. 2020)
Magnetic (photopolymerized) hydrogel	Cd ²⁺	140.85 mg/g	0.2 g adsorbent, 12 h, room temperature	(Ozay et al. 2009)
Magnetic poly(acrylic acid–acrylamide–butyl methacrylate) (P(AAB)) hydrogel	Crystal Violet	10.787 mg/g	10 mg adsorbent, pH = 7, 25 °C	(Li et al. 2011)
Eggshell/starch/Fe ₃ O ₄ magnetic nanocomposite	Pb ²⁺	97.86% removal (10 mg/L)	pH = 6, 25 °C, 60 min, 1 g/L adsorbent	(Hosseini et al. 2022)
Fe ₃ O ₄ /poly(HEMA-co-AMPS) magnetic hydrogel	MB	94% removal (50 mg/L, after 10 cycles)	pH = 6.5, 1 mg/mL adsorbent, 1 h	(Ludeña Huaman et al. 2024)
Fe ₃ O ₄ /poly(HEMA-co-IA) magnetic hydrogel	MB	91% removal (200 mg/L)	pH = 6.8, 1 mg/mL adsorbent, 10 min	(Ludeña et al. 2024)
Fe ₃ O ₄ -TMSPM/HG	MB	270.27 mg/g (50 mg/L) 92.6% removal	pH = 8, 0.5 mg/mL adsorbent, 24 h, 15 °C	(Ccoyo Ore et al. 2024)
Hydrogel CNS/P(AAc-MAC)	MB	2249 mg/g (400 mg/L) 98% (50 mg/L)	pH = 8, 0.5 mg/mL adsorbent, 1 h, 15 °C	(Tang et al. 2021)
Magnetic graphene oxide/poly(NVI-co-AA) hydrogel	MB	97% removal (100 mg/L) 65% removal (after 5 cycles)	10 mg adsorbent, pH = 12, 100 min, 40 °C	(Yao et al. 2020)
Fe ₃ O ₄ -APTES–acryloyl chloride/IA–HEMA magnetic nanocomposite	MB	>95% in 15 min	pH = 11, 30 mg adsorbent, 20 mg/L, 15 min	(Mehdizadeh et al. 2022)

A major advantage of magnetic hydrogels is their reuse capacity, which lowers the operational costs and minimizes secondary waste generation (Yao et al. 2020). Furthermore, the embedded Fe₃O₄ nanoparticles enable fast separation of solids after adsorption, avoiding complex filtration or additional centrifugation steps (Li et al. 2011). Several studies have reported adsorption efficiencies above 80% after multiple regeneration cycles using mild desorption agents, such as HCl, NaOH, or ethanol in aqueous solution (Makhado et al. 2018). For instance, Fe₃O₄/poly(HEMA-co-AMPS) hydrogel showed a MB removal efficiency of 85% after 5 regeneration cycles (Ludeña et al. 2024). Despite these promising findings, important knowledge gaps remain concerning the regeneration mechanisms and long-term structural stability of biopolymer-based magnetic hydrogels during repeated use (Safavi-Mirmahalleh et al. 2019, Mittal et al. 2016). Additionally, many studies do not evaluate physicochemical changes such as Fe₃O₄ oxidation, nanoparticle leaching, or polymer network degradation, which can critically affect the adsorbent performance and recyclability (Dong et al. 2020). Furthermore, most research is focused on single-component pollutant systems, often neglecting proof-of-concept studies in real wastewater matrices containing complex organic–inorganic mixtures (Mittal et al. 2016).

In this work, a novel magnetic hydrogel based on native Peruvian potato starch and magnetite nanoparticles was synthesized via a simple copolymerization followed by a coprecipitation process and then was applied for the removal of MB from model aqueous solutions. The study evaluated the adsorption performance, key operating parameters, and the textural, structural and chemical-surface properties of the synthesized adsorbent, as well as its reusability, adsorption kinetics, and adsorption isotherms. Density Functional Theory (DFT) studies and thermodynamic analyses were also conducted. Additionally, the hydrogel's applicability was validated using real wastewater matrices. In summary, this study prioritizes durability and recyclability of the material by assessing the long-term retention of structural, kinetic, and magnetic properties, thereby contributing to the practical implementation of magnetic hydrogels within the framework of circular economy and sustainable adsorption technologies.

2. Materials and methods

2.1 Materials

Starch was extracted from the peel of the Peruvian Amarilla Reyna (AR) potato, collected from the fields of the village of Champaccocha, located at 13°39'5.6" S, 73°18'15.3" W and 3440 m altitude in the district of San Jeronimo, province of Andahuaylas, Apurímac, Peru. For this precursor, a mass fraction of 42.09 wt.% of apparent amylose has been reported (Choque-Quispe et al. 2024).

Acrylic acid (AA), N, N'-methylene-bisacrylamide (MBA), sodium hydroxide (NaOH), hydrochloric acid (HCl) solution, ammonium persulfate (APS), ethanol, and MB were obtained from Sigma-Aldrich. The reagents used for the magnetite preparation were ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Reagent Plus®, 98%, Sigma-Aldrich), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Reagent Plus®, 98%, Sigma-Aldrich), and ammonia (puriss., anhydrous, $\geq 99.9\%$, Sigma-Aldrich). All chemicals were used at an analytical grade.

2.2 Synthesis of the hydrogel

In this work, the hydrogel was synthesized following the method reported by Chen et al. (2021), with some modifications. Briefly, 5.0 g of starch, 1.0 g of NaOH, and 50 mL of distilled water was mixed at 25°C in a three-necked flask, equipped with a mechanical stirrer and a thermometer. The mixture was continuously stirred at 300 rpm for approximately 20 min, and the temperature increased from 25 to 55°C. Then, 5.0 mL of AA solution was added while the temperature was raised up to 65°C. Then, the stirring speed was lowered to 150 rpm. At the same time, 6.0 mL of APS solution (10 g/L) was added and allowed to react for 40 min under N_2 atmosphere. Subsequently, 5 mL of MBA solution (10 g/L) and 5 mL of AA solution (34% neutralization degree) were added to the reaction mixture, which was then stirred for 40 min. The temperature then increased to 70°C, and the reaction was allowed to continue for an additional 60 min without stirring. The obtained hydrogel was cut into smaller pieces and then stirred in 500 mL of distilled water for 24 h to remove unreacted AA monomers and impurities. It was subsequently immersed at least three times in a 200 mL solution of 75% w/v ethanol. Finally, the resulting hydrogel was dried in an oven at 40°C for 24 h. From 5 g of native AR potato starch, 8.55 g of hydrogel were obtained, yielding 7 g with particle sizes between 2 and 3 mm.

2.3 Magnetization process of the hydrogel

The preparation of the magnetic hydrogel was conducted by the co-precipitation method, as follows: 80 mL of ultrapure water, saturated with N_2 for 30 min, was mixed with 0.1 g of hydrogel, 0.26 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and 0.13 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a three-necked flask at 80°C, under constant N_2 bubbling. After 30 min of contact between the precursors and the hydrogel,

approximately 2.5 mL of 25% ammonia solution was added. The mixture was stirred for 30 min to form a colloidal magnetite (Fe₃O₄)/hydrogel solution. The colloidal solution was separated from the liquid using a magnet and washed with ultrapure water until the washing water reached pH 7. The magnetized hydrogel and the free magnetite were sonicated for 5 min, then separated and dried in an oven at 40°C for 24 h. The hydrogel/precursor ratio was 1:4 to ensure an adequate magnetic response upon swelling in water, as can be seen in Figure S1 of the Supplementary Material.

2.4 Adsorption Experiments

The batch adsorption experiments were accomplished as follows: 0.01 g of magnetic hydrogel was put in contact with 25 mL of MB solution ($C_0 = 20$ mg/L), using ultrapure water as solvent, and yielding an initial pH of 10. The system was maintained at constant temperature (30°C) and stirring rate (300 rpm) in a programmable orbital shaker (LabMate, model 96108607; Aapptec LLC, Louisville, KY, USA) for 24 h. Samples were filtered before UV-Vis measurements. The MB concentration was determined using a UV-Vis spectrophotometer (Biochrom Libra S22, Biochrom Ltd., UK) at a wavelength of 664 nm. The equilibrium adsorption capacity (q_e , mg/g) and removal efficiency (E , %) were calculated according to the Equations (1) and (2):

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (1)$$

$$E = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

where C_0 (mg/L) is the initial MB concentration, C_e (mg/L) is the MB concentration at equilibrium time, V (L) is the volume of MB solution, and W (g) indicates the mass of adsorbent. The optimal adsorption conditions were determined to facilitate future adsorption research. Thus, the effect of varying initial pH values (8-10) on the adsorption capacity was examined. Additionally, the adsorption capacity dependence on contact time was measured, as well as the influence of the initial MB concentration on adsorption kinetics was investigated over 24 h. Likewise, the MB adsorption isotherm was obtained at 30°C, with initial concentrations ranging from 8 to 400 mg/L. Also, the thermodynamic studies were carried out at 30, 40, and 60°C.

