Removal of methylene blue from wastewater using hydrogel nanocomposites: A review

Nompumelelo Malatji¹, Edwin Makhado¹, Kwena D Modibane¹, Thabiso C Maponya¹, Gobeng R Monama¹ and Mpitloane J Hato¹

Abstract
Water pollution by organic dyes continues to pose a serious health and environmental threat to the ecosystem. Although adsorption using biopolymer-based hydrogels has proven to be an ideal technique for the treatment of these dye contaminants from aqueous solutions, these hydrogels suffer from lack of mechanical stability and recovery as compared to synthetic polymers. Herein, we review the low-cost synthesis of hydrogel incorporated with inorganic components mainly focusing on strategies to improve the mechanical stability and separation of the hydrogel in removing methylene blue (MB) dye from aqueous solution. The literature shows that hydrogel nanocomposites are a class of materials that have flourished significant consideration, especially concerning water treatment. In adsorption technology, hydrogel nanocomposites act as absorbents, prominent to enhance their removal efficiency towards contaminants. This review highlights the preparation and use of hydrogel nanocomposites as efficient adsorbents. In-depth discussions on adsorption and diverse synthetic routes of hydrogels have been devoted to applications of these nanocomposites and are compared in this contribution to the removal efficiency of MB dye from wastewater.

Keywords
Adsorption, hydrogel, inorganic components, methylene blue, nanocomposites

Introduction
Water is very important for the survival of living things on earth.¹ Despite the need for this resource, water pollution continues to be a problem in most countries including South Africa, where the mainstream water supplies are underground and surface water.² Water pollution may be defined as any water that is unsafe for drinking by humans and animals.² There are two classes of water contaminants, namely, point sources and non-point sources in which they are defined as a source of pollution at a fixed location (mines, industries, power stations, water treatment station,

¹Nanotechnology Research Lab, Department of Chemistry, School of Physical and Mineral Sciences, University of Limpopo (Turffloop), Polokwane, Sovenga 0727, South Africa

Corresponding authors:
Edwin Makhado, Department of Chemistry, University of Limpopo, N-Block 1014, Private Bagx1106, Sovenga 0727, South Africa. Email: edwin.makhado@ul.ac.za or edwinmakhado@yahoo.com
Mpitloane J Hato, Department of Chemistry, University of Limpopo, N-Block 1012, Private Bagx1106, Sovenga 0727, South Africa. Email: mpitloane.hato@ul.ac.za
Kwena D Modibane, Department of Chemistry, University of Limpopo, N-Block 1010, Private Bagx1106, Sovenga 0727, South Africa. Email: kwena.modibane@ul.ac.za
etc.) and pollution from moving sources (cars, buses and trains), respectively.1,4 In point source, water pollutants may be classified as either inorganic (fertilizers and toxic metals), organic (dyes) or microbial (viruses and bacteria).5 For example, dyes are organic complexes mostly used by textile industries to give colour to fabrics and contribute largely to pollution.6 Other applications may include use in medical, pharmaceutical, paper, rubber, plastics, leather, food and cosmetics industries.7 Dyes contain aromatic rings in their structure and can be made up of either chromophores or auxochromes.7,8 Chromophores are responsible for the production of colour (OH, NH2, NHR, NR2, Cl, COOH and R =alkyl group), and auxochromes (NO2, NO and N = N) improve chromophores, make molecules soluble in water and improve their affinity to bind materials.8 The discharging of dye effluents into either surface and/or groundwater sources leads to contamination which ultimately results in various health and environmental problems.8,9 Consumption of contaminated water by humans can lead to vomiting, mutation, cancer, breathing problems, diarrhoea, eyes burn, nausea shock, cyanosis, jaundice and tissue necrosis.7,8–10 The environmental issues include the death of aquatic organisms, leading to the development of foul smell,11,12 hence the need to eliminate dyes from waste effluents before discharging them into rivers and other water streams.

Conventional methods used to remove dyes from water include adsorption, membrane filtration, ion-exchange, photochemical method, electrochemical destruction and anaerobic bioremediation systems (Table 1).13 The membrane filtration technique separates pollutants using a physical barrier that allows permeability by water only such that contaminants are retained on the membrane surface. Factors influencing the separation behaviour of the membrane filtration may include sieving, size of contaminants, adsorption and electrostatic interactions.14 Its advantage is that it is fast with low space requirement and it removes all dye types.15 However, the disadvantage is its limited lifetime before fouling, high costs of the membrane and sludge production.15 During ion-exchange for treatment of dye effluents, the concentration of the dye is reduced through the use of anionic or cationic resins whose ions exchange with the dye molecules to form solid particles that are easy to remove.16 The advantage of ion-exchange is that it has high removal capacity for dyes, but the major disadvantage is its inability to remove all dye types and high costs.13,16 The photochemical method uses UV light and most use Fenton reagent.17 It offers the advantage of no sludge production and odour elimination.13,16 The main advantage of dye degradation using heterogeneous photocatalysts is the ability to use the sunlight in the production of hydroxyl radicals. Its drawback is the formation of by-products.18 The electrochemical destruction method applies electrical current for the destruction of dye molecules.19,20 This method does not generate sludge and does not require the addition of any chemical reagent.13,19 However, it has the disadvantage of high flow rates, which consequently reduce the removal efficiency of dyes, sludge production and causing a secondary pollution problem.13,21 It is worth mentioning that above-mentioned conventional methods are also applicable for recovery of metals from wastewater. Apart from the aforementioned processes, cementation processes have been well documented in the literature for recovering metals from wastewater. Several researchers have investigated this process in the recovery of copper (Cu), gold (Au), aluminium (Al) and zinc (Zn) from wastewater.22 Anaerobic bioremediation involves degradation of organic contaminants under anaerobic conditions in the presence of anaerobic microorganisms.23 The advantage of this technique is that water-soluble dyes can be decolourised; however, this method results in the production of sulphide and methane.24 Amongst these techniques, the adsorption technique is most favoured owing to its cheap operation costs, easy design and fast removal of dye.25,26 During this process, dye molecules are attached on the surface of a solid material (adsorbent) through either physical interactions (hydrogen bonding, weak Van der Waals forces) or chemical bonding.27

The most used commercial adsorbent is activated carbon (AC) (powder or granular).6,25 The application of AC as an adsorbent is possible due to its high adsorption capacity, high removal efficiency, large surface area and high porosity.29 It effectively removes various types of organic micropollutants as well as their secondary oxidation products and inorganic compounds.29 The main disadvantage of this adsorbent, however, is the high cost and its regeneration problems.6 To reduce the cost of using commercial AC, agricultural by-products including shells

### Table 1. Methods of removing dyes from water.

| Adsorbent method                        | Disadvantages                                           | References |
|-----------------------------------------|---------------------------------------------------------|------------|
| Membrane filtration                     | Membrane fouling and production of concentrated sludge  | 25         |
| Ion-exchange                            | Ineffective for all dye types                           | 6,13       |
| Photochemical method                    | Production of by-products                               | 25         |
| Electrochemical destruction             | Moderately high flow rates that decrease the amount of dye removed | 25         |
| Anaerobic bioremediation systems        | Lead to the production of methane and hydrogen sulphide which are harmful | 13,28     |
| Adsorbent using activated carbon        | The adsorbent is expensive                               | 28         |
and seeds of fruits have been used for production of AC.\textsuperscript{30,31} For example, a study by Geçgel et al. (2012) generated AC from Pea Shells (\textit{Pisum sativum}) and removed 246.91 mg/g of methylene blue (MB) from water.\textsuperscript{32} Further, to improve regeneration of AC, a study by Park et al. (2019) regenerated spent AC obtained from wastewater treatment plant through heat treatment and KOH chemical activation.\textsuperscript{33} The group reported an increased specific surface area from 680 m\textsuperscript{2}/g (spent AC) to 710 m\textsuperscript{2}/g (regenerated AC). Despite these improvements, AC still suffers the problem of separation from water bodies and that it produces secondary pollution.\textsuperscript{33} In an attempt to improve separation of AC from water bodies, many studies have introduced magnetic nanoparticles into the AC material, to enable recovery through exposure to an external magnetic field.\textsuperscript{29,34,35} Considering the evidence that biological materials could be used for dyes removal, many researchers were prompted to investigate the use of biological materials such as polysaccharides, agricultural waste and fruit peels as cheap and effective adsorbents for MB removal.\textsuperscript{5} Compared to AC and other materials, polysaccharides (cellulose, chitin, chitosan, sodium alginate, etc.) offer greater advantages for use as adsorbents for removal of MB.\textsuperscript{7} The advantages include non-toxicity, cheap cost, and eco-friendliness, sustainability due to their abundant availability, high chemical reactivity, biodegradability, polyfunctionality and biocompatibility.\textsuperscript{36–38} However, due to their lack of stability, most researchers have explored their application as hydrogels.\textsuperscript{7,10,39,40} For example, Zhou et al.\textsuperscript{40} prepared cellulose based hydrogels and removed 2197 mg/g of MB.

Hydrogels are a class of three-dimensional (3D) soft polymeric materials, which can imbibe a substantial amount of liquids.\textsuperscript{41} In this direction, their innate ability to absorb and hold a high volume of liquid qualifies them as ideal materials for the adsorption of aquatic pollutants.\textsuperscript{41} Hydrogels attracted a great deal of attention in various fields (gas sensing,\textsuperscript{42} drug delivery\textsuperscript{43} and cosmetics\textsuperscript{44}) owing to their non-toxicity, low cost, permeability and biocompatibility.\textsuperscript{10} However, the applicability of hydrogels has been overshadowed due to their weak mechanical properties and partial adsorption capacity.\textsuperscript{10} The yearning for enhancing inherent shortcomings exhibited by hydrogels has instigated tremendous research interest in the development of hydrogel nanocomposite, which is a robust process to improve the disadvantages without losing the advantage of hydrogels. In the past decades, the use of hydrogel nanocomposites for the removal of MB dyes in aqueous environment has increased considerably. In the past 10 years, a developing trend of publications in hydrogel nanocomposites for removal of MB dyes is shown in Figure 1. The literature survey statistics show an exponential increase in the number of publications per year considering hydrogel nanocomposites for the removal of MB dye.
This review summarizes the recent advances and developments of hydrogel nanocomposites as adsorbents for wastewater treatment. This is realized by doing a detailed review of the reactions and mechanisms of adsorption including an overview of the adsorption of MB dye. Then, we introduce hydrogel nanocomposite as an adsorbent for MB removal with great emphasis on the structure and synthetic routes.

**Adsorption**

**Background**

The attachment or adherence of molecules on the surface of solid material is known as adsorption. The adsorbent material contains active adsorptive sites on its surface to which molecules (gas or liquid) from the bulk solution (adsorbate solution) bind to. Adsorption of molecules may occur either physically or chemically. The mass transfer process may occur in the form of migration, diffusion or convection, in which liquid or gaseous molecules are transferred to a solid phase. Interactions such as Lewis acid-base, van der Waals and Columbic are characteristic of physisorption whereas chemisorption is distinguished through the development of new adsorbate–adsorbent bonds. The adsorptive sites can have the same or different energy, depending on the nature of the material. Owing to its principle, adsorption has gained interest for application in hydrogen storage, sensing, drug delivery, gas capture and water treatment.

The recent interest in applying adsorption for the treatment of dyes from wastewater was attracted by its low operation costs, easy design, efficiency and fast removal of dye. Before applying an adsorbent material on an industrial scale (column adsorption), it is first optimized in batch mode experiments; then if it possesses a high removal efficiency, it can be employed for column adsorption studies. Factors that affect the adsorption process in wastewater treatment include the following:

1. The adsorbent and adsorbate charges,
2. The solution pH,
3. Temperature,
4. Dye concentration,
5. Adsorbent dose and
6. The surface area of the solid material.

When an adsorption process reaches equilibrium, it means the active sites of the adsorbent are saturated with adsorbate molecules and no further adsorption can take place.