Finally, the reusability of the adsorbent was assessed as follows: 0.01 g of the hydrogel was immersed in 25 mL of MB solution ($C_0 = 20$ mg/L) at an initial pH of 10 until equilibrium was reached. Subsequently, the saturated hydrogel was put in contact with a 0.1 M HCl solution, then washed with 0.1 M NaOH solution, and rinsed with distilled water. Following this procedure, five consecutive adsorption-desorption cycles were accomplished. The desorption efficiency values (DE , %) was calculated using the following equation:

$$DE = \frac{100 \cdot C_d \cdot V \cdot m}{q_a} \quad (3)$$

where C_d (mg/L) is the MB concentration after the hydrogel desorption in the same cycle, V (mL) is the volume of desorption solution, q_a (mg/g) is the adsorption capacity in the same cycle, and m (g) is the mass of hydrogel.

2.5 Characterization of the materials

The swelling capacity of the magnetized hydrogel was measured by immersing it in 50 mL of distilled water at room temperature for 24 h. The swelling capacity (g/g) was then calculated according to Equation (4):

$$\text{Swelling capacity} = \frac{100 \cdot (W_2 - W_1)}{W_1} \quad (4)$$

where W_2 (g) represents the weight of the swollen sample and W_1 (g), the weight of the dry sample.

The point of zero charge (pH_{PZC}) of the adsorbent was determined by the pH drift method. Briefly, 0.01 g of the hydrogel was put in contact with 25 mL of ultrapure water at different pH values ranging from 5 to 10, and maintained under stirring for 24 h. The final pH (pH_f) of the solutions was measured with an electronic pH meter. The pH_{PZC} value (at $\Delta\text{pH} = 0$) for each sample was determined from a plot of ΔpH ($\text{pH}_i - \text{pH}_f$) versus pH_i (initial pH).

SEM micrographs of the magnetic hydrogel were obtained using a field emission scanning electron microscope (FE-SEM, Scios 2 LoVac, Thermo Fisher Scientific), equipped with an Energy Dispersive X-ray Spectroscopy (EDS) (UltraDry, with an energy resolution of 129 eV) and an Electron Backscatter Diffraction (EBSD) (Quasor II sensor) system. The achieved resolution was 0.7 nm at 30 kV in STEM mode and 1.4 nm at 1 kV in FE-SEM mode. Moreover, the surface chemistry of the materials was explored using a Thermo Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer, working at a wavelength range from 400 to 4000 cm^{-1} . At the same time, the structural properties of the material were analysed by X-ray diffraction (XRD) technique, using a Bruker D8 Advance A25 diffractometer. Finally, Vibrating Sample Magnetometer (VSM) Microsense (sensitivity of 10^{-5} to 10^{-7} emu) measurements were performed at room temperature. Measurements were performed by applying a maximum magnetic field of 1.8 T in 10-Oe steps, using mass values of 0.02474 g for magnetite and 0.02906 g for the magnetic hydrogel composite to normalize the magnetization values obtained.

2.6 Proof of concept

Two different samples of real wastewater effluents: a surface water and a wastewater treatment plant (WWTP) effluent, were collected (see their characterization in Table 2). The kinetic and adsorption isotherm studies using the real water matrices were accomplished under the same conditions used for the adsorption tests in ultrapure water, as described in Section 2.4. It should be noted that the real effluents were spiked with the same concentration of MB than used for ultrapure water tests, $C_0 = 20$ mg/L, in order to study the competitive effect between the dye and the organic and inorganic compounds present in the wastewater matrices.

Table 2. Physic-chemical parameters of the tested real water matrices.

Parameter	Surface water	WWTP effluent
pH	7.3	8.8
Chemical Oxygen Demand, COD (mg/L)	<15.0	23.0
Total Organic Carbon, TOC (mg/L)	3.2	13.2
Total Carbon, TC (mg/L)	7.4	26.0

Total Nitrogen, TN (mg/L)	0.6	4.8
Total Dissolved Solids, TDS (mg/L)	64.0	596.0
Conductivity, at 20 °C (μS/cm)	38.2	484.6

After the adsorption process, the liquid samples were subjected to toxicity tests using the internationally standardized aquatic ecotoxicity assay performed with a Microtox M500 analyzer. The assays were conducted according to the standard procedure for measuring bioluminescence inhibition in the marine bacterium *Vibrio fischeri* (*V. fischeri*) using the Biotox test kit, in accordance with ISO 11348-3:2009. The toxicity of each sample was determined as the percentage inhibition of bioluminescence relative to an uncontaminated blank (ultrapure water). All samples were analyzed at 15 °C, with the pH adjusted to between 6 and 8 and the osmotic pressure adjusted using a 2% NaCl solution. In accordance with the standard, bioluminescence was measured after 5 and 15 min of exposure, and the results were expressed as Toxicity Units (TU) based on the 5 min exposure.

2.7 Density Functional Theory studies

Density Functional Theory (DFT) calculations were carried out using Gaussian 16 (Frisch et al. 2016) with the MN12-SX functional (Peverati and Truhlar 2012) and the aug-cc-pVTZ basis set (Dunning Jr. 1989, Kendall et al. 1992). The SMD implicit solvation model (Marenich et al. 2009) was employed to include the effects of water as the solvent. The optimized structures were visualized using GaussView 6.0 (Dennington et al. 2016). The Multiwfn program (Lu and Chen 2012, Lu and Chen 2022) was used to generate the molecular electrostatic potential (MEP) surface, the isosurface plots of HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital), at an isovalue of 0.02 a.u., and the representation of the natural bond orbital (NBO) atomic charges. Their Cartesian coordinates are provided in Table S1 (Supplementary Material). Energetic data, electronic parameters and chemical descriptors—calculated using the Koopmans in DFT approximation from HOMO and LUMO energies (Geerlings et al. 2003)—for optimized structure of Methylene Blue cation are collected in Table S2 of the Supplementary Material.

3. Results and discussion

3.1 Characterization of the materials

The FTIR spectrum of the magnetized hydrogel showed a broad O–H stretching band close to 3322 cm⁻¹, which is indicative of adsorbed and structural water retained within the hydrophilic hydrogel network (see Figure 1). Also, it was observed the presence of a peak at 2926 cm⁻¹ due to C–H stretching vibrations in alkane or alkene groups, an ionized H–O–H/C=O bending peak at 1645 cm⁻¹, and C–O–C/C–O vibrations within 1150–994 cm⁻¹ wavelength, indicating esterification and grafting between the glycosidic matrix and acrylic chains. Regarding the magnetic properties, the observed Fe–O lattice vibration at approximately 570 cm⁻¹ confirmed the presence of iron spinel in the hydrogel structure. The absence of a clear carbonyl band at approximately 1700 cm⁻¹ indicated that most carboxyl groups are either ionized or esterified, demonstrating successful polymer modification of the material. Likewise, in the FTIR spectrum of the precursor (starch) can be seen the same

absorption bands, with a more attenuated signal, and with the exception of the peak observed at 570 cm^{-1} , attributed to the presence of iron in the hydrogel structure.

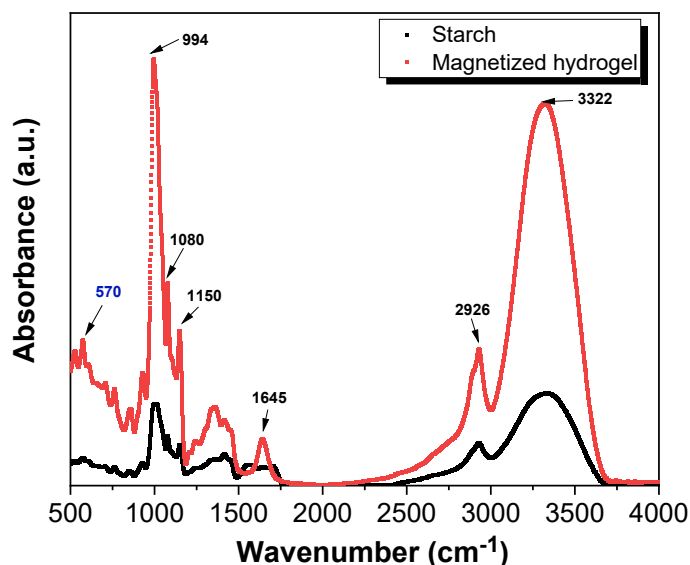


Figure 1. FTIR spectra of the potato peel starch and the synthesized magnetic hydrogel.

SEM micrographs of the magnetic hydrogel are shown in Figure 2. It can be observed the carbon-rich polymer matrix coated with iron oxide nanoparticles (red in Fig. 2), which were identified as magnetite by XRD (see Figure 4). As can be seen in Figure 3a, these particles assemble into irregularly shaped submicron aggregates distributed relatively evenly across the surface. Notably, there are no large clumps or extensive free areas, indicating an effective *in situ* coprecipitation and robust anchoring within the hydrogel network. Moreover, the size of the synthesized magnetite particles ranged from 10 to 22 nm (Fig. 3b).

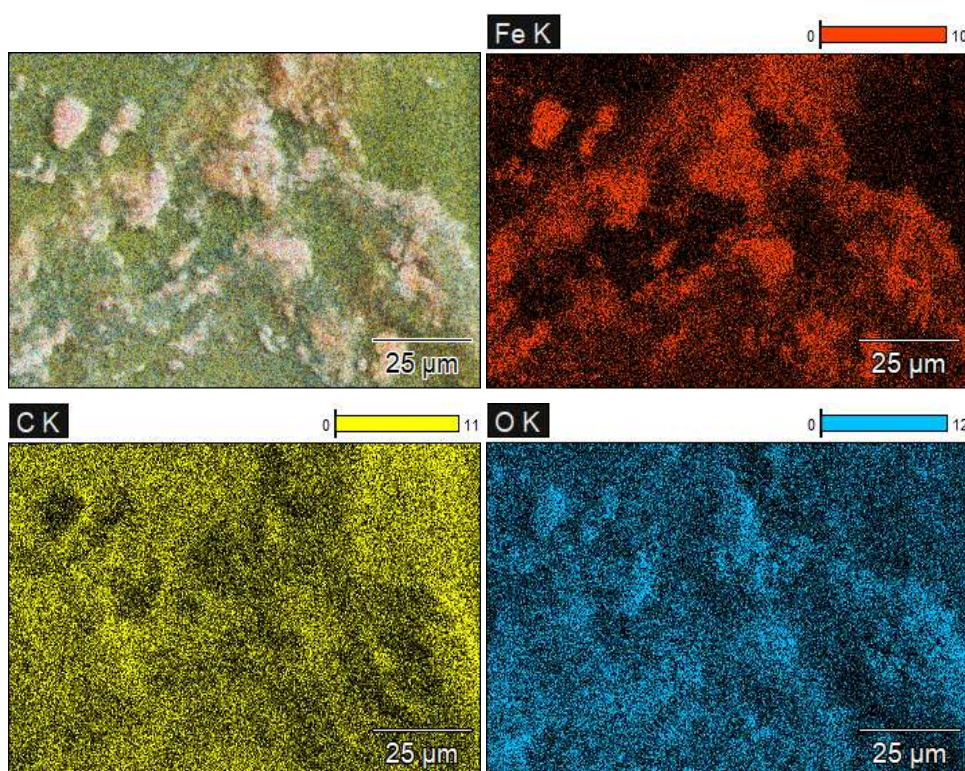


Figure 2. SEM-EDS elemental mapping of the magnetic hydrogel, showing the spatial distribution of iron oxide nanoparticles homogeneously dispersed across the carbon-rich polymer matrix.

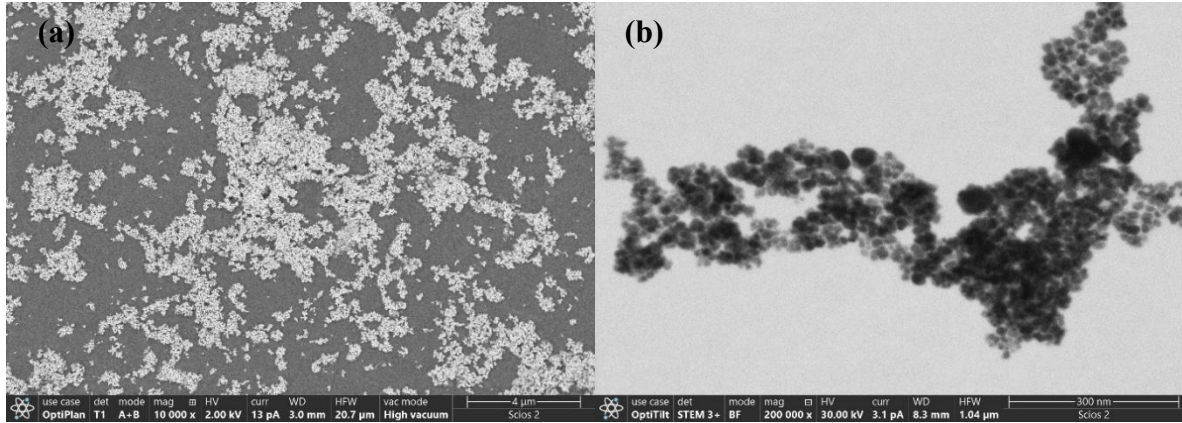


Figure 3. (a) SEM image of the magnetic hydrogel surface showing the rough morphology and distribution of Fe₃O₄ aggregates on the polymer network; and (b) STEM micrograph of the isolated magnetite nanoparticles (used for particle size determination).

The XRD patterns of the unmodified starch, the synthesized magnetite, and the magnetic hydrogel can be seen in Figure 4. For the case of the precursor, the XRD profile showed three pronounced peaks at 17, 19, and 22 (2θ). The XRD pattern of the synthesized magnetite showed characteristic diffraction peaks at $2\theta = 30.1, 35.4, 43.1, 53.4, 57.1,$ and 62.7° , indexed to the (220), (311), (400), (422), (511), and (440) planes of the inverse cubic spinel structure, confirming the formation of crystalline Fe₃O₄ nanoparticles. While, the XRD pattern of the magnetic hydrogel showed only some of those peaks attenuated, being 35.4° the most visible. Upon incorporation into the hydrogel, the magnetite diffraction peaks were attenuated, reflecting the dilution of the crystalline phase within the amorphous polymer matrix.

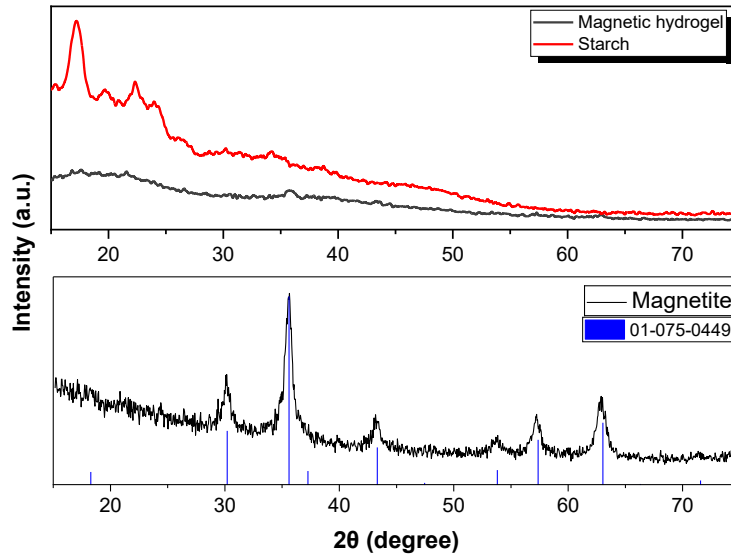


Figure 4. XRD patterns of the used precursor (starch), magnetite, and the magnetic hydrogel.

The magnetization hysteresis curves of the magnetite and the synthesized magnetic hydrogel are shown in Figures 5a-b. In both cases, the curves showed a magnetically soft behaviour; this is, very low coercivity values, $H_c = 15\text{-}16\text{ Oe}$, and small remanence, which is consistent with reduced-size magnetite particles and/or with a significant contribution from surface disorder. In fact, the magnetite presented a M_s value of $55.96 \pm 0.23\text{ emu/g}$, clearly below of the typical value reported for bulk magnetite ($\sim 92\text{ emu/g}$). Usually, this decrease is attributed to size effects and surface spin disorder/canting which reduce saturation magnetization by decreasing particle size (Arun et al. 2013). In the case of magnetite-hydrogel material, the decrease up to $M_s = 0.94 \pm 0.22\text{ emu/g}$ suggested that the magnetic filler is strongly diluted by the polymer matrix — potentially by residual moisture—, rather than a drastic change in the magnetic character of the oxide. In fact, a simple estimation by mass normalization indicated an effective fraction of approximately $0.94/55.93 \sim 1.7\%$ w/w of active magnetite in the measured sample. This value is comparable to other low-response magnetized hydrogels found in the literature. For example, a M_s value of 1.68 emu/g was determined for a $\text{Fe}_3\text{O}_4/\text{poly}(\text{HEMA-co-IA})$ hydrogel, vs. 34.97 emu/g was determined for the reference, Fe_3O_4 (Arun et al. 2013).