**Adsorption parameters**

**Adsorption isotherms.** The isotherms of adsorption are significant for describing the adsorbate–adsorbent interactions. Additionally, they provide information about the mechanisms of adsorption, adsorption capacity and surface properties. This study employs the Langmuir, Freundlich and Temkin isotherm models. Below are their brief descriptions including their linear and non-linear equations.

**Langmuir isotherm model.** Irving Langmuir established the Langmuir isotherm in 1916. The model theory assumes that the active sites on the solid surface have the same energy, leading to homogeneous adsorption of adsorbate molecules (monolayer coverage). Graphically, adsorption equilibrium is observed by a plateau, which is a point where all active sites are fully occupied and no further adsorption can occur. The model is expressed as follows, non-linear (equation (1)) and linear (equation (2)) forms

\[
q_e = \frac{q_m b C_e}{1 + b C_e} \quad (1)
\]

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (2)
\]

where \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the amount adsorbed at equilibrium (mg/g), \(K_L\) (L/mg) is the adsorption equilibrium constants of Langmuir, the Langmuir constants \(q_m\) (mg/g) represent the monolayer adsorption capacity and \(b\) relates to the heat of adsorption. The values of \(q_m\) and \(K_L\) can be determined from the linear plot of \(C_e/q_e\) against \(C_e\). The essential features of the Langmuir isotherm can be employed to predict the affinity between the sorbate and the sorbent using the dimensionless equilibrium constant (\(R_L\)).

The \(R_L\) is a dimensionless constant denoted as the separation factor. \(R_L\) is calculated using the following equation (3)

\[
R_L = \frac{1}{1 + b C_o} \quad (3)
\]

If \(R_L > 1\), adsorption is not favoured. If \(R_L = 1\), adsorption is linear. If \(R_L < 1\), adsorption is favoured, and if \(R_L = 0\), the reaction is irreversible.

**Freundlich isotherm.** The model assumes multilayer coverage of the adsorbent. The model is expressed by the following equations in a non-linear (equation (4)) and linear (equation (5)) form

\[
q_e = K_F C_e^{1/n} \quad (4)
\]

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)
\]

where \(q_e\) (mg/g) and \(C_e\) (mg/L) are the amounts adsorbed and the solution concentration, respectively, at equilibrium. \(K_F\) is the sorption enthalpy and varies with temperature. \(K_F\) and n
are the sorption capacity and sorption intensity.\textsuperscript{67} It determines the non-linear relation between adsorption and the concentration of the solution.\textsuperscript{67}

**Temkin isotherm.** The Temkin isotherm theory ignores the concentration values and assumes that the decrease in heat of adsorption concerning the temperature is linear instead of decreasing logarithmically as suggested in the Freundlich equation. The non-linear (equation (6)) and linear (equation (7)) forms of the Temkin model are expressed as follows below

\[
q_e = \frac{RT}{b_T} \ln (K_T C_e)
\]  
(6)

\[
q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e
\]  
(7)

where \(A_T\) is the equilibrium binding constant corresponding to the maximum binding energy (L/g), \(b_T\) is the Temkin constant related to the heat of adsorption (kJ/mol), \(R\) is the universal gas constant (8.314 J/mol K) and \(T\) is the absolute temperature (K).\textsuperscript{68}

**Kinetic isotherms.** Adsorption is a process that involves the transfer of mass of a solute from the liquid phase to the surface of the adsorbent.\textsuperscript{69} The mechanism of adsorption can be researched using either Lagergren’s pseudo-first-order equation or pseudo-second-order equation. The amount of contaminant adsorbed with time can be analysed provided an appropriate model is used.\textsuperscript{70} To identify which model is appropriate, the correlation coefficient (\(R^2\)) is measured and must be close or equal to 1. The model with a higher \(R^2\) is the most suitable model for the adsorption kinetics of contaminants.

The non-linear (equation (8)) and linear (equation (9)) equations for the pseudo-first-order kinetic model are

\[
q_e = q_e[1 - \exp(K_f t)]
\]  
(8)

\[
\ln(q_e - q_t) = \ln(q_e) - K_f t
\]  
(9)

where \(q_e\) and \(q_t\) refer to the amount of dye adsorbed (mg/g) at equilibrium and at any time, \(t\) (min). \(K_f\) is the equilibrium rate constant of pseudo-first-order sorption (1/min). \(K_f\) will be determined using the slope and intercept of the plot of \(\ln(q_e - q_t)\) versus \(t\).\textsuperscript{71}

The non-linear and linear equations for the pseudo-second-order kinetic model are

\[
q_e = \frac{K_2 q_t^2 t}{1 + K_2 q_t t}
\]  
(10)

\[
\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]  
(11)

where \(K_2\) is the equilibrium rate constant of pseudo-second-order adsorption (g/mmol min). \(K_2\) will be determined using the slope and intercept of the plot of \(t/q_t\) versus \(t\).

**Thermodynamics.** During the adsorption process, thermodynamic parameters such as enthalpy (\(\Delta H^0\)), entropy (\(\Delta S^0\)) and Gibbs free energy (\(\Delta G^0\)) are required to determine spontaneity and heat change.\textsuperscript{72} Thermodynamics parameters may be calculated according to the formulas below

\[
K_D = \frac{q_e}{C_e}
\]  
(12)

\[
\Delta G^0 = -RT \ln K_D
\]  
(13)

\[
\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]  
(14)

where \(K_D\) represents the distribution coefficient of the adsorbate, \(q_e\) and \(C_e\) represent the equilibrium concentration (mg/g) and in the solution (mg/L). \(R\) represents the universal gas constant (8.314 J/mol K), and \(T\) is the temperature (K). \(\Delta H^0\) and \(\Delta S^0\) may be calculated from the slope and intercept of the plot \(\ln K_D\) versus 1/\(T\). Negative \(\Delta G^0\) values at different temperatures are an indication of a spontaneous adsorption process.\textsuperscript{71,73} If \(\Delta G^0\) decreases when the temperature is increased, it means there is a more efficient interface during adsorption. A positive \(\Delta H^0\) value indicates an endothermic adsorption process.\textsuperscript{74}

**Adsorbent materials for MB**

Although the adsorption technique is effective for dye removal, the type of adsorbent used limits its efficiency.\textsuperscript{75} Various materials have been used for MB dye removal. For example, AC is reported to be the most frequently used nano-adsorbent for removing a variety of inorganic and organic contaminants owing to its high surface area, porous structure, thermal stability and amphoteric nature.\textsuperscript{76,77} However, AC has some drawbacks such as intraparticle resistance in industrial application, high production costs and regeneration costs.\textsuperscript{77–79} Recent research studies have attempted to find ways to improve the regeneration of AC and produce it at a lower cost.\textsuperscript{77} On the other hand, alternative adsorbents such as fly ash, graphene, clay, carbon nanotubes and polysaccharides were reported for removal of MB.\textsuperscript{80–87} Among these adsorbents, Mittal et al.\textsuperscript{80} reported that using polysaccharides-based adsorbents is a promising strategy for MB dye removal from aqueous solutions. This is due to their enhanced adsorption capacity amongst other attractive properties.

**Polysaccharides.** Polysaccharides can be defined as highly hydrophilic and non-toxic natural polymers made up of multiple small units of saccharides that are connected through glycosidic bonds.\textsuperscript{83–85} These biopolymers are
found and used in plants or animals for structural support and energy storage. Examples of polysaccharides include carboxymethyl cellulose (CMC), alginate, carrageenan, chitosan, guar gum, starch and locust bean gum. These natural polymers offer the advantages of high absorption capacity, biodegradability and cheap synthesis. However, due to low solubility and other physical drawbacks, synthetic polymers are incorporated into the biopolymeric backbone to improve their properties. Polysaccharides-based materials have recently attracted use for adsorption of dyes and toxic metals because of their non-toxic nature, biodegradability, easy availability and low-cost synthesis. Amongst other polysaccharides, CMC and alginate offer more attractive properties for application as dye adsorbents.

**Carboxymethyl cellulose.** Cellulose is the main component of most plants. Carboxymethyl cellulose is a highly reactive, hydrophilic, water-dissolving derivative of cellulose with many carboxyl groups on its surface. Commercially it can be obtained as sodium CMC with different degrees of saturation (DS), which may range from 0.6–0.95 depending on how it was prepared, and the solvent used. Carboxymethyl cellulose is mostly used in paper, packaging, textile, food, cosmetics and pharmaceuticals. Due to its sensitivity to pH, non-toxic nature, hydrophilicity, low cost and ability to form gels, CMC has been applied on its own or in a composite form as an adsorbent for removing inorganic and organic contaminants.

Carboxymethyl cellulose (Figure 2) is a cellulose derivative with carboxymethyl groups at carbon 2, 3 and 6. 

![Figure 2. Structure of sodium carboxymethyl cellulose](image)

![Figure 3. $^{13}$C NMR of CMC](image)
In a study conducted by Kono, the resonances of CMC were determined using carbon-13 nuclear magnetic resonance (13C NMR) as shown in Figure 3. In the spectrum of CMC, the carbonyl carbon (C1, C4), overlap of C2, C3, C5, the carboxymethyl groups, and C6 were assigned to broad 13C resonances at 178, 104, 83, 75 and 63 ppm. The existence of carboxylic groups (COO−) on the polymer chains of CMC allows for interactions with multivalent metal cations (Al3+ and Fe3+) which results in the formation of stabilized ionotropic hydrogels. Interactions with metal ions through the hydroxyl groups of the CMC may improve the water insolubility and stability of the polymer aggregates.

The reaction of cellulose with monochloroacetic acid (MCA) or its sodium salt in the presence of an organic solvent under basic conditions produces NaCMC. There are various materials from which CMC can be derived; for example, Petri prepared CMC from pineapple peels, and in another study, Begum et al. prepared CMC from sugarcane bagasse. The synthesis of CMC occurs in three steps: (1) alkalization, (2) carboxymethylation and (3) neutralization as outlined in the steps below.

**Step 1.** Cell-OH + NaOH → Cell-OH.NaOH

**Step 2.** Cell-OH.NaOH + ClCH2COONa → Cell-O−CH2COO−Na+ + NaCl + H2O

**Step 3.** NaOH+ Cl−CH2COONa → HO-CH2COONa + NaCl

During the synthesis process, carboxymethyl groups replace hydroxyl groups at positions 2, 3 and 6 of cellulose. In the synthesis of CMC, it is important to consider the degree of substitution, which will govern the porosity, and adsorption capacity of CMC. Degree of Substitution (DS) refers to the number of hydroxyl groups replaced by carboxymethyl groups. Each β-glucopyranose unit of cellulose has three hydroxyl groups; therefore, hypothetically DS value will range between 0 and 3.0. Various factors may affect the DS of CMC such as the solvent, temperature and the NaOH concentration. For example, most researchers report that the use of isopropanol as the solvent yields CMC with very high DS. Huang et al. synthesized CMC from the pulp of six different plants; the conditions that yielded the best CMC were 20% NaOH concentration, the temperature of 60°C and 3–5 g of MCA. The group reported that CMC yield increased with increasing MCA content. The degree of saturation influences the application of CMC. The hydrophilicity of CMC increases with an increase in DS. When DS > 0.4 (higher), CMC becomes soluble in water, has better viscosity, enhanced cationic exchangeability and improved covalent crosslinking through radiation. Whereas when DS < 0.4 (lower), CMC is insoluble, and it swells in solution.