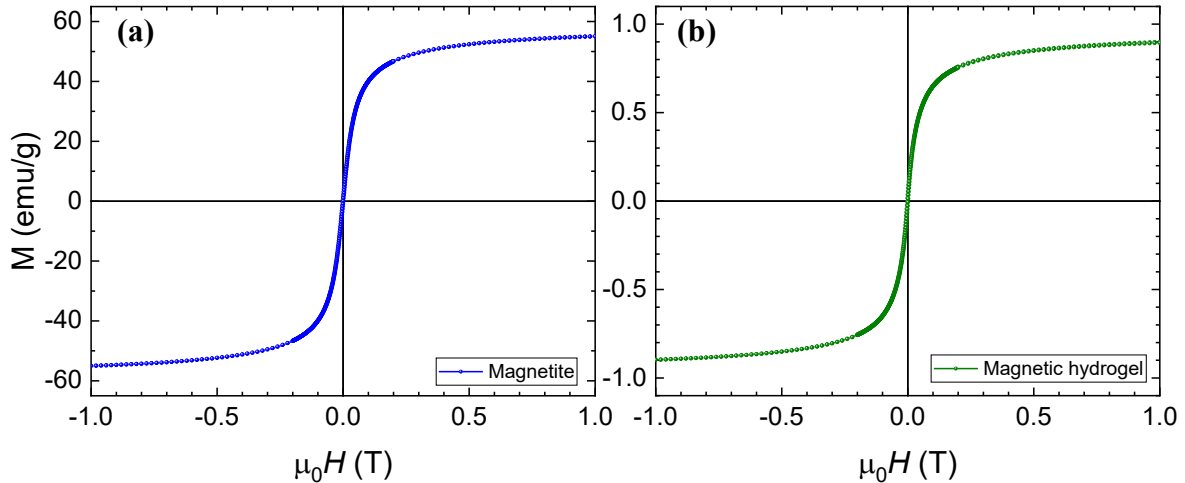


Figure 5. Magnetization hysteresis loop of (a) magnetite; and (b) the synthesized magnetic hydrogel, measured at room temperature. M_s values = 55.96 emu/g (magnetite); 0.94 emu/g (magnetic hydrogel).

As can be observed in Figure 6, the magnetic starch-poly(acrylic acid) hydrogel exhibited highly pH-dependent superabsorbent characteristics. At pH 3, with a highly protonated network, the swelling capacity is approximately 9 g/g because the ionization of $-\text{COOH}$ groups are suppressed, causing the network to collapse due to internal hydrogen bonding. Furthermore, upon the disappearance of the charge, the strong electrostatic attraction vanishes, leaving only a weak interaction with the MB cations through $n-\pi$ interactions, in which the non-bonding electron pairs of the adsorbent act as electron density donors and the LUMO orbitals of the cation function act as acceptors (Figure 7).

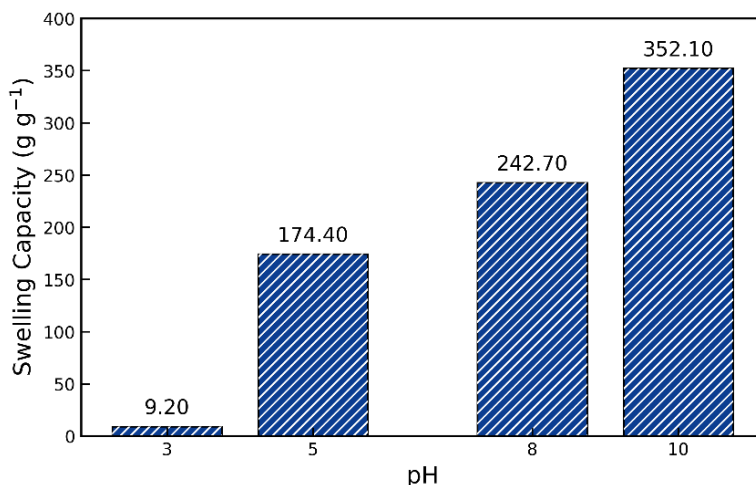


Figure 6. Swelling capacity of the magnetized hydrogel as a function of pH.

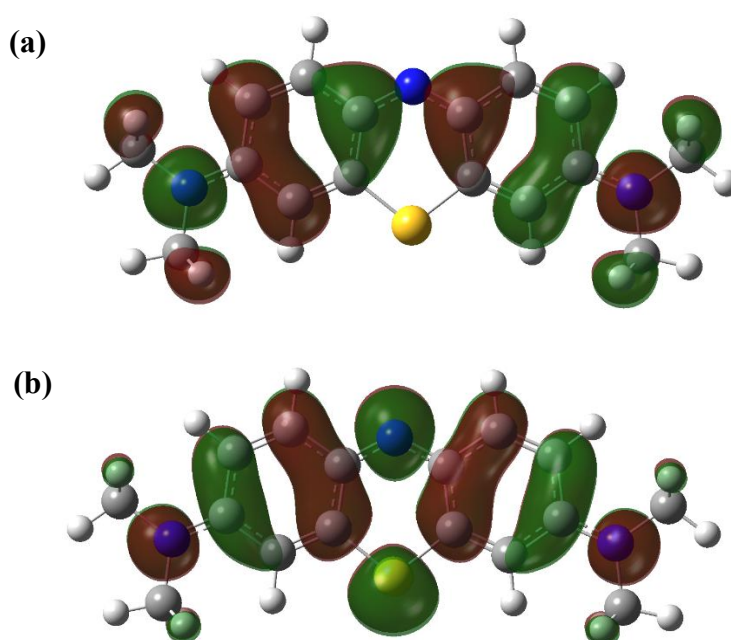


Figure 7. Isosurface plot of (a) HOMO; and (b) LUMO orbitals.

When the pH surpassed 5, deprotonation of the carboxyl groups led to electrostatic repulsions and increased internal osmolarity, resulting in higher swelling capacity (174.4 g/g). Despite not having reached the point of zero charge (pH_{PZC}) yet, the presence of carboxylate ions generated a strong electrostatic attraction towards the MB cations, thereby enhancing dye adsorption. At pH 10, the swelling capacity value increased to 352 g/g, at which ionization of the material is nearly complete. This pattern suggested that the poly(acrylate) phase primarily governs absorption via its anionic charge, whereas the starch component provides mechanical strength to the material. As a reference, Chen et al. (2021) reported a maximum swelling capacity value of 253.42 g/g for a commercial starch-based hydrogel. Thus, in this case, native AR potato starch-based hydrogel exhibited a higher swelling capacity.

Moreover, the obtained pH_{PZC} value of 7.92 (see Figure 8) indicated that the hydrogel surface tends to be negatively charged above this value, favouring the capture of cationic dyes via electrostatic attraction forces. Otherwise, below this pH, the surface becomes protonated and

more positively charged, thereby favouring the retention of anionic species. As it has been reported in the literature, the pH_{PZC} values of magnetic adsorbents/hydrogels usually fall in the neutral-slightly basic range, depending on their surface chemistry and the contribution of magnetite (Ccoyo Ore et al. 2025).

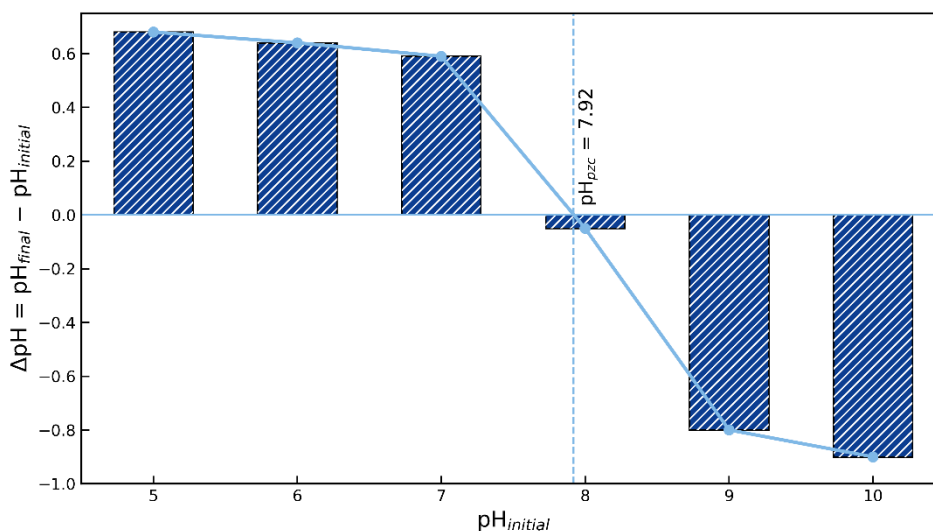


Figure 8. Point of zero charge (pH_{PZC}) of the magnetic hydrogel (determined by the pH drift method).

Regarding the textural properties of the magnetic hydrogel, it exhibited a total pore area of 16.906 m^2/g , a pore volume of 26.039 mL/g , and an average pore diameter of 6.161 μm (Chen et al. 2021).

3.2 Effect of initial pH and MB concentration on the removal efficiency

For initial MB concentration values ranging from 10 to 40 mg/L , the magnetized hydrogel consistently removed more than 80% of MB across pH 8-10. Likewise, at the highest tested pH ($pH = 10$), it was observed a marked increasing of the removal efficiency, reaching up a maximum of 96%, for 10 and 20 mg/L initial concentrations (see Figure 9). This marginal pH sensitivity indicated that, above pH 8, most carboxyl groups of the adsorbent remained deprotonated, thereby providing negatively charged sites that attract the cationic dye via electrostatic interactions.

Chemical interactions are less likely at such pH soft fluctuations. These results are consistent with others found in the literature; for example, hydrogels based on chitosan grafted with gelatin/SWCNTs and another based on starch, both of them showed the best performance at pH 10 (Chen et al. 2021, Farasati Far et al. 2024). So, although increasing the initial concentration slightly decreased the adsorption efficiency, likely due to the progressive occupation of the active sites, the overall MB removal performance consistently exceeded 80%.

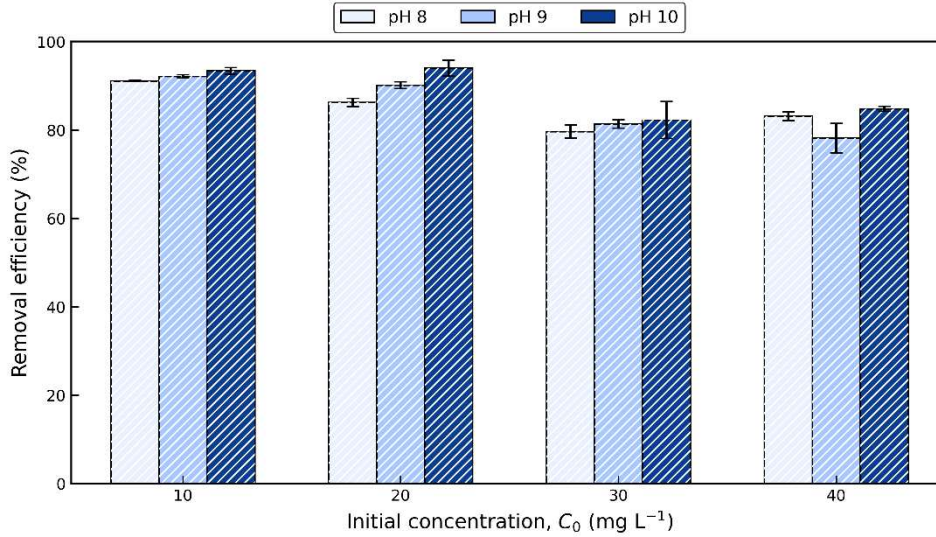


Figure 9. Effect of initial MB concentration and initial pH on the MB removal efficiency onto the magnetic hydrogel.

3.3 Adsorption kinetics

Kinetic analysis demonstrated that the adsorption system was best described by the pseudo-first order (PFO) kinetic model (Equation 5), indicating that the deceleration of the process followed an exponential trend as available sites of the adsorbent became saturated (see Table 3). This observation matches the natural limits of mass transfer and the unevenness found in hydrogels (Seida and Tokuyama 2022). A best fitting to the PFO model indicated that, within the experimental parameters, the predominant mechanism involves mass transfer—external film and/or diffusion—encompassing a general interaction of physisorption or electrostatic attraction type, rather than kinetics governed by a specific surface reaction.

Under the tested experimental conditions, the equilibrium was reached at 3 h, yielding an adsorption capacity (q_e) of 48 mg/g. Moreover, as can be seen in Figure 10, the experimental equilibrium MB adsorption capacity predicted by the PFO model was of $q_{e,calc} = 47.53$ mg/g ($R^2 = 0.9619$), thus supporting the goodness of the fitting. The following equations (5-7) describe the kinetic models used in this work, e.g., pseudo-first order (PFO), pseudo-second order (PSO), and the intraparticle diffusion (Weber-Morris) models.

$$q_t = q_e \cdot (1 - e^{-k_1 \cdot t}) \quad (5)$$

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \quad (6)$$

$$q_t = k_i \cdot \sqrt{t} + C \quad (7)$$

where q_t and q_e are the MB adsorption capacity values at any time and equilibrium time, respectively (mg/g), k_1 is the kinetic constant in the PFO model (1/h), k_2 is the pseudo-second-order kinetic constant (g/mg.h), k_i (mg/g $\times$ h^{0.5}), and C (mg/g) are the rate constant and a constant associated with the thickness of the boundary layer, respectively, in the intraparticle diffusion model.

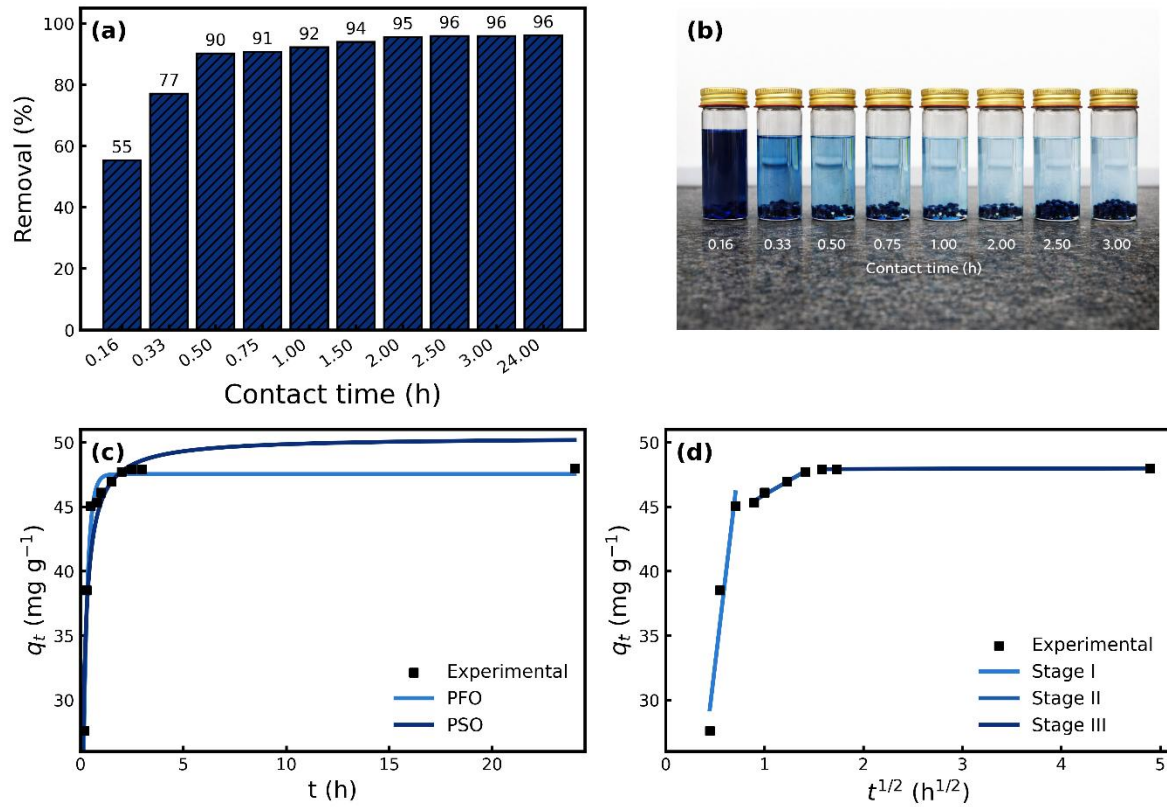


Figure 10. (a) Effect of contact time on the MB removal efficiency; (b) photograph of visual color changes at different contact times; (c) experimental and predicted kinetic curves for MB adsorption, and (d) linear relationship for the intraparticle diffusion model.

Also, as can be seen in Figure 10(d), and according to the intraparticle diffusion model, the adsorption behaviour of the magnetic hydrogel for MB adsorption can be divided into three distinct linear phases, each with a different slope, and none passing through the origin. This indicated that a multistep control mechanism governs the kinetics of the MB adsorption process (Doğan et al. 2009). The first phase involves a rapid transfer of MB molecules across the hydrogel surface via boundary-layer diffusion. The second phase involves intraparticle diffusion, where MB molecules keep moving into the inner pores of the hydrogel. In the final phase, the adsorption capacity remains constant as the active sites become occupied by the MB molecules, reaching the equilibrium.

Table 3. Kinetic parameters for MB adsorption onto the magnetic hydrogel.

Model	Parameter	Value	Units	R ²
Experimental value	q _{e,exp}	48.0	mg/g	—
Pseudo-first-order (PFO)	q _e	47.53	mg/g	0.9619
	k ₁	4.929	h ⁻¹	
Pseudo-second-order (PSO)	q _e	50.41	mg/g	0.8731
	k ₂	0.177	g/mg.h	
Intraparticle diffusion (Weber–Morris), Stage I (0.2–0.5 h)	k _{i,1}	64.77	mg/g.h ^{0.5}	0.9270
	C ₁	0.32	mg/g	
Intraparticle diffusion (Weber–Morris), Stage II (0.8–2 h)	k _{i,2}	4.450	mg/g.h ^{0.5}	0.9833
	C ₂	41.48	mg/g	
Intraparticle diffusion (Weber–Morris), Stage III (2.5–24 h)	k _{i,3}	0.017	mg/g.h ^{0.5}	0.9866
	C ₃	47.90	mg/g	

3.4 Adsorption isotherm, thermodynamic, and reusability studies

In Figure 11(a) can be seen the effect of MB initial concentration on the dye removal; likewise, the experimental and theoretical MB adsorption isotherms onto the magnetic hydrogel are shown in Figure 11(c). Experiments conducted at an optimal pH of 10 revealed a maximum MB removal efficiency of 96% and an equilibrium adsorption capacity value of 1148.3 mg/g, much higher value than most of those obtained in similar works (Table 1).