**Alginate.** Alginate is a sentimental term used in the dietic, cosmetic, pharmaceutical and biotechnological industries. The alginate can be found in salts of magnesium (Mg), potassium (K), calcium (Ca) and sodium (Na). E.C.C Stanford who was a pharmacist discovered alginites in 1929. SA is found in brown algae, marine algae and produced by some bacteria, hence abundant in nature. Applications of sodium alginate include drug delivery, thicker, gel-forming agent, binder during the production of tablets, use as a stabilizer and mixing agent. The recent use of polysaccharides as adsorbents for dyes and other pollutants is mostly due to the attractive properties that polysaccharides possess, such as high hydrophilic structures, non-toxic nature, biodegradability and cheap synthesis. Sodium alginate (SA, Figure 4) is made up of poly-β-1, 4-D- mannuronic acid and α-1, 4-L-guluronic acid. The structure consists of carboxylic groups and hydroxyl groups, which can react with metal ions or crosslinking agents to form hydrogels. Alginate can be extracted from its salt forms by ion-exchange methods. Because of the
presence of divalent ions, monovalent, water-soluble salts of alginates can transform into water-insoluble salts. The COO\(^-\) and -OH functional groups on the alginate backbone will allow adsorption of cationic dye pollutants.\(^{115}\) However, sodium alginate just like other polysaccharides suffers from a lack of stability.\(^{111}\) To enhance the stability of SA and its adsorption capacity, the biopolymer may be cross-linked with synthetic polymers into forming a hydrogel.\(^{116,117}\) This will allow their use as adsorbents without them dissolving in the adsorbate solution. The major disadvantage of polysaccharides as adsorbents is that they dissolve in water and have low mechanical stability.\(^{116,117}\) To resolve this problem, polysaccharides are cross-linked to form hydrogels, which do not dissolve in water.

**Hydrogels**

**Background**

Hydrogels are hydrophilic polymer chains that are cross-linked to form gel structures that swell in aqueous solution and trap fluids for a long period without dissolving.\(^{83,84}\) Hydrogels may contain carboxylic, amine, imide, hydroxyl and sulfonyl groups in their 3D structure that are responsible for the hydrophilicity and swelling capacity.\(^{118}\) Depending on the nature of the hydrogel, it can be classified based on various properties. Classification of hydrogels (Figure 5) can be based on whether they are synthetic (involves the use of synthetic monomers), natural (involves using biopolymers) or a combination of synthetic and natural monomers resulting in a hybrid hydrogel.\(^{119}\) The polymeric composite classification can be based on the method used to synthesize the hydrogel.\(^{119}\)

Figure 5. Classification of hydrogels.

- Homopolymeric hydrogels: they are hydrogels consisting of the same type of monomer.
- Copolymeric hydrogels: these hydrogels comprise two or more different kinds of monomers such that the network would have at least one hydrophilic component on the polymer network chain.
- Multipolymer interpenetrating polymeric hydrogel (IPN): the hydrogel network consists of two components (natural and/or a synthetic polymer) that are independently cross-linked.

It was also demonstrated that hydrogels can be categorized based on whether they are\(^{120}\)

- crystalline,
- amorphous or
- semi-crystalline: showing properties of both crystalline and amorphous phases.

The other classification is based on whether the cross-linking of hydrogels occurs via chemical or physical means. Briefly,

- physical crosslinking in hydrogels may be through (1) formation of a hydrogen bond, (2) hydrophobic interactions between chains, in which the dissipation energy of the bond prevents breakage and improves the hydrogel strength, and (3) crystallization where gels are subjected to freeze and thaw process in PVA/PVP solution 10h at 15°C and then placed at room temperature for 2h. Lastly (4) between oppositely charged groups.\(^{84}\)
b. Chemical crosslinking can be achieved by (1) using aldehydes such as acetaldehyde, glutaraldehyde (GA) and formaldehyde and (2) radiation using an electron beam, gamma rays or ultraviolet rays at room temperature in which a free radical is formed, monomers are added to the chain for growth and the gel forms at the critical gelling point. Lastly (3) free-radical polymerization using a cross-linker, for example, MBA. In this method, an initiator such as potassium persulfate (KPS) generates free radicals, the radicals react with other monomers and then MBA is added to the polymer chain to form the hydrogel.

In addition, the hydrogels may be classified based on the charge on their cross-linked polymer network. The charge may be

- ionic (cationic/anionic),
- non-ionic (neutral),
- amphoteric (comprising both basic and acidic groups) and
- zwitterionic (contains anionic and cationic components on each repeating structural unit). The net charge of the gel is zero.

Lastly, hydrogels can also be categorized according to what stimulates their response. These hydrogels are sometimes called smart hydrogels. There are two categories of stimulus, namely, physical stimuli and chemical stimuli as stipulated in Table 2. The swelling or de-swelling of hydrogels caused by changes in the environment can be too much to a point that the hydrogel changes phase (volume collapse).

### Application of hydrogels

Hydrogels have gained much attention for use in various applications owing to their outstanding qualities; these include use in the making of disposable diapers, absorbent pads, in hydrogen storage, sensing, CO₂ capture, biomedical field (drug and cell delivery systems), immobilization of enzymes, wastewater treatment and agriculture for trapping water. The ideal properties of a hydrogel depend on its specific application. For application in water treatment, the hydrogel must have the following properties below:

1. High absorption capacity;
2. low residue monomer and soluble content;
3. cost-effective;
4. reusable;
5. high biodegradability and not produce harmful by-products;
6. must retain neutral pH after swelling in water and
7. easy recoverability.

The swelling capacity of hydrogels is indicative of their absorptive capacity which may be affected by factors such as the intermolecular spaces in the 3D network, the existence of hydrophilic groups on the hydrogel polymer backbone and the pore size of the hydrogel surface. Hence, parameters such as the amount of initiator, cross-linker, polymer, monomer and solvent volume are optimized during the preparation of the hydrogel to obtain optimum conditions for preparing an ideal hydrogel.

### Preparation methods

As stated previously, biopolymers suffer poor mechanical, thermal stability and they dissolve in water. Most researchers have reported that crosslinking, grafting and modification with inorganic constituents such as metal oxides and clay improves solubility and stability problems associated with biopolymers. The type of method used to prepare the hydrogel, therefore, affects its structural make-up or physical properties. Amongst several physical and chemical techniques used for hydrogel synthesis, the most widely used methods are discussed below.

**Grafting**. Grafting is the modification of the polymer backbone using synthetic polymers such as acrylamide, acrylic acid, methacyrlamide and vinyl alcohol as support materials. During grafting, an initiator creates a free radical site, and then a monomer unit is added to the generated free radical site. Grafting can occur via either a chemical or radiation. Chemical grafting involves using chemical reagents such as ammonium persulfate, KPS or other chemical initiators. Radiation grafting involves initiating free radicals using UV visible or microwave radiation.

It was shown in the literature that using a microwave radiation method for synthesizing hydrogels produces sterilized hydrogels. Naturally, polysaccharides suffer from poor chemical and physical stability. Grafting has been reported to solve these issues including enhancing the performance of hydrogels through the introduction of new functionalities from grafted monomers.
study conducted by Tally and Atassi,\textsuperscript{86} it could be observed from the thermogravimetric analysis (TGA) curves of (a) SA and (b) SA-g-P (AA-co-AM)/PVP semi-IPN SAP (Figure 6) that grafting with synthetic polymers enhanced the thermal stability of hydrogels by more than 20% weight loss at above 200°C.

A study of the modification of CMC by grafting with poly (3-sulfopropyl methacrylate), P (SPMA), in the presence of KPS initiator for MB removal was carried out.\textsuperscript{93} The main vibrational peaks at C =O (1718 cm\(^{-1}\)), S =O (1085 cm\(^{-1}\)) and S-O (626 cm\(^{-1}\)) were observed in Figure 7(a) of the Fourier transform infrared (FTIR) of the CMC-g-P (SPMA) hydrogel.\textsuperscript{93} The scanning electron microscopy (SEM) image showed the well-defined pores and 3D interconnections of CMC-g-P (SPMA) hydrogel, for which the hydrogel could allow easy penetration of dye molecules in solution through its pores as observed in Figure 7(b).\textsuperscript{93} The adsorption of MB by the hydrogel was characterized by an absorption peak at 664 nm corresponding to the characteristic absorption band of MB (Figure 7(c)). From the X-ray diffraction (XRD) (Figure 7(d)), the partially crystalline structure of CMC was characterized by sharp peaks at \(2\theta = 9.4\) and 20.1° resulting from the intermolecular and intramolecular hydrogen bonding between carboxylic groups and hydroxyl groups of the biopolymer. Upon grafting on the CMC-g-P (SPMA), it could be observed that the peaks were broader, indicating the hydrogen bonds were destructed, allowing grafting to take place.\textsuperscript{93}

**Crosslinking.** The process of crosslinking can occur through physical or chemical interactions. Physical interactions are irreversible and include electrostatic interactions, hydrogen bonding and the van der Waals forces.\textsuperscript{128} Chemical cross-linking involves forming irreversible covalent bonds in the hydrogel polymer chain usually through the reaction of complementary groups.\textsuperscript{129} Chemically cross-linked hydrogels are mostly used in medical applications. For example, Liu et al.\textsuperscript{130} synthesized chitosan-based hydrogels from PEG for application in drug delivery. In another study by Kumar et al.,\textsuperscript{131} cross-linked hydrogels were produced from GA as a covalent cross-linker (Scheme 1).

The most commonly used chemical cross-linkers include ethylene glycol dimethyl-acrylate, N, N-methylene-bis-acrylamide (MBA), tetra-ethylene glycol dimethyl-acrylate (EGDMA) or tri-propyleneglycol diacrylate (TPGDA).\textsuperscript{132} However, these cross-linkers are usually toxic and result in non-biodegradable hydrogels.\textsuperscript{133} In addition, because of the lack of internal structural homogeneity and an effective mechanism for energy dissipation, chemically cross-linked hydrogels are very brittle.\textsuperscript{134} This prompted many researchers to consider introducing nanocomposites, ionic interactions, hydrogen bonding and hybrid hydrogel systems to improve the hydrogel properties.\textsuperscript{135–137} A hybrid system consists of physical interactions that will aid in energy dissipation and chemical interaction, which will mainly improve structural properties.\textsuperscript{138} Figure 8 illustrates the preparation of hydrogel beads through ionic interactions by Rahmani et al.\textsuperscript{139} Briefly, a mixture containing gum tragacanth (GT), graphene oxide (GO) and calcium carbonate (CaCO\(_3\)) was added dropwise into a concentrated solution of Cu\(^{2+}\) which interacted with \(-\)OH
and COO\(^-\) groups on the GT and GO to form hydrogel beads. Ionic crosslinking offers the advantage of less toxicity.\(^{133}\)

In a study by Eftekhari-sis et al.,\(^{140}\) hybrid hydrogels constructed from poly (N-isopropyl acrylamide-co-itaconic acid) and non-toxic octa-vinyl polyhedral oligomeric silsesquioxane (OV-POSS) cross-linker were prepared. Their obtained SEM (Figure 9), XRD and TGA (Figure 10) results are discussed. The rough non-homogeneous surface was observed on the SEM image (a) of poly (NIPAM-co-IA). Upon hybridization with 8\% POSS (b), 12\% POSS (c) and 12\% POSS (d), the morphology changed to a honeycomb like structure with homogeneous pores of varying pore sizes as POSS content was increased. The study reported that at 12\% POSS the honeycomb pattern was disrupted, indicating that the degree of uniformity in the hydrogel hybrid can be controlled by changing the crosslinking content.\(^{140}\)

For example, the XRD patterns in Figure 10(a) showed a successful hybridization and a uniform dispersion of the cross-linker as confirmed by the disappearance of characteristic crystalline diffraction peaks of OV-POSS at 2\(\theta\) = 9.8, 23.1 and 23.9°.\(^{140}\) The TGA thermogram (Figure 10(b)) showed that the crosslinking with POSS in the hybrid hydrogels increased the thermal stability, wherein the weight loss at temperatures 340–500°C was less than weight loss obtained for poly (NIPAM-co-IA) at the same temperature.\(^{140}\) From the obtained literature, it could be observed that the chemical and physical properties of the hydrogels were improved, including creating porous structures that enable penetration of adsorbate molecules.

**Free-radical polymerization.** Free-radical polymerization is a technique in which polymerization is achieved by generating free radicals to which chain growth occurs in
succession.\textsuperscript{141} This method involves a combination of grafting and crosslinking. The decomposition of the initiator may occur using temperature, light or photon, which then forms a free radical.\textsuperscript{142} Decomposition by photon offers advantages such as low costs; it allows better spatial and time-based control of the reaction process and does not use chemical solvent.\textsuperscript{143} Scheme 2 shows a schematic representation of an overview of free-radical polymerization for synthesizing hydrogels. Firstly, there is the generation of free radicals by an initiator (initiation). Secondly, the free radicals react with the monomer to generate vacant active sites (propagation) and lastly, the formation of a polymer network through crosslinking (termination).\textsuperscript{144}

Free-radical polymerization is the most frequently used procedure in the polymer industry.\textsuperscript{1} The advantages of using free-radical polymerization are that it is easy to carry out, convenient, it is not easily affected by impurities and it is suitable for designing and preparing polymers that can be used for a variety of applications. Free-radical polymerization allows well-characterized reaction kinetics and achievement of in situ properties.\textsuperscript{145}

**Modification with inorganic materials.** Depending on the intended application of the hydrogels, their physical properties can be further enhanced through the incorporation of inorganic materials. For example, for use in removing contaminants from aqueous solutions, the hydrogel must be mechanically and thermally stable for application especially for removing effluents from industries that utilize water for cooling reactions,\textsuperscript{146,147} wherein the contaminants may be introduced at that point. In addition, the hydrogels must be easy to recover. Many recent studies have incorporated nanofillers such as clay-based materials, carbon-based materials and metal oxides into the hydrogel matrix during the polymerization process to improve stability and recoverability. The blended product is then called a hydrogel nanocomposite.

**Carbon-based.** Carbon-based hydrogel nanocomposites are hydrogels synthesized by incorporating materials such as graphene oxide (GO), biochar, AC and carbon nanotubes.\textsuperscript{148,149} GO is a carbon material prepared by oxidizing graphene through chemical or thermal reduction processes. It contains highly hydrophilic groups such as hydroxyl, carboxylic and epoxy groups that are essential for adsorbing dyes and toxic metals.\textsuperscript{150} GO may interact with contaminants through pi-to-pi interactions, electrostatic interactions or hydrogen bonding.\textsuperscript{151} Owing to its outstanding mechanical, electrical and thermal properties, GO has attracted its use in the biomedical, energy and environmental field.\textsuperscript{152}

Carbon nanotubes are simply graphene sheets rolled up in cylinders of 1 nm in diameter.\textsuperscript{153} As a result of their porous structure, large surface area, high tensile strength

---

**Figure 8.** Scheme showing the preparation of gum tragacanth–based hydrogel beads.\textsuperscript{117}
Figure 9. SEM images of poly (NIPAM-co-IA) hydrogel (a) and hybrid poly (NIPAM-co-IA)/OV-POSS (8%, 10% and 12% POSS) (b–d).\textsuperscript{118} SEM: scanning electron microscopy; OV-POSS: octa-vinyl polyhedral oligomeric silsesquioxane.

Figure 10. X-ray diffraction and thermogravimetric analysis.\textsuperscript{118}
(0.15 TPa) and elastic modulus (0.91 TPa), CNTs have attracted interests in use for adsorption of pollutants such as dyes, dichlorobenzene, ethylbenzene and some heavy metals. CNTs can be categorized into two forms, namely, single-walled carbon nanotubes (SWCNTs), which are made up of single layers of graphene sheets, and multi-walled carbon nanotubes (MWCNTs), which are made up of multiple layers of concentric cylinders. For example, the incorporation of CNTs in gels improves the mechanical properties; however, the rate of degradation decreases. This is because carbon-based materials have high hydrothermal stability, which makes them resistant to harsh environments. Scheme 3 shows various interactions or applications that carbon-based materials can take part in such as surface complexation, physical adsorption through its surfaces and electrostatic interactions. Amongst recent studies that have used carbon-based materials to modify properties of the hydrogel, the incorporation of MWCNTs into XG/PAA hydrogel improved the surface hydrophilicity and specific area of xanthan gum. Makhado et al. conducted studies on xanthan gum polymer cross-linked with polyacrylic acid and incorporated with reduced graphene oxide (rGO); the successful synthesis was confirmed by FTIR. Various carbon-based nanocomposite hydrogels and their adsorption properties for removing contaminants from aqueous solutions are listed in Table 3.

Clay-based hydrogels. Natural clays and their improved forms have recently been used for removing pollutants from water. The most commonly used clays, especially for treating toxic metals and dyes, are modified kaolinite and montmorillonite. However, these clays are difficult to regenerate and reuse because of their colloidal dimensions. This prompted the functionalization of these clays, for example, the modification of montmorillonite to form Cloisite 30B clay. In a study where C30B clay was incorporated onto polypropylene grafted with maleic anhydride (PP-g-MA) and thermoplastic starch (TPS), it was reported that the biodegradability of the materials was improved. Modification of adsorbents by introducing functionalized clay components may improve both the physical and chemical properties of adsorbents. Other modifications with clay results improve the number of adsorbing active sites, enhanced porosity and low levels of mineral impurities. In a recent study, C30B was mixed with a culture obtained from an anaerobic sludge to remove hexavalent chromium, where the removal capacity of nearly 100% was obtained. Peng et al. prepared cellulose-MMT hydrogels for removing MB. The hydrogels had a maximum removal capacity of 1065 mg/g (Table 4). Their viscoelasticity studies from the sweep measurements (Figure 11(a)) showed that when \( G' < G'' \) the cellulose-MMT systems were in a viscous liquid form; however with

### Table 3. Carbon-based adsorbent hydrogels and their adsorption properties in removing contaminants from aqueous solution.

| Adsorbent      | Cross-linker | Dye            | \( q_e \) (mg/g) | pH | Dosage (mg) | Isotherm   | Kinetics          | Reference |
|----------------|--------------|----------------|-----------------|----|-------------|------------|------------------|-----------|
| CMC-AAm-GO     | MBA          | Acid black-133 | 185.45          | 6  | 100         | —          | —                | 9         |
| XG-cl-pAA/o-MWCNTs | MBA         | MB             | 521             | 6  | 30          | —          | —                | 10        |
| XG-cl-pAA/rGO  | MBA          | MV             | 1052.63         | 5  | 10          | Langmuir  | Pseudo-second-order | 119       |
|                |              | MB             | 793.65          | 5  | 20          | Langmuir  | Pseudo-first-order | 158       |
| CS/CNTs beads  | Alkaline mixture | CR         | 450.4           | 5  | 20          | —          | —                | —         |
| p (AAm)-CB     | MBA          | Phenol         | 1112            | 10 | 50          | Langmuir  | Pseudo-first-order | 159       |
| p (AAm)-WB     | MBA          | CV             | 118             | 5–8| 200         | —          | —                | 160       |

### Table 4. Clay-based adsorbent hydrogels and their adsorption properties in removing contaminants from aqueous solution.

| Adsorbent      | Cross-linker | Dye | \( q_e \) (mg/g) | pH | Dosage (mg) | Isotherm     | Kinetics          | Reference |
|----------------|--------------|-----|-----------------|----|-------------|--------------|------------------|-----------|
| CMC-MMT        | ECH          | MB  | 1065            | 1–10| 500         | Langmuir     | Pseudo-second-order | 166       |
| K-Carra-AAm-MMT | APS         | MB  | 49.52           | 7  | 50          | Langmuir     | Pseudo-second-order | 167       |
| P (AA-co-AMPS)/MMT | MBA       | MB  | 192             | 10 | —           | Redlich–Peterson | Pseudo-second-order | 168       |
| CS-g-IA/BT     | MBA          | MB  | 500             | 6  | 30          | Langmuir     | Pseudo-second-order | 169       |
increasing time when \( G' > G'' \), the materials were in a gel form. Figure 11(b) in this case revealed that increasing clay content decreased the gel formation. Figure 11(c) revealed that the storage moduli \( (G') \) of hydrogels containing clay was higher than that of unmodified hydrogel and was proportional to the clay content from 10 to 15 wt.%. The incorporation of clay, however, increased the gel strength from 0.3 KPa to 4.7 KPa as shown in Figure 11(d) and (e), which was approximately 16 times higher. Furthermore, the study reported that an increase in clay content from 10–15 wt. % reduced the swelling capacity of the hydrogel (Figure 9(f)), reportedly due to a high degree of crosslinking. Increasing the crosslinking density of the hydrogel enhanced mechanical properties.\(^{166}\)
**Metal oxide–based hydrogels.** Metal oxide–based nanoparticles have been reported to have a high density and restricted size, which are responsible for their very interesting and unique chemical and physical properties. Examples of metal oxides include titanium dioxide (TiO₂), iron oxide (Fe₃O₄), magnesium oxide (MgO) and aluminium oxide (Al₂O₃). Owing to their non-toxic nature, high surface area, high chemical stability and economical friendliness, Fe₃O₄ nanoparticles are widely used for the removal of toxic metals and organic pollutants from water. Ion-oxide and zinc oxide nanoparticles are some of the most frequently used metal oxides in treating dyes from aqueous solutions.

**Magnetic (Fe₃O₄) nanocomposite hydrogels.** Magnetite (Fe₃O₄) also known as black iron oxide amongst other transition metals has the strongest magnetism and is stable at ambient temperatures. Magnetite is prepared from the co-precipitation of iron oxide salts that result in an inverse spinel crystal structure consisting of half of the Fe³⁺ in tetrahedral coordination and the other half Fe²⁺ ions in octahedral coordination (Figure 12). The co-precipitation method is the most useful and suitable technique in preparing magnetite at both lab-scale and industrial scale.

Due to their cheap synthesis costs, susceptibility, stability, high porosity, magnetic properties, biocompatibility and easy chemical modification, MNPs have attracted much use in the wastewater treatment field. The introduction of MNPs into polymer structures to produce nanocomposite hydrogels leads to a hybrid hydrogel with advantages of both components, thus improving chemical and physical properties. An example of such hybridized hydrogel is Fe₃O₄-g-pAA hydrogel synthesized via radical polymerization in the presence of MBA cross-linker, which resulted in a highly adsorptive hydrogel of 507.7 mg/g removal capacity for MB as shown in Table 5. However, according to Flory’s theory, the swelling degree of a hydrogel depends on the density of crosslinking, the ionic osmotic pressure and the attraction of the gel for the liquid. When the crosslinking density is high, the space between the polymer chains decreases making the gel to be stiff due to small nonexpendable pores. Additionally, an increase for MNPs increases the thermal properties but consequently reduces the swelling capacity as the Fe⁺ from the incorporated MNPs may act as a physical crosslinking agent. The greatest advantage of incorporating MNPs into the hydrogel matrix is the improved stability and easy recovery of the material after application.

**Zinc oxide–based hydrogels.** Zinc oxide (ZnO) can be found in nature as a zincite mineral; however, the majority of it is prepared synthetically. Its crystal structure can be found in a hexagonal wurtzite form or cubic zinc blende form (Figure 13). The form that is most stable and commonly found at ambient temperature is the wurtzite structure. ZnO is commonly used for treating skin-related problems such as nappy rash, dandruff and incorporation in ointments used in wound dressing. Other applications of ZnO include use in catalysis, batteries, sensors and adsorption of contaminants. Khan et al. reported their application as adsorbent material in a study, where a guar gum adsorbent hydrogel incorporated with ZnO nanoparticles was used for removing chromium (VI) from water. The group reported that incorporating ZnO nanoparticles improved the recovery of the adsorbent from the aqueous solution after the removal of Cr (VI). In another study, CMC hydrogel was modified with ZnO for antimicrobial activity, which was influenced by their inexpensiveness and lacks colour. Therefore, looking at these properties, the ZnO would be ideal for preparing hydrogels for adsorbing dyes.