Adsorption isotherm models help explain how adsorbates interact with the adsorbent surface. In this work, the obtained experimental equilibrium data were fitted to three widely used equilibrium adsorption models: Langmuir, Freundlich, and Temkin (Equations (8-10)).

$$q_e = \frac{q_{\max} \cdot k_L \cdot C_e}{(1 + k_L \cdot C_e)} \quad (8)$$

$$q_e = k_F \cdot C_e^{1/n} \quad (9)$$

$$q_e = \frac{R \cdot T}{b_T} \cdot \ln K_T + \frac{R \cdot T}{b_T} \cdot \ln C_e \quad (10)$$

where q_e is the equilibrium adsorption capacity (mg/g), q_{max} is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (L/mg), for Langmuir equation; K_F represents the Freundlich constant (mg/g.(L/mg)^{1/n}), and n is a parameter in the Freundlich equation. Finally, K_T is the Temkin constant (L/g), T is the temperature (K), R is the universal gas constant (8.314 J/mol.K), and b_T is the heat of adsorption (J/mol).

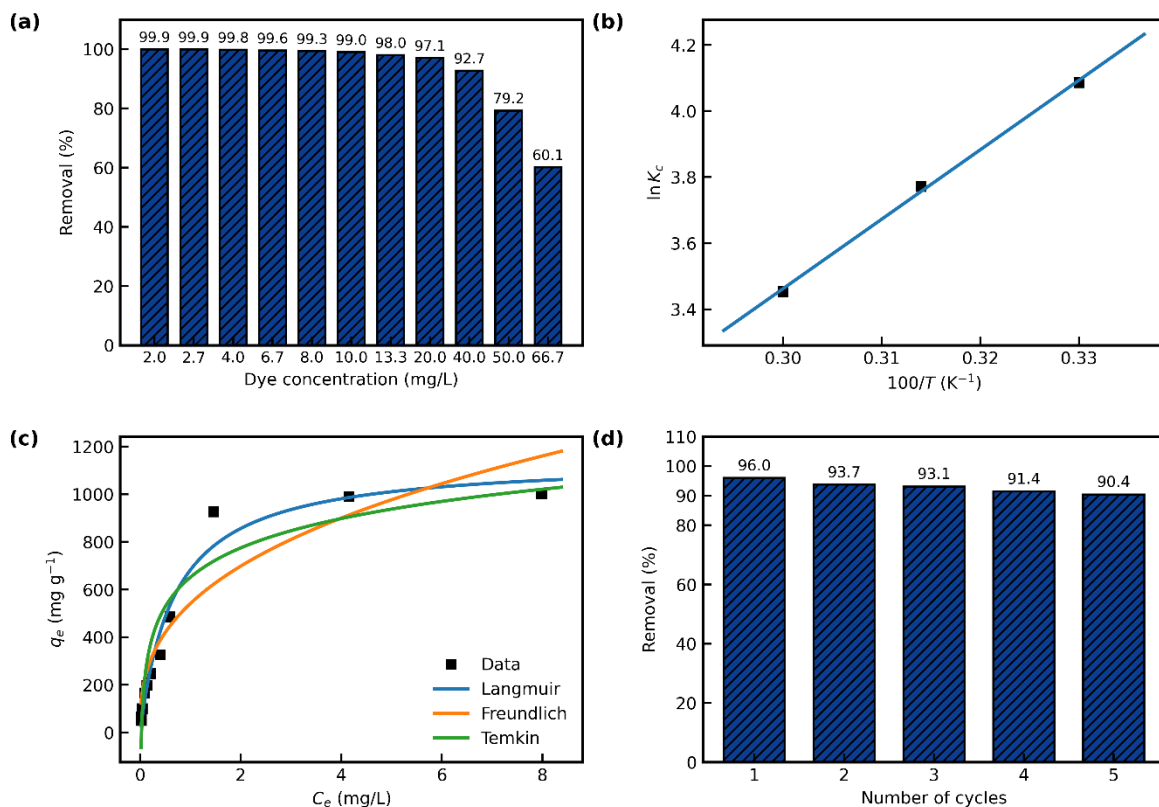


Figure 11. (a) Effect of the MB initial concentration on the removal efficiency; (b) van't-Hoff linear relationship for determining thermodynamic parameters, (c) experimental and predicted adsorption isotherms for MB removal onto the magnetic hydrogel; and (d) reusability of the magnetic hydrogel within five consecutive adsorption cycles.

The adsorption isotherm parameters for the adsorption of MB onto the synthesized magnetic hydrogel are collected in Table 4. As can be seen, the experimental adsorption equilibrium data best-fitted to the Langmuir model. This model suggested that the adsorbate molecules adsorb homogeneously, since the adsorption occurs as a monolayer onto the adsorbent surface, assuming that all surface sites are equivalent.

Table 4. Adsorption isotherm parameters for MB adsorption onto the magnetic hydrogel.

Model	Parameter	Value	Units	R ²
Experimental value	$q_{e,exp}$	1000	mg/g	—
Langmuir	q_{max}	1148.3	mg/g	0.9722
	k_L	1.464	L/mg	
Freundlich	k_F	541.4	mg/g.(L/mg) ^{1/n}	0.8937
	n	2.727	-	
Temkin	b_T	14.2	J/mol	0.9102
	K_T	39.12	L/mg	

Compared to other magnetic hydrogels recently reported in the literature, the synthesized in this work showed a notably superior adsorption performance. For instance, for poly(acrylic acid)-based magnetic hydrogel nanocomposites a q_{max} value of 507.7 mg/g was achieved for MB removal (Pooresmaeil et al. 2018), which is half of the adsorption capacity found in this study. Other tested polymer matrices, such as PAM/SA/HA/Fe₃O₄@Lignite beads (Lizhuang et al. 2026), alginate/fruit-waste/Fe₃O₄ hydrogel biobeads (Parlayıcı and Baran 2025), and

Fe₃O₄/Poly(HEMA-co-IA) hydrogels (Ludeña et al. 2024), have exhibited adsorption capacity values significantly lower than 200 mg/g for the same pollutant. This substantial difference indicated that the polymer network of the synthesized magnetic hydrogel possessed a high density of active sites and interconnected porosity, thereby greatly enhancing the affinity towards MB molecules.

On the other hand, the thermodynamic analysis of the adsorption process was conducted at 30, 40, and 60°C. Thermodynamic adsorption parameters, c.a. Gibbs energy change (ΔG° , kJ/mol), enthalpy change (ΔH° , kJ/mol), and entropy change (ΔS° , J/mol·K), were determined using Equations (11), (12), and (13), respectively.

$$\Delta G^\circ = -R \cdot T \cdot \ln k_c \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (12)$$

$$\ln k_c = \ln \frac{q_e}{C_e} = -\frac{\Delta H^\circ}{R \cdot T} + \frac{\Delta S^\circ}{R} \quad (13)$$

In the given equations, enthalpy (ΔH°), entropy (ΔS°), Gibbs free energy (ΔG°), k_c is the equilibrium constant, R denotes the universal gas constant (8.314 J/mol K), and T is the absolute temperature (K).

According to the results shown in Figure 11(b), the adsorption process can be considered as exothermic; this is, the MB adsorption capacity decreased with increasing temperature. Therefore, this statement was confirmed by the calculated negative value of ΔH° (-17.66 kJ/mol). Furthermore, it can be established that the adsorption of MB molecules onto the surface of the adsorbent was driven by ion-exchange-dominated physisorption mechanism – COO⁻/MB⁺ – as indicated by a ΔH° value lower than 40 kJ/mol (Inglezakis and Zorpas 2012). The negative value of ΔS° (-24.26 J/mol K) indicated that random interactions decreased during the adsorption process. Finally, the obtained negative values of ΔG° (-10.29 kJ/mol < ΔG° < -9.56 kJ/mol) confirmed the spontaneous nature of the adsorption process.

This behaviour resembles that of magnetic hydrogels, which also exhibit spontaneity and exothermicity to varying extents. For example, it was found in the literature that the CMS/GO magnetic hydrogel showed $\Delta H^\circ = -3.54$ kJ·mol⁻¹, positive ΔS° , and negative ΔG° values (Jiang et al. 2021). Conversely, some magnetic hydrogels used for MB removal exhibited endothermic, entropy-driven processes, typically linked to mechanisms in which increasing temperature promoted swelling, penetration, or reorganization of the polymer network and the hydration layer (Wu et al. 2024). In this case, the combination of negative ΔH° and ΔS° values suggested a dominant process driven by bonding interactions, such as electrostatics, hydrogen bonds, or microdomain partitioning, that orders the system. This process becomes less favourable as the temperature rises, which is plausible given the heterogeneity and internal mass transfer occurring within the hydrogel network.