**Titanium dioxide–based hydrogels.** Titanium dioxide is a naturally occurring oxide of titanium. It exists in three crystalline phases, namely, brookite, anatase and rutile. The rutile phase is thermodynamically stable compared to

---

**Figure 12.** The inverse spinel structure of magnetite Fe₃O₄.  

**Figure 13.** The inverse spinel structure of magnetite Fe₃O₄.
the anatase and brookite phases, which are metastable.\textsuperscript{195} The advantages of TiO\textsubscript{2} are that it is non-toxic, chemically stable, highly reactive, biocompatible, cost-effective, contains electrochemical properties and is safe to produce.\textsuperscript{195,196} In addition, TiO\textsubscript{2} possesses antimicrobial and UV-protection properties.\textsuperscript{196} Applications of titanium dioxide include the use of a photocatalyst for water-dye degradation, in food and pharmaceuticals as a white colourant, in sensors, ceramic industries, inorganic membranes and biological implants.\textsuperscript{195,196} For example in a study by Kangwansupamonkon et al.,\textsuperscript{197} TiO\textsubscript{2}/poly [acrylamide-co-(acrylic acid)] hydrogel was reported to have 91.6% removal for MB using 5% TiO\textsubscript{2} as an inorganic initiator. Another study by Ari et al.\textsuperscript{195} used P (AMPS)-TiO\textsubscript{2} composite hydrogel for photocatalytic degradation of MB and reported high catalytic performance and high thermal stability due to the incorporated TiO\textsubscript{2} nanoparticles. The group also reported over 80% removal capacity for MB after repeated cycles of more than five, hence improved reusability and regeneration. Another study by Han et al.\textsuperscript{198} also reported excellent performance in terms of regeneration, self-cleaning and recovery of the prepared hydroxyethyl-titanium dioxide-CMC (HEC-TiO\textsubscript{2}-CMC) hydrogel cage for the removal of MB.\textsuperscript{198} Adsorption of MB onto polyacrylamide-grafted gum ghatti (PAAm-g-Gg)/TiO\textsubscript{2} hydrogel nanocomposite prepared by Mittal and Ray was reported to be greatly dependent on the adsorbent dose, the

### Table 5. Metal oxide–based adsorbents for organic dyes removal.

| Adsorbent | Cross-linker | Dye | qₑ (mg/g) | pH | Dosage (mg) | Isotherm | Kinetics | References |
|-----------|--------------|-----|----------|----|------------|---------|----------|------------|
| PAA-grafted MNPs | MBA | MB | 507.7 | 4 | 20 | Langmuir | Pseudo-second-order | 179 |
| Fe\textsubscript{3}O\textsubscript{4}-CS-Clay | Clay | MB | 82 | 9–12 | 500 | — | — | 181 |
| SA-PAAc/ZnO | MBA | MB | 1530 | 6–9 | 10 | Langmuir | Pseudo-second-order | 182 |
| Fe\textsubscript{3}O\textsubscript{4}/p (Am-co-Na Ac) | MBA | MB | 641 | 7 | 50 | Langmuir | Pseudo-second-order | 170 |
| CMC coated Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} nanocomposite | — | MB | 22.7 | 11 | 30 | Langmuir | Pseudo-second-order | 183 |
| Fe\textsubscript{3}O\textsubscript{4}/CA gel beads | CaCl\textsubscript{2} | MV | 713 | — | 20–40 | modified Langmuir–Freundlich | Pseudo-second-order | 184 |
| ZnO–clay–alginate hydrogel beads | Clay | CR | 546.89 | 5–7 | 200 | Temkin | Pseudo-first-order | 185 |
| ZnO-PPy nanocomposite | — | BG | 140.8 | — | 50–200 | Langmuir | Pseudo-second-order | 186 |
| chitosan/silica/ZnO NC | — | MB | 293.3 | — | — | Langmuir | Pseudo-second-order | 187 |

![Figure 13. Crystal structure of zinc oxide.\textsuperscript{162}](image-url)
ionic strength, pH and temperature of the solution. The pair reported a removal capacity of 1305.5 mg g⁻¹ dominated by pseudo-second-order rate model and Langmuir adsorption isotherm. The incorporation of TiO₂ NPs onto sodium alginate cross-linked polyacrylic acid (SA-cl-poly (AA) hydrogel) was reported to have improved removal capacity from 80% using hydrogel with no TiO₂ to 94.1% and 99.4% for nanocomposites containing 0.05 and 0.2 g of TiO₂ NPs, respectively. XRD patterns from this study showed the disappearance of some TiO₂ peaks after MB absorption indicating a reduction in the crystallinity of the nanocomposite that is said to be caused by the trapping of dye molecules within the micropores and macropores of the absorbent.

In recent years, efforts have been made to confirm the effectiveness of using NCHs as adsorbent for wastewater treatment. In this context, Malatji and co-workers fabricated clay/magnetic hydrogel nanocomposites via free-radical polymerization method; their material exhibited improved thermal stability and mechanical strength in comparison to the pure hydrogel. However, their adsorption studies showed that the incorporation of Fe₃O₄ and Cloisite 30B in the polymeric hydrogel networks reduced the adsorption capacity. The prepared clay/magnetic hydrogel nanocomposites exhibited an adsorption capacity of 1081.60 mg/g, which is low when compared to the adsorption capacity (1109.55 mg/g) of pure hydrogel. Surprisingly, Zhang et al. prepared PAAm/CS/Fe₃O₄ composite hydrogel via in situ polymerization for the removal of MB dye from aqueous solution, and the obtained results demonstrated that the incorporation of Fe₃O₄ magnetic nanoparticles in the hydrogel matrices improved both swelling and adsorption capacity. Another study by Makhado et al. synthesized sodium alginate/ZnO hydrogel nanocomposites by the

| Adsorbent Filler | Advantages | Disadvantages | References |
|------------------|------------|---------------|------------|
| (PAAm-g-Gg)/TiO₂ hydrogels nanocomposite | TiO₂ NPs | Recyclability, adsorption capacity | — | 199 |
| SA-cl-poly (AA)-TiO₂ O/I-hydrogels nanocomposite | TiO₂ NPs | Mechanical properties and adsorption capacity | Swelling capacity | 200 |
| CMC-p (AA)/Fe₃O₄ hydrogels nanocomposite | Fe₃O₄ NPs | Mechanical properties and thermal stability | Swelling and adsorption capacity | 201 |
| Poly (acrylamide-chitosan)/Fe₃O₄ hydrogels | Fe₃O₄ NPs | Adsorption capacity, low cost and swelling capacity | — | 202 |
| Sodium alginate-chitosan/Fe₃O₄ hydrogel nanocomposite | ZnO NPs | Thermal stability, swelling and adsorption capacity | Mechanical properties | 182 |
| SA/p (AAC)/o-MWCNTs hydrogels nanocomposite | o-MWCNTs | Thermal stability, swelling and adsorption capacity | Mechanical properties | 203 |
| GK-cl-P (AA-cl-AAM)/SiO₂ nanocomposite | SiO₂ NPs | Surface area, adsorption capacity | Pore size | 204 |
| GumT-cl-HEMA/TiO₂ hydrogel | TiO₂ NPs | Adsorption capacity, surface area, thermal stability and regeneration | Swelling capacity | 205 |

Scheme 1. Crosslinking using glutaraldehyde to produce hydrogel.
in situ free-radical polymerization method. They applied the as-prepared material as an adsorbent for MB dye removal from the aqueous phase. According to their results, sodium alginate/ZnO hydrogel nanocomposites showed high adsorption capacity (1529.6 mg/g) for MB in contrast to adsorption capacity (1129.0 mg/g) exhibited by the pure hydrogel. In addition, sodium alginate/ZnO hydrogel nanocomposites displayed relatively high thermal stability and excellent recycling performance than pure hydrogel. Nonetheless, the incorporation of ZnO NPs in the SA-poly

**Scheme 2.** An overview of thermal free-radical polymerization and crosslinking.\textsuperscript{122}

**Scheme 3.** Showing possible interactions of carbon-based materials.\textsuperscript{135}
(AA) hydrogel matrix increased the swelling capacity, which sequentially led to a decrease in the mechanical strength.\textsuperscript{182} Table 6 shows the advantages and disadvantages of variously reported hydrogel nanocomposites in the removal of MB from wastewater.\textsuperscript{199–205}

Conclusions

This review discusses recent studies applied for removing MB from aqueous solution using biopolymer-based hydrogel nanocomposites. Owing to various advantages such as low cost and easy design, the adsorption method is recognized as the most promising treatment technique for the removal of MB dye. This work discussed the principle behind the adsorption method, common adsorbent materials used and its advantages. We also briefly explained the hydrogels and methods to improve their properties. Three isothermal models: Langmuir, Freundlich and Temkin models have been thoroughly explained with their respective principles. From this review, it was observed that the preparation of hydrogels can be affected by various factors and its removal capacity is affected by pH, temperature and dye concentration. This contribution emphasized the importance of incorporating metal oxide nanoparticles in hydrogels for the removal of dyes and also their advantages and disadvantages towards the gel structure and properties. Concerning the research up to date, it has been observed that the realization of hydrogels for practical purposes needs more research, especially the preparation of hydrogel nanocomposites with the ability to remove organic contaminants such as dyes. It was seen that both magnetic nanoparticles and ZnO nanoparticles have contributed greatly to improving stability and enabling easy separation of adsorbent materials after application. Although the actual wastewaters are complex to be treated because they possess various ions and pollutants, it is more pivotal to conduct analysis on wastewater for adsorption studies using the actual industrial water samples. This is mainly because the adsorbent performance may be noticeably different from the one carried out in batch mode in the laboratory.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The authors immensely acknowledge the financial support from the National Research Foundation (NRF) (Grant Nos. 116679, 117727, and 118113), Sasol Foundation and University of Limpopo, South Africa.

ORCID iD

Kwena D Modibane \(\text{https://orcid.org/0000-0003-4502-122X}\)

References

1. Gupta VK, Ali I, Saleh TA, et al. Chemical treatment technologies for waste-water recycling-an overview. \textit{RSC Adv} 2012; 2: 6380–6388.
2. Muller M. Understanding the origins of Cape Town’s water crisis. \textit{Civil Eng} 2017; 2017(5): 11–16.
3. Park Y, Ayoko GA, and Frost RL. Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. \textit{J Colloid Interf Sci} 2011; 354(1): 292–305.
4. Abu Shmeis RM. Water chemistry and microbiology. \textit{Compr Anal Chem} 2018; 81: 1–56.
5. Bodzek M. Membrane technologies for the removal of micropollutants in water treatment. \textit{Advances in Membrane Technologies for Water Treatment: Materials, Processes and Applications}. Woodhead Publishing Series in Energy, 2015, pp. 465–517.
6. Yagub MT, Sen TK, Afroze S, et al. Dye and its removal from aqueous solution by adsorption: a review. \textit{Adv Colloid Interf Sci} 2014; 209: 172–184.
7. Liu C, Omer AM, and Ouyang X-k. Adsorptive removal of cationic methylene blue dye using carboxymethyl cellulose/k-carrageenan/activated montmorillonite composite beads: isotherm and kinetic studies. \textit{Int J Biol Macromol} 2018; 106: 823–833.
8. Dawood S and Sen TK. Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents. \textit{J Chem Process Eng} 2014; 1(1): 1–11.
9. Varaprasad K, Jayaramudu T, and Sadiku ER. Removal of dye by carboxymethyl cellulose, acrylamide and graphene oxide via a free radical polymerization process. \textit{Carbohydr Polym} 2017; 164: 186–194.
10. Makhado E, Pandey S, Nomngongo PN, et al. Preparation and characterization of xanthan gum-cl-poly(acrylic acid)/o-MWCNTs hydrogel nanocomposite as highly effective reusable adsorbent for removal of methylene blue from aqueous solutions. \textit{J Colloid Interf Sci} 2018; 513: 700–714.
11. Arami M, Limaee NY, Mahmoodi NM, et al. Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. \textit{J Hazard Mater} 2006; 135(1–3): 171–179.
12. Ukaogo PO, Ewuzie U, and Onwuka CV. Environmental pollution: causes, effects, and the remedies. In: \textit{Microorganisms for sustainable environment and health}. 2020, pp. 419–429.
13. Adegoke KA and Bello OS. Dye sequestration using agricultural wastes as adsorbents. \textit{Water Resour Industry} 2015; 12: 8–24.
14. Nascimben SE, László Z, Hodúr C, et al. Photocatalytic membrane filtration and its advantages over conventional...
approaches in the treatment of oily wastewater: a review. *Asia-Pac J Chem Eng* 2020; 15(5): e2533.