On the other hand, within the successfully accomplished regeneration tests, the MB adsorption efficiency decreased slightly, from 96 to 90.4%, over five consecutive adsorption-desorption cycles (see Figure 11(d)). This behaviour is indicative that MB retention was mainly due to reversible electrostatic interactions between the hydrogel's carboxylate groups and the cationic dye. Acid washing with HCl solution allowed to re-protonate the surface, removing most of the dye without damaging the polymer network. The slight decline in

removal efficiency is likely due to some molecules becoming trapped within the hydrogel inner structure, blocking anionic sites from the eluent, and minor structural fatigue from repeated swelling and shrinking caused by acid-base treatments. With MB removal efficiency values remaining above 90%, the hydrogel was demonstrated to be reusable multiple times without chemical degradation and to still provide effective magnetic separation.

3.5 Real water matrix studies: Proof of concept

MB adsorption studies using two real water matrices, e.g., a surface water and a WWTP effluent, were accomplished. In these cases, a decrease in the removal efficiency from 96% for ultrapure water, to 38 and 30% for surface water and the WWTP effluent, respectively, was observed (see Figures 12a-b). This behaviour underscored the fragility of hydrophilic polymer networks under the electrochemical forces that are characteristic of real water matrices.

As shown in Table 2, high TDS concentrations and conductivity levels (approaching 600 mg/L TDS and 484.6 $\mu\text{S}/\text{cm}$ in the case of the WWTP effluent) synergistically compressed the Debye double layer and induced ionic competition for carboxylic acid-active sites. The positive charge in the MB cation is extensively delocalized across its conjugated π -system. This delocalization is clearly illustrated by the electrostatic potential (ESP) surface (see Figure 13), which shows a predominantly positive potential distributed over the entire molecular framework. Also, NBO atomic charge analysis (see Fig. 14) revealed that the partial positive charges are distributed over multiple atoms, with no individual atomic charge exceeding 0.5e. This confirmed a highly delocalized charge distribution rather than a concentrated point charge, in sharp contrast to the highly localized point charges of small inorganic cations typically found in real water samples. Consequently, these inorganic cations interact more strongly and specifically with the negatively charged active sites of the adsorbent, resulting in more effective competition and a significant reduction in the MB removal efficiency in real water matrices.

Furthermore, for WWTP effluent, moderate values of TOC and COD contributed to blockages that impede the interstitial penetration of MB molecules in the adsorbent structure (Qiu et al. 2019). Kinetic studies revealed that the adsorption process tended to follow the pseudo-first-order model but was also closer to the pseudo-second-order model, showing a significant decrease in the MB adsorption rate in comparison to the results obtained with ultrapure water (see Table 5). This is due to the fact that, in these competitive environments, contaminant retention requires overcoming higher energy barriers to displace hydration water molecules and competing ions present in the environmentally-relevant wastewater matrices (Shah et al. 2022).

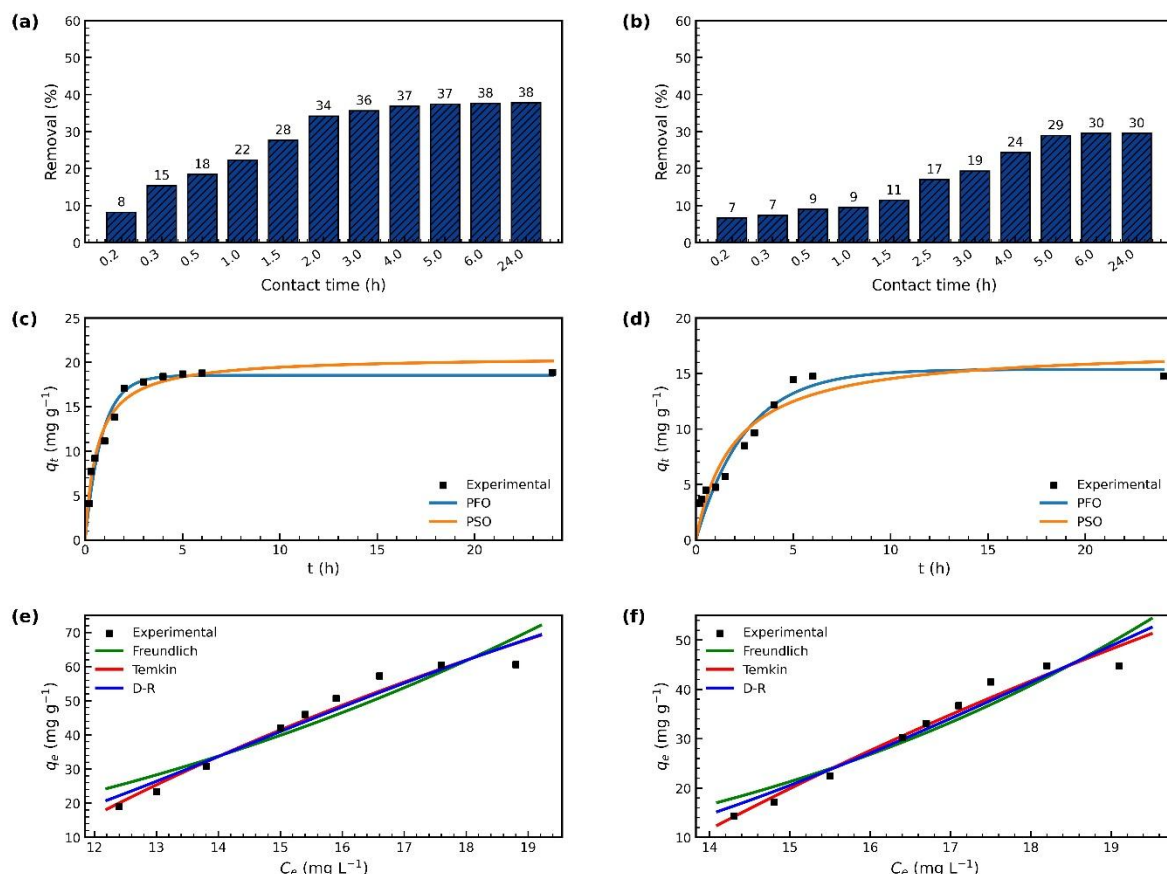


Figure 12. MB removal by the magnetic hydrogel vs. contact time in two wastewater matrices: (a) surface water, and (b) WWTP effluent; experimental and predicted kinetic adsorption curves in: (c) surface water, and (d) WWTP effluent; nonlinear fitting to Freundlich, Temkin, and D–R equilibrium adsorption models in: (e) surface water, and (f) WWTP effluent.

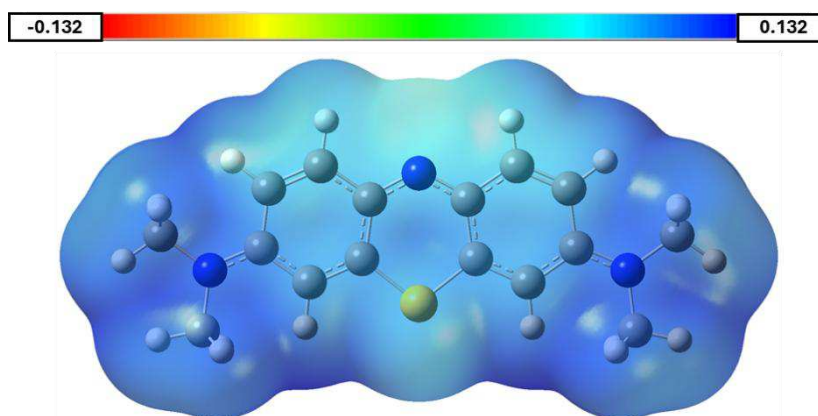


Figure 13. Molecular electrostatic potential (ESP) surface of the Methylene Blue cation (red = negative, blue = positive).

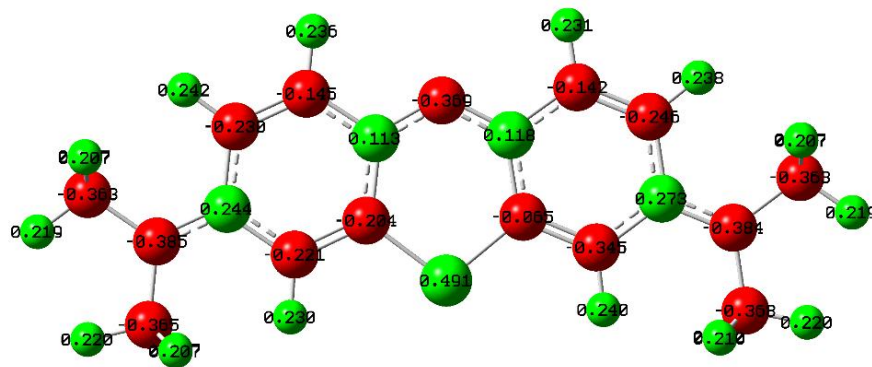


Figure 14. NBO atomic charges of the Methylene Blue cation. Values are in units of e . Colours indicate the sign of the partial charge (red = negative, green = positive).