15. Thamaraiselvan C and Noel M. Membrane processes for dye wastewater treatment: recent progress in fouling control. *Crit Rev Environ Sci Technol* 2015; 45(10): 1007–1040.

16. Jawzakieh Z and Hubicki Z. Anion exchange resins as effective sorbents for removal of active, reactive, and direct dyes from textile wastewaters. In: *Ion Exchange-Studies and Applications*. 2015, pp. 37–72.

17. Priya R, Stanly S, Kavitharani T, et al. Highly effective photocatalytic degradation of methylene blue using PrO2-MgO nanocomposites under UV light. *Optik* 2020; 206: 164318.

18. Shaban M, Abukhmad MR, Ibrahim SS, et al. Photocatalytic degradation and photo-Fenton oxidation of Congo red dye pollutants in water using natural chromite-response surface optimization. *App/ Water Sci* 2017; 7(8): 4743–4756.

19. Riera-Torres M and Gutiérrez M-C. Colour removal of three reactive dyes by UV light exposure after electrochemical treatment. *Chem Eng J* 2010; 156(1): 114–120.

20. Lahghrib F, Bakasse M, Lahrich S, et al. Advanced oxidation processes: photo-electro-Fenton remediation process for wastewater contaminated by organic azo dyes. *Int J Environ Anal Chem* 2020; 1–16, doi:10.1080/03067319.2020.1711892.

21. Ashraf RS, Abid Z, Shahid M, et al. Methods for the treatment of wastewaters containing dyes and pigments. In: *Water Pollution and Remediation: Organic Pollutants*. 2021, pp. 597–661.

22. Crane R and Sapsford D. Tunable formation of copper metal, oxide, chloride and hydroxyl chloride nanoparticles from aqueous copper solutions using nanoscale zerovalent iron particles. *Nanomater Nanotechnology* 2019; 9: 1–16.

23. Nzila A. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons under anaerobic conditions: overview of studies, proposed pathways and future perspectives. *Environ Pollut* 2018; 239: 788–802.

24. Okoniewska E. Removal of selected dyes on activated carbons. *Sustainability* 2021; 13(6): 4300.

25. Salleh MAM, Mahmoud DK, Karim WAWA, et al. Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. *Desalination* 2011; 280(1–3): 1–13.

26. Kathiresan V, Kansedo J, and Lau SY. Efficiency of various recent wastewater dye removal methods: a review. *J Environ Chem Eng* 2018; 6: 4676–4697.

27. Rathi BS and Kumar PS. Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environ Pollut* 2021; 280: 116995.

28. Mohammadzadeh Pakdel P and Peighambardoust SJ. A review on acrylic based hydrogels and their applications in wastewater treatment. *J Environ Manage* 2018; 217: 123–143.

29. Moosavi S, Lai CW, Gan S, et al. Application of efficient magnetic particles and activated carbon for dye removal from wastewater. *ACS Omega* 2020; 5(33): 20684–20697.

30. Amaya A, Medero N, Tancred N, et al. Activated carbon briquettes from biomass materials. *Bioresour Technol* 2007; 98(8): 1635–1641.

31. Ioannidou O and Zabaniotou A. Agricultural residues as precursors for activated carbon production-A review. *Renew Sustain Energ Rev* 2007; 11(9): 1966–2005.

32. Gegeł U, Özcan G, and Giürpınar GÇ. Removal of methylene blue from aqueous solution by activated carbon prepared from pea shells (Pisum sativum). *J Chem* 2013; 2013: 1–9.

33. Park JE, Lee GB, Hong BU, et al. Regeneration of activated carbons spent by waste water treatment using KOH chemical activation. *Appl Sci* 2019; 9(23): 5132.

34. Zhang Z, Wang T, Zhang H, et al. Adsorption of Pb(II) and Cd(II) by magnetic activated carbon and its mechanism. *Sci The Total Environment* 2021; 757: 143910.

35. Yang Z, Zhao Z, Yang X, et al. Xanthate modified magnetic activated carbon for efficient removal of cationic dyes and tetracycline hydrochloride from aqueous solutions. *Colloids Surf A: Physicochem Eng Aspects* 2021; 615: 126273.

36. Nasrollahzadeh M, Sajjadi M, Iravani S, et al. Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano)materials for sustainable water treatment: a review. *Carbohydr Polym* 2020; 251: 116986.

37. Bealer EJ, Onisemsa-Karimu S, Rivera-Galletti A, et al. Protein-polysaccharide composite materials: fabrication and applications. *Polymers* 2020; 12(2): 464.

38. Russo T, Fucile P, Giacometti R, et al. Sustainable removal of contaminants by biopolymers: a novel approach for wastewater treatment. Current state and future perspectives. *Processes* 2021; 9(4): 719.

39. Crini G, Torri G, Lichtfouse E, et al. Cross-Linked Chitosan-based hydrogels for dye removal. In: *Sustainable Agriculture Reviews*. Cham: Springer, 2019, Vol. 36, pp. 381–425.

40. Zhou Y, Fu S, Liu H, et al. Removal of methylene blue dyes from wastewater using cellulose-based superabsorbent hydrogels. *Polym Eng Sci* 2011; 51(12): 2417–2424.

41. Makhdo E, Pandey S, Nompongong P, et al. Xanthan-gum-epoly (acrylic acid/reduced graphene oxide hydrogel nanocomposite as adsorbent for dye removal. In: 9th Int’l conference on advances in science, engineering, technology and waste management (ASETWM-17), Parya, South Africa, 27–28 November 2017, pp. 159–164.

42. Zhi H, Gao J, and Feng L. Hydrogel-based gas sensors for NO2 and NH3. *ACS Sensors* 2020; 5(3): 772–780.

43. Alvarez-Lorenzo C, Grinberg VY, Burova TV, et al. Stimuli-sensitive cross-linked hydrogels as drug delivery systems: impact of the drug on the responsiveness. *Int J Pharmaceutics* 2020; 579: 119157.

44. Mitura S, Sionkowska A, and Jaiswal A. Biopolymers for hydrogels in cosmetics: review. *J Mater Sci Mater Med* 2020; 31(6): 50.
adsorbents for wastewater treatment. *Environ Chem Sustain World* 2019; 18: 23–71.
46. Crini G and Morcellet M. Synthesis and applications of adsorbents containing cyclodextrins. *J Sep Sci* 2002; 25: 789–813.
47. Lavrenko VA, Podchernyaeva IA, and Shchur DV. Nanostructured materials features of physical and chemical adsorption during interaction polycrystalline nanocrystalline mater gases 2018; 56(517): 504–511.
48. Yan F, Chu Y, Zhang K, et al. Determination of adsorption isotherm parameters with correlated errors by measurement error models. *Chem Eng J* 2015; 281: 921–930.
49. Foo KY and Hameed BH. Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 2010; 156(1): 2–10.
50. Milonjic S. A consideration of the correct calculation of thermodynamic parameters of adsorption. *J Serbian Chem Soc* 2007; 72: 1363–1367.
51. Hibbitts DD and Iglesia E. Hydrogen chemisorption isotherms on platinum particles at catalytic temperatures: Langmuir and two-dimensional gas models revisited. *J Phys Chem* 2019; 123: 8447–8462.
52. Balis N, Zaky AA, Perganti D, et al. Dye sensitization of Titania compact layer for efficient and stable perovskite solar cells. *ACS Appl Energy Mater* 2018; 1: 6161–6171.
53. Worch E. *Adsorption Technology in Water Treatment Fundamentals, Processes, and Modeling.* © 2012. Berlin/Boston: Walter de Gruyter GmbH & Co. KG, 2012 (ISBN 978-3-11-024022-1).
54. State K, State E, and State K. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk. *J Appl Chem* 2012; 3(1): 38–45.
55. Seidel-morgenstern A. Experimental determination of single solute and competitive adsorption isotherms. *J Chromatogr A* 2004; 1037: 255–272.
56. Oguz Erdogan F, Freundlich, Langmuir, Temkin and Harkins-Jura Isotherms Studies of H2 adsorption on porous adsorbents. *Chem Technol 2019; 13(2): 129–135.
57. Ng C, Losso JN, Marshall WE, et al. Freundlich adsorption isotherms of agricultural by-product-based powdered activated carbons in a geosmin-water system. *Bioresour Technol* 2002; 85: 131–135.
58. Azizian S. Kinetic models of sorption: a theoretical analysis. *J Colloid Interf Sci* 2004; 276: 47–52.
59. Ho YS and Mckay G. Pseudo-second order model for sorption processes. *Process Biochem* 1999; 34: 451–465.
60. Salvestrini S. Analysis of the Langmuir rate equation in its differential and integrated form for adsorption processes and a comparison with the pseudo first and pseudo second order models. *React Kinet, Mech Catal* 2018; 123(2): 455–472.
61. Yusuff SM, Khim OK, Zin W, et al. Isotherms and thermodynamics of CO₂ adsorption on thermally treated alum sludge. *Nat Environ Pollut Technol* 2019; 18(1): 247–250.
62. Wu P, Cai Z, Jin H, et al. Adsorption mechanisms of five bisphenol analogues on PVC microplastics. *Sci Total Environ* 2019; 650: 671–678.
63. Zhao Z, Bai P, Li L, et al. The reaction thermodynamics during plating Al on graphene process. *Materials (Basel)* 2019; 12(2): 330.
64. Cheng SY, Show P-L, Lau BF, et al. New prospects for modified algae in heavy metal adsorption. *Trends Biotechnol* 2019; 37(11): 1255–1268.
65. Sham AYW and Notley SM. Adsorption of organic dyes from aqueous solutions using surfactant exfoliated graphene. *J Environ Chem Eng* 2018; 6(1): 495–504.
pore structure development and characterization. *Bioresour Technol* 2005; 96: 1364–1369.
78. Lillo-Rodensas MA, Carzrola-Ameros D, and Linares-Solano A. Chemical reactions between carbons and NaOH and KOH – an insight into chemical activation mechanisms. *Carbon* 2003; 41: 265–267.
79. Kyzas GZ, Bornis G, Kosheleva RI, et al. Nanobubbles effect on heavy metal ions adsorption by activated carbon. *Chem Eng J* 2019; 356: 91–97.
80. Mittal H, Ray SS, and Okamoto M. Recent progress on the design and applications of polysaccharide-based graft copolymer hydrogels as adsorbents for wastewater purification. *Macromol Mater Eng* 2016; 301: 496–522.
81. Moreno-López AY, González-López ME, Manríquez-González R, et al. Evaluation of the Cr(VI) adsorption performance of xanthate polysaccharides supported onto agave fiber-LDPE foamed composites. *Water Air Soil Pollut* 2019; 230: 133.
82. Largitte L and Pasquier R. A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chem Eng Res Des* 2016; 109: 495–504.
83. Gupta VK and Suhas. Application of low-cost adsorbents for dye removal - A review. *J Environ Manage* 2009; 90(8): 2313–2342.
84. Guilherme MR, Aouada FA, Fajardo AR, et al. Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: a review. *Eur Polym J* 2015; 72: 365–385.
85. Zheng Y, Monty J, and Linhardt RJ. Polysaccharide-based nanocomposites and their applications. *Carbohydr Res* 2015; 405: 23–32.
86. Tally M and Atassi Y. Optimized synthesis and swelling properties of a pH-sensitive semi-IPN superabsorbent polymer based on sodium alginate-g-poly (acrylic acid-co-acrylamide) and polyvinylpyrrolidone and obtained via microwave irradiation. *J Polym Res* 2015; 22: 181.
87. Mohammadzadeh Pakdel P and Peighambardoust SJ. A review on acrylic based hydrogels and their applications in wastewater treatment. *J Environ Manage* 2018; 217: 123–143.
88. Essawy HA, Ghazy MBM, El-Hai FA, et al. Superabsorbent hydrogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients. *Int J Biol Macromol* 2016; 89: 144–151.
89. Chen P, Liu X, Jìn R, et al. Dye adsorption and photo-induced recycling of hydroxpropyl cellulose/molybdene disulfide composite hydrogels. *Carbohydr Polym* 2017; 167: 36–43.
90. Benhalima T, Ferfiera-Harrar H, and Lerari D. Optimization of carboxymethyl cellulose hydrogels beads generated by an anionic surfactant micelle templating for cationic dye uptake: Swelling, sorption and reusability studies. *Int J Biol Macromol* 2017; 105: 1025–1042.
91. Yu W, Song D, Li A, et al. Control of gypsum-dominated scaling in reverse osmosis system using carboxymethyl cellulose. *J Membr Sci* 2019; 577: 20–30.
92. Shi C, Tao F, and Cui Y. Evaluation of nitriloacetic acid modified cellulose film on adsorption of methylene blue. *Int J Biol Macromol* 2018; 114: 400–407.
93. Salama A. Preparation of CMC-g-P(SPSMA) super adsorbent hydrogels: Exploring their capacity for MB removal from waste water. *Int J Biol Macromol* 2018; 106: 940–946.
94. Colombo P, Bettini R, Santi P, et al. Swellable matrices for controlled drug delivery: gel-layer behaviour, mechanisms and optimal performance. *Pharm Sci Technol Today* 2000; 3: 198–204.
95. Son Y-R, Rhee KY, and Park S-J. Influence of reduced graphene oxide on mechanical behaviors of sodium carboxymethyl cellulose. *Composites Part B: Eng* 2015; 83: 36–42.
96. Kono H. Characterization and properties of carboxymethyl cellulose hydrogels crosslinked by polyethylene glycol. *Carbohydr Polym* 2014; 106: 84–93.
97. Zhu X, Bao L, Wei Y, et al. Removal of toxic indigo blue with integrated biomaterials of sodium carboxymethyl cellulose and chitosan. *Int J Biol Macromol* 2016; 91: 409–415.
98. Petri DFS. Carboxymethyl cellulose/poly (acrylic acid) interpenetrating polymer network hydrogels as multifunctional adsorbents. *Cellulose* 2019; 26(1): 597–615.
99. Begum HA and Mahbub MKB. Effectiveness of carboxymethyl cellulose for the removal of methylene blue from aqueous solution. *Dhaka Univ J Sci* 2013; 61(2): 193–198.
100. Lee J, Park S, Roh H, et al. Preparation and characterization of superabsorbent polymers based on starch aldehydes and carboxymethyl cellulose. *Polymers* 2018; 10(605): 1–16.
101. Saputra AH, Qadhayna L, and Pitaloka AB. Synthesis and characterization of carboxymethyl cellulose (cme) from water hyacinth using ethanol-isobutyl alcohol mixture as the solvents. *Int J Chem Eng Appl* 2014; 5(1): 36–40.
102. Huang CMY, Chia PX, Lim CSS, et al. Cellulose chemistry and technology synthesis and characterisation of carboxymethyl cellulose from various agricultural wastes. *Cellul Chem Technol* 2017; 51: 665–672.
103. Nizam El-Din HM, Abd Alla SG, and El-naggar AWM. Swelling and drug release properties of acrylamide/carboxymethyl cellulose networks formed by gamma irradiation. *Radiat Phys Chem* 2010; 79(6): 725–730.
104. Tonnesen HH and Karlsen J. Alginates in drug delivery systems. *Drug Deve Ind Pharm* 2002; 28(6): 621–630.
105. Ertesvag H and Valla S. Biosynthesis and applications of alginates. *Polym Degrad Stab* 1998; 59(1–3): 85–91.
106. Cadé F, Rizvi R and Peters RW. Feasibility studies for the removal of heavy metals from solution using tailored bentonite. *Hazardous and industrial wastes, Proceedings of the twenty-second mid-Atlantic industrial waste conference*. Drexel University, 1990, pp. 77–79.
107. Gupta S and Abu-Ghannam N. Bioactive potential and possible health effects of edible brown seaweeds. *Trends Food Sci Technol* 2011; 22(6): 315–326.
108. Liu S, Li Y, and Li L. Enhanced stability and mechanical strength of sodium alginate composite films. *Carbohydr Polym* 2017; 160: 62–70.
109. Liu Y-g, Hu X-j, Wang H, et al. Photoreduction of Cr(VI) from acidic aqueous solution using TiO2-impregnated glutaraldehyde-crosslinked alginate beads and the effects of Fe(III) ions. Chem Eng J 2013; 226: 131–138.