Table 5. Kinetic adsorption parameters for MB adsorption onto the magnetic hydrogel in the wastewater matrices.

Waste water matrices.				
Model	Parameter	Value	Units	R ²
Surface water				
Experimental value	q _{e,exp}	~19.0	mg/g	—
Pseudo-first-order (PFO)	q _e	18.54	mg/g	0.9600
	k ₁	1.161	h ⁻¹	
Pseudo-second-order (PSO)	q _e	20.68	mg/g	0.9676
	k ₂	0.077	g/mg.h	
WWPT effluent				
Experimental value	q _{e,exp}	~15.0	mg/g	—
Pseudo-first-order (PFO)	q _e	15.37	mg/g	0.9174
	k ₁	0.393	h ⁻¹	
Pseudo-second-order (PSO)	q _e	17.39	mg/g	0.9016
	k ₂	0.029	g/mg.h	

On the other hand, for the description of the experimental equilibrium adsorption data obtained for the real aqueous matrices, the Dubinin-Radushkevich (D-R) model (Equations (14) to (16)) has been tested. The D-R equation is an empirical isotherm model originally designed to describe adsorption on microporous solids, which assumes a Gaussian energy distribution at the adsorption sites. Unlike the Langmuir model, it does not assume a homogeneous surface or a constant adsorption potential, making it ideal for heterogeneous systems.

$$q_e = q_s \cdot \exp(-K_{D-R} \cdot \varepsilon^2) \quad (14)$$

$$\varepsilon = R \cdot T \cdot \ln \left(1 + \frac{1}{C_e} \right) \quad (15)$$

$$E = \frac{1}{\sqrt{2 \cdot K_{D-R}}} \quad (16)$$

where q_s is a constant (mg/g) related to the adsorption capacity, K_{D-R} is a constant associated to the mean free energy of adsorption (mol^2/kJ^2), R is the universal gas constant (kJ/mol K),

and T is the absolute temperature (K). Also, in Equation 15 ϵ is the Polanyi potential (kJ/mol), and E (Eq. 16) is the adsorption energy (kJ/mol).

The experimental equilibrium data obtained in the experiments with the real matrices were fitted to Freundlich, Temkin, and D-R models (Figures 12(e)-(f)). It was observed that the Temkin and D-R models best-fitted the experimental data (see Table 6), indicating that the magnetic hydrogel surface becomes progressively less homogeneous and increasingly saturated with interfering substances (due to the competition effect), requiring additional energy to overcome the electrostatic repulsions (Temkin model), and to trap MB molecules within the smallest micropores (Dubinin-Radushkevich equation).

Enhancements in this regard probably would require magnetic hydrogels with more flexible networks that respond more effectively to saline osmotic gradients (Jery et al. 2024). Additionally, because the calculated E value was lower than 8 kJ/mol in both cases (Table 6), it confirmed that the MB adsorption process is of physical nature (Zhou et al. 2021). Also, the low b_T values determined in Temkin equation indicated a weak interaction between the magnetic hydrogel surface and the MB molecules. Additionally, the positive values of this parameter are indicative that the adsorption process is exothermic, with bond energy decreasing linearly as adsorbent surface coverage increases.

In the domain of hydrogel research, including magnetic variants incorporating Fe_3O_4 or composites used for the removal of MB, comparative analyses are often frequently contrasted with water matrices containing interferents such as salts or NOM. For instance, MB adsorption on recyclable gels varies with coexisting species and is influenced by the physical state and microstructure of the gel, which means that real matrix behaviour cannot be linearly extrapolated from ultrapure water data (Qiu et al. 2019). In batch processes, reduction in the removal efficiency caused by matrix effects such as ionic competition, NOM/colloids, and increased transfer resistances is common, as demonstrated by the removal obtained with the cellulose hydrogel in a textile effluent (64.76%), which is substantially lower than the values observed in synthetic solution under optimized conditions (Majamo et al. 2024). Some systems, such as gels or hydrogels used in monolithic columns can achieve very high removal efficiencies in real-world samples when operational parameters were optimized, resulting in removal rates approaching 99.9% but adsorption capacities around 25 mg/g, lower than in this work, even in real samples (Taweekarn et al. 2023). This suggested that, beyond adsorbent chemistry, factors including architecture and operational mode -batch versus continuous, hydrodynamics, and residence time- can mitigate or amplify matrix effects. Consequently, results from real-world water samples provide a challenging benchmark for batch processes and serve as a foundation for the development of optimization strategies, such as pre-filtration, ionic or pH adjustments, or alternative column or monolith configurations to allow the scalability of the adsorption process.

Table 6. Equilibrium adsorption parameters for MB adsorption onto the magnetic hydrogel.

Model	Parameter	Value	Units	R ²
Surface water				
Experimental value	q _{e,exp}	~60	mg/g	—
Freundlich	k _F	0.060	mg/g.(L/mg) ^{1/n}	0.8922
	n	0.417	-	
	q _s	162.8	mg/g	
D-R	K _{D-R}	52.1	mol ² /J ²	0.9490
	E	0.098	kJ/mol	
Temkin	b _T	22.4	J/mol	0.9618
	K _T	0.096	L/mg	
WWPT effluent				
Experimental value	q _{e,exp}	~45	mg/g	—
Freundlich	k _F	0.001	mg/g.(L/mg) ^{1/n}	0.9107
	n	0.280	-	
	q _s	215.8	mg/g	
D-R	K _{D-R}	88.9	mol ² /J ²	0.9475
	E	0.075	kJ/mol	
Temkin	b _T	21.1	J/mol	0.9685
	K _T	0.079	L/mg	

Also, toxicity evaluation tests were performed using the *Vibrio fischeri* bioassay on three samples after be treated with the magnetic hydrogel: surface water, wastewater treatment plant (WWTP) effluent, and the MB in ultrapure water. The obtained toxicity values were of 0.94, 1.17, and 0.24 TU, respectively. According to the commonly accepted classification (TU < 1: non-toxic; 1 ≤ TU < 10: slightly toxic), the treated surface water and MB in aqueous solution can be classified as non-toxic, whereas the WWTP effluent exhibited very slight toxicity (very close of the lower limit). Overall, these results indicated that the adsorption treatment did not generate significant toxic effects in the treated effluents.

4. Conclusions

A novel starch-based magnetic hydrogel was successfully synthesized from native Peruvian Amarilla Reyna potato starch via radical copolymerization with acrylic acid and N,N'-methylenebisacrylamide as a crosslinker, followed by *in situ* Fe₃O₄ co-precipitation. FTIR studies confirmed successful esterification and grafting of acrylic chains onto the starch backbone; XRD pattern identified the characteristic inverse spinel peaks of Fe₃O₄ within the composite, while SEM-EDS revealed a homogeneous Fe₃O₄ nanoparticle distribution. VSM analysis showed that the material showed weak magnetic properties, which were, however, enough for it to be separated magnetically from the solution after use. The hydrogel exhibited outstanding superabsorbent properties (up to 352.1 g/g at pH 10) and a pH_{PZC} value of 7.92, conferring a negatively charged surface under working conditions that promoted the electrostatic attraction of cationic MB molecules. Adsorption experiments showed a maximum removal efficiency of 96% and an equilibrium adsorption capacity of 1148.3 mg/g, surpassing most analogous adsorbents in the literature. Adsorption kinetics were best-described by the PFO model, indicating a mass-transfer-governed mechanism. Thermodynamic data confirmed a spontaneous, exothermic process driven by electrostatic and H-bonding interactions. DFT/NBO analysis supported dominant electrostatic and n-π interactions. Also, the adsorbent maintained >90% MB removal efficiency over five consecutive adsorption-desorption cycles, demonstrating structural stability and reusability.

Proof-of-concept studies using real water matrices showed a significant reduction in the MB removal efficiency (30–38%) attributable to ionic competition, Debye layer compression, and organic matter blocking of the hydrogel structure. Also, the toxicity results demonstrated that the magnetic hydrogel is an environmentally safe adsorbent, as no significant toxicity was observed after the adsorption treatment. Overall, the developed material represents a promising bio-based, recyclable adsorbent within the circular economy framework for dyes removal from environmentally-relevant water matrices.

Supplementary Information The online version contains supplementary material available at

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Data availability The data supporting the findings of this study are available from the corresponding author upon request.

Declarations

Ethical approval Not applicable.

Consent to participate Not applicable.

Consent for publication All authors have read and approved the manuscript and provided consent to publish.

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