110. Li J, Ma J, Chen S, et al. Adsorption of lysozyme by alginate/graphene oxide composite beads with enhanced stability and mechanical property. Mater Sci Eng C 2018; 89: 25–32.

111. Li C, Wang X, Meng D, et al. Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide for selective and efficient removal of cationic dyes. Int J Biol Macromol 2018; 107: 1871–1878.

112. Wang W and Wang A. Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly (sodium acrylate) and polyvinylpyrrolidone. Carbohydr Polym 2010; 80(4): 1028–1036.

113. Rashidzadeh A, Olad A, and Salari D. The effective removal of methylene blue dye from aqueous solutions by NaAlg-g-poly(acrylic acid-co-acryl amide)chloropropylsilane hydrogel nanocomposite. Fibers Polym 2015; 16: 354–362.

114. Sterner M, Ribeiro MS, Gröndahl F, et al. Cyclic fractionation process for Saccharina latissima using aqueous chelator and ion exchange resin. J Appl Phycol 2017; 29(6): 3175–3189.

115. Hefnawy ME, Ali KA, and Allah MMD. Preparation and properties of a novel eco-friendly carboxymethylcellulose/k-carrageenan/graphene oxide gel beads for the removal of heavy metals from water. Chem Process Eng Res 2018; 58: 6–16.

116. Ren H, Gao Z, Wu D, et al. Efficient Pb(II) removal using sodium alginate-carboxymethyl cellulose gel beads: preparation, characterization, and adsorption mechanism. Carbohydr Polym 2016; 137: 402–409.

117. Lan W, He L, and Liu Y. Preparation and properties of sodium carboxymethyl cellulose/sodium alginate/chitosan composite film. Coatings 2018; 8(8): 291.

118. Shirsath SR, Patil AP, Patil R, et al. Removal of brilliant green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: a comparative study. Ultrason Sonochem 2014; 20(3): 914–923.

119. Makhado E, Pandey S, and Ramontja J. Microwave assisted synthesis of xanthan gum-c1-poly (acrylic acid) based-reduced graphene oxide hydrogel composite for adsorption of methylene blue and methyl violet from aqueous solution. Int J Biol Macromol 2018; 119: 255–269.

120. Garg S and Garg A. Hydrogel: classification, properties, preparation and technical features. Asian J Biomater Res 2016; 2(6): 163–170.

121. Çankaya N. Synthesis of graft copolymers onto starch and its semiconducting properties. Results Phys 2016; 6: 538–542.

122. Ahmed EM. Hydrogel: preparation, characterization, and applications: a review. J Adv Res 2015; 6(2): 105–121.

123. Liang Y, Zhao X, Ma PX, et al. pH-responsive injectable hydrogels with mucosal adhesiveness based on chitosan-grafted-dihydrocaffeic acid and oxidized pullulan for localized drug delivery. J Colloid Interf Sci 2019; 536: 224–234.

124. Singh V, Kumar P, and Sanghi R. Use of microwave irradiation in the grafting modification of the polysaccharides - A review. Prog Polym Sci 2012; 37(2): 340–364.

125. Makhado E, Pandey S, Nomngongo PN, et al. Fast microwave-assisted green synthesis of xanthan gum grafted acrylic acid for enhanced methylene blue dye removal from aqueous solution. Carbohydr Polym 2017; 176: 315–326. DOI: 10.1016/j.carbpol.2017.08.093.

126. Cook JP, Goodall GW, Khutoryanskaya OV, et al. Microwave-assisted hydrogel synthesis: a new method for crosslinking polymers in aqueous solutions. Macromol Rapid Commun 2012; 33(4): 332–336.

127. Anah L and Astrini N. Influence of pH on Cr (VI) ions removal from aqueous solutions using carboxyethyl cellulose-based hydrogel as adsorbent. IOP Conf Ser Earth Environ Sci 2017; 60: 012010.

128. Ismail H, Irani M, and Ahmad Z. Starch-based hydrogels: present status and applications. Int J Polym Mater Polyme Biomater 2013; 62(7): 411–420.

129. Shen C, Shen Y, Wen Y, et al. Fast and highly efficient removal of dyes under alkaline conditions using magnetic chitosan-Fe (III) hydrogel. Water Res 2011; 45(16): 5200–5210.

130. Liu L, Gao Q, Lu X, et al. In situ forming hydrogels based on chitosan for drug delivery and tissue regeneration. Asian J Pharm Sci 2016; 11(6): 673–683.

131. Kumar T, Thakur A, Alexander A, et al. Modified chitosan hydrogels as drug delivery and tissue engineering systems: present status and applications. Acta Pharm Sin B 2012; 2(5): 439–449.

132. Song L, Zhu M, Chen Y, et al. Temperature- and pH-sensitive nanocomposite gels with semi-interpenetrating organic/inorganic networks. Macromol Chem Phys 2008; 209(15): 1564–1575.

133. Zhu M, Xiong L, Wang T, et al. High tensibility and pH-responsive swelling of nanocomposite hydrogels containing the positively chargeable 2-(dimethylamino) ethyl methacrylate monomer. Reactive Funct Polym 2010; 70(5): 267–271.

134. Xu J, Liu X, Ren X, et al. The role of chemical and physical crosslinking in different deformation stages of hybrid hydrogels. Eur Polym J 2018; 100: 86–95.

135. Ye X, Li X, Shen Y, et al. Self-healing pH-sensitive cytosine- and guanosine-modified hyaluronic acid hydrogels via hydrogen bonding. Polymer 2017; 108: 348–360.

136. Huang T, Xu HG, Jiao KX, et al. A novel hydrogel with high mechanical strength: a macromolecular microsphere composite hydrogel. Adv Mater 2007; 19: 1622–1626.

137. Sun J-Y, Zhao X, Illeperuma WRK, et al. Highly stretchable and tough hydrogels. Nature 2012; 489: 133–136.

138. Hu M, Gu X, Hu Y, et al. Low chemically cross-linked paml-c-dot hydrogel with robustness and superstretchability in both as-prepared and swelling equilibrium states. Macromolecules 2016; 49: 3174–3183.

139. Rahmani Z, Sahraei R, and Ghaemy M. Preparation of spherical porous hydrogel beads based on ion-crosslinked...
140. Effekhari-sis B, Rahimkhoei V, Akbari A, et al. Cubic poly-
141. hedral oligomeric silsesquioxane nano-cross-linked hybrid
142. hydrogels: synthesis, characterization, swelling and dye ad-
143. sorption properties. Reactive Funct Polym 2018; 128: 47–57.
144. Braun D. Origins and development of initiation of free radical
145. polymerization processes. Int J Polym Sci 2009; 2009: 1–10.
146. Dannert C, Stokke BT, and Dias RS. nanoparticle-hydrogel
147. composites: from molecular interactions to macroscopic
148. behavior. Polymers 2016; 8(01): 034–042.
149. Jung W, Riahimehzad H, Duever TA, et al. Case studies with
150. mathematical modeling of free-radical multi-component bulk/solution polymerizations: part 1. J Macromol Sci Part A 2015; 52(9): 659–698.
151. Ranganathan N, Joseph Bensingh R, Abdul Kader M, et al.
152. Synthesis and properties of hydrogels prepared by various pol-
153. ymerization reaction systems. In: Mondal M (ed) Cellulose-based
154. superabsorbent hydrogels, polymers and polymeric composites: a reference series. Cham: Springer; 2018, 1–25.
155. Dannert C, Stokke BT, and Dias RS. nanoparticle-hydrogel
156. composites: from molecular interactions to macroscopic behavior. Polymers 2019; 11(2): 275.
157. Guanghui J, Wang L, Yu H, et al. Recent progress on study of
158. hybrid hydrogels for water treatment. Colloids Surf A: Physicochem Eng Aspects 2013; 416: 86–94.
159. Smith SC and Rodrigues DF. Carbon-based nanomaterials for
160. removal of chemical and biological contaminants from water: a review of mechanisms and applications. Carbon 2015; 91: 122–143.
161. Biswas S, Sen TK, Yeneneh AM, et al. Synthesis and charac-
162. terization of a novel Ca-alginate-biochar composite as efficient zinc (Zn2+) adsorbent: thermodynamics, process design, mass transfer and isotherm modeling. Sep Sci Technol 2019; 54(7): 1106–1124.
163. Hai H, Li C, Wang X, et al. A pH-sensitive graphene oxide
164. composite hydrogel. Chem Commun 2010; 46: 2376–2378.
165. Wang X, Liu X, Yuan H, et al. Non-covalently functionalized
166. graphene strengthened poly (vinyl alcohol). Mater Des 2018; 139: 372–379.
167. Fazil S, Bangesh M, Rehman W, et al. Mechanical, thermal, and
dielectric properties of functionalized graphene oxide/polyimide nanocomposite films. Nanomater Nanotechnology 2019; 9: 1–8.
168. Elhissi AMA, Ahmed W, Hassan IU, et al. Carbon nanotubes
169. in cancer therapy and drug delivery. J Drug Deliv 2012; 2012: 1–10.
170. Zhou Y, Tang L, Zeng G, et al. Mesoporous carbon nitride
171. based biosensor for highly sensitive and selective analysis of
172. phenol and catechol in compost bioremediation. Biosens Bioelectron 2014; 61: 519–525.
173. Demczyk BG, Wang YM, Cumings J, et al. Direct mechanical
174. measurement of the tensile strength and elastic modulus of
175. multiwalled carbon nanotubes. Mater Sci Eng A 2002; 334: 173–178.
176. Aqel A, El-nour KMMA, Ammar RAA, et al. Carbon nanotubes, science and technology part (I) structure, synthesis and characterisation. Arabian J Chem 2012; 5(1): 1–23.
177. Yang X, Wan Y, Zheng Y, et al. Surface functional groups of
178. carbon-based adsorbents and their roles in the removal of
179. heavy metals from aqueous solutions: a critical review. Chem Eng J 2019; 366: 608–621.
180. Chatterjee S, Lee MW, and Woo SH. Adsorption of Congo red by chitosan hydrogel beads impregnated with carbon nanotubes. Bioresour Technol 2010; 101(6): 1800–1806.
181. Karakoyun N, Kubilay S, Aktas N, et al. Hydrogel-biochar
182. composites for effective organic contaminant removal from
183. aqueous media. Desalination 2011; 280: 319–325.
184. Hosseinzadeh H. Synthesis of carrageenan/multi-walled carbon nanotube hybrid hydrogel nanocomposite for ad-
185. sorption of crystal violet from aqueous solution. Polish J Chem Technol 2015; 17(2): 70–76.
186. Cadena F, Rizvi R and Peters RW. Feasibility studies for the
187. removal of heavy metals from solution using tailored bentonite. Hazardous and industrial wastes, Proceedings of the twenty-second mid-Atlantic industrial waste conference. Drexel University, 1990, pp. 77–9.
188. Gopal K and Sen S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv Colloid Interf Sci 2008; 140: 114–131.
189. Yuan G, Theng BKG, North P, et al. Clays and clay minerals
190. for pollution control. Dev Clay Sci 2013; 1: 624–675.
191. Abreu AS, Oliveira M, and Machado AV. Effect of clay mineral addition on properties of bio-based polymer blends. Appl Clay Sci 2015; 104: 277–285.
192. Lytras G, Lytras C, Argyropoulou D, et al. A novel two-phase bioreactor for microbial hexavalent chromium removal from wastewater. J Hazard Mater 2017; 336: 41–51.
193. Peng N, Hu D, Zeng J, et al. Superabsorbent cellulose-clay nanocomposite hydrogels for highly efficient removal of dye in water. ACS Sustainable Chem Eng 2016; 4: 7217–7224.
methylene blue from aqueous solutions. *Adsorpt Sci Technol* 2013; 31(5): 397–419.

171. Pasqui D, Atrei A, Giani G, et al. Metal oxide nanoparticles as cross-linkers in polymeric hybrid hydrogels. *Mater Lett* 2011; 65(2): 392–395.

172. Stankic S, Suman S, Haque F, et al. Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties. *J Nanobiotechnol* 2016; 14(1): 73.

173. Rao KG, Ashok CH, Rao KV, et al. Structural properties of MgO nanoparticles: synthesized by co-precipitation technique. *Int J Sci Res* 2014: 2319–7064.

174. Markides H, Rotherham M, and El Haj AJ. Biocompatibility and toxicity of magnetic nanoparticles in regenerative medicine. *J Nanomater* 2012; 2012: 1–11.

175. Majewski P and Thierry B. Functionalized magnetite nanoparticles—synthesis, properties, and bio-applications. *Crit Rev Solid State Mater Sci* 2007; 32(3–4): 203–215.

176. Rivani DA, Retnosari I, Kusumandari TE, et al. Influence of TiO2 addition on the magnetic properties of carbon-based iron oxide nanocomposites synthesized using submersed arc-discharge. *Magnetism properties of carbon-based iron oxide nanocomposites synthesized using submersed arc-discharge. IOP Conf Ser Mater Sci Eng* 2019; 509(1): 012034.

177. Frimpong RA and Hilt JZ. Poly(n-isopropylacrylamide)-based hydrogel coatings on magnetite nanoparticles via atom transfer radical polymerization. *Nanotechnology* 2008; 19(17): 175101.

178. Leslie-Pelecky DL and Rieke RD. Magnetic properties of nanomaterials. *Chem Mater* 1996; 8(8): 1770–1783.

179. Pooresmacel M, Mansoori Y, Mirzaeinejad M, et al. Efficient removal of methylene blue by novel magnetic hydrogel nanocomposites of poly (acrylic acid). *Adv Polym Technol* 2018; 37(1): 262–274.

180. Koetting MC, Peters JT, Steichen SD, et al. Stimulus-responsive hydrogels: theory, modern advances, and applications. *Mater Sci Eng R: Rep* 2016; 93: 1–49.

181. Bée A, Obeid L, Mbolantenaina R, et al. Magnetic chitosan/clay beads: a magsorbent for the removal of cationic dye from water. *J Magn Magn Mater* 2017; 421: 59–64.

182. Makhado E, Pandey S, Modibane KD, et al. Sequestration of methylene blue dye using sodium alginate poly(acrylic acid) @ZnO hydrogel nanocomposite: kinetic, isotherm, and thermodynamic investigations. *Int J Biol Macromol* 2020; 162: 60–73.

183. Zirak M, Abdollahiyan A, Eftekhari-Sis B, et al. Carbomethyl cellulose coated Fe3O4@SiO2 core-shell magnetic nanoparticles for methylene blue removal: equilibrium, kinetic, and thermodynamic studies. *Cellulose* 2018; 25(1): 503–515.

184. Asadi S, Eris S, and Azizzian S. Alginate-based hydrogel beads as a biocompatible and efficient adsorbent for dye removal from aqueous solutions. *ACS Omega* 2018; 3(11): 15140–15148.

185. Vahidhabanu S, Karuppasamy D, Adeogun AI, et al. Impregnation of zinc oxide modified clay over alginate beads: a novel material for the effective removal of Congo red from wastewater. *RSC Adv* 2017; 7(10): 5669–5678.

186. Zhang M, Chang L, Zhao Y, et al. Fabrication of Zinc Oxide/Polypyrrole Nanocomposites for brilliant green removal from aqueous phase. *Arabian J Sci Eng* 2019; 44(1): 111–121.

187. Hosseini H and Mashaykhi M. New chitosan/silica/zinc oxide nanocomposite as adsorbent for dye removal. *Int J Biol Macromol* 2019; 131: 520–526.

188. Stefaniuk I, Cieniek B, Rogalska I, et al. Magnetic properties of ZnO-Co layers obtained by pulsed laser deposition method. *Mater Sci Pol* 2018; 36(3): 439–444.

189. Ahmad M, Yingying S, Nisar A, et al. Synthesis of hierarchical flower-like ZnO nanostructures and their functionalization by Au nanoparticles for improved photocatalytic and high performance Li-ion battery anodes. *J Mater Chem* 2011; 21(21): 7723–7729.

190. Nassar MY, Ali AA, and Amin AS. A facile Pechini sol-gel synthesis of TiO2/Zn2TiO2/ZnO/C nanocomposite: an efficient catalyst for the photocatalytic degradation of Orange G textile dye. *RSC Adv* 2017; 7(48): 30411–30421.

191. Young S-J and Tang W-L. Wireless zinc oxide based pH sensor system. *J Electrochem Soc* 2019; 166(9): B3047–B3050.

192. Farrokhi M, Hosseini SC, Yang JK, et al. Application of ZnO–Fe 3 O 4 nanocomposite on the removal of azo dye from aqueous solutions: kinetics and equilibrium studies. *Water Air Soil Pollut* 2014; 225(9): 1–12.

193. Khan TA, Nazir M, Ali I, et al. Removal of Chromium (VI) from aqueous solution using guar gum-nano zinc oxide bio- composite adsorbent. *Arabian J Chem* 2017; 10: S2388–S2398.

194. Li J, Fang L, Tait WR, et al. Preparation of conductive composite hydrogels from carbomethyl cellulose and polyaniline with a non-toxic crosslinking agent. *Rsc Adv* 2017; 7(86): 54823–54828.

195. Ari B, Sengel SB, and Sahiner N. The use of titanium dioxide particles embedded in anionic hydrogel composite for photocatalytic degradation of methylene blue. *SPE Polym* 2021; 2(2): 97–109.

196. Anaya-Esparza LM, Villagran-de la Mora Z, Ruvalcaba-Gomez JM, et al. Use of Titanium Dioxide (TiO2) Nanoparticles as reinforcement agent of polysaccharide-based materials. *Processes* 2020; 8(11): 1395.

197. Kangwansupamonkon W, Kliaikaew N, and Kiatkamjornwong S. Green synthesis of titanium dioxide/acylamide-based hydrogel composite, self degradation and environmental applications. *Eur Polym J* 2018; 107: 118–131.
199. Mittal H and Ray SS. A study on the adsorption of methylene blue onto gum ghatti/TiO2 nanoparticles-based hydrogel nanocomposite. *Int J Biol Macromol* 2016; 88: 66–80.

200. Thakur S, Pandey S, and Arotiba OA. Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of methylene blue. *Carbohydr Polym* 2016; 153: 34–46.

201. Malatji N, Makhado E, Ramohlola KE, et al. Synthesis and characterization of magnetic clay-based carboxymethyl cellulose-acrylic acid hydrogel nanocomposite for methylene blue dye removal from aqueous solution. *Environ Sci Pollut Res* 2020; 27(35): 44089–44105.

202. Zhang C, Dai Y, Wu Y, et al. Facile preparation of polyacrylamide/chitosan/Fe3O4 composite hydrogels for effective removal of methylene blue from aqueous solution. *Carbohydr Polym* 2020; 234: 115882.

203. Makhado E and Hato MJ. Preparation and characterization of sodium alginate-based oxidized multi-walled carbon nanotubes hydrogel nanocomposite and its adsorption behaviour for methylene blue dye. *Front Chem* 2021; 9: 576913.

204. Mittal H, Maity A, and Ray SS. Synthesis of co-polymer-grafted gum karaya and silica hybrid organic-inorganic hydrogel nanocomposite for the highly effective removal of methylene blue. *Chem Eng J* 2015; 279: 166–179.

205. Sharma B, Thakur S, Mamba G, et al. Titania modified gum tragacanth based hydrogel nanocomposite for water remediation. *J Environ Chem Eng* 2021; 9(1): 104608.