

Biocompatible Self-Healing Hydrogels Based On Boronic Acid-Functionalized Polymer And Laponite Nanocomposite Applied For Water Pollutant Removal

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Abstract

The problem of global water pollution is becoming more and more severe, among which organic dyes and heavy metal ions are two typical types of the most common pollutants. The adsorption method for water purification and wastewater treatment is widely studied and applied. Hydrogel has unique advantages in the field of adsorption due to its three-dimensional porous structure. In this paper, a new type of self-healing hydrogels based on reversible covalent bond were prepared by mixing poly(vinyl alcohol) (PVA) and 2-aminophenylboronic acid modified polyacrylic acid (PAA-2APBA). In addition, the introduction of laponite nanoparticles into the hydrogel can increase both the mechanical strength and adsorption efficiency. This low-cost PAA-2APBA/PVA/laponite nano-composite hydrogel could efficiently remove the organic dyes and heavy metal ions in model waste water through simple immersion, which makes it have application prospects in the fields of both biomedical and environmental engineering.

Introduction

Organic dyes and heavy metal ions are two of the most common water pollutants. Many types of organic dyes are biologically toxic and difficult to degrade, especially that some cationic dyes are more harmful to hydrosphere (Bae and Freeman 2007). Compared to organic dyes, heavy metal ions such as copper and cadmium are more difficult to eliminate, which can be easily accumulate in organisms (Sekhar, Chary et al. 2004). Heavy metal ions are completely non-degradable, and always cause irreversible pollution (Nagajyoti, Lee et al. 2010). It can be enriched in organisms and spread along the food chain, causing heavy metal poisoning at various levels as well as large scales. For these two types of pollutants, the adsorption method for water purification and wastewater treatment is widely studied and applied (Barry, Mane et al. 2017).

Hydrogel is composed of a cross-linked network formed by water-soluble polymers, and a large amount of water swells in this quasi-steady network (Ahmed 2015), which gift it suitable properties to serve as an adsorption material. Due to their special mechanical properties and excellent hydrophilicity, hydrogels are widely used in the preparation and modification of tissue engineering scaffold, water purification materials, oil-water separation membranes, sensors, adsorption materials, and some other industrial devices (Deepthi, Viha et al. 2014, Chu, Feng et al. 2015, Deng, Attalla et al. 2018, Zhou, Guo et al. 2019) .

In different application scenarios, specific working conditions such as temperature, moisture content, and pH etc. are always required specifically for certain types of hydrogels in order to maintain their stability (Zhou, Chen et al. 2019). However, in the practical application scenarios like wastewater treatment, the changing of the conditions and factors are often unpredictable and uncontrollable. One solution to adapt the environmental change is to employ some special dynamic covalent bond. One common type of reversible covalent bonds is the B-O bond between boronic acids and 1,2- or 1,3-diols, which is often used as a synthetic self-healing material (Tarus, Hachet et al. 2014). However, the formation of B-O always requires relatively high pH ($\text{pH} > \text{pK}_a$), and most B-O bond-based self-repairing behaviors occur in high pH range ($\text{pH} \sim 8.5$) which is sometimes difficult to maintain. 2-aminophenylboronic acid (2APBA) can

change its structure to form intramolecular coordination under different pH, which has unique advantages in adapting to special pH environments (Yang, Lee et al. 2006, Deng, Attalla et al. 2018, Smithmyer, Deng et al. 2018). We have previously synthesized 2-aminophenylboronic acid modified hyaluronic acid (HA-2APBA), and prepared HA-2APBA/poly(vinyl alcohol) (PVA) plus alginate/calcium interpenetrating network (IPN) hydrogels, which possessed both self-healing properties and good biocompatibility (Deng, Attalla et al. 2018). The preparation of this IPN hydrogel is a bit complicated, hence a more simplified method is required.

Laponite (LAP) is a synthetic layered silicate nanodisc incorporated with inorganic polyphosphate dispersing agent. It hydrates and swells in water to give clear and colorless colloidal dispersions of low viscosity. Haraguchi et al. were the first one to use laponite as a crosslinking agent to form a hydrogel (Haraguchi, Takehisa et al. 2002). Nowadays, laponite has been widely used in drug delivery, wastewater treatment and other fields (Haraguchi, Takehisa et al. 2002, Rajabi, Kharaziha et al. 2020). It has permanent negative charge, good biocompatibility, high transparency, and good dispersity in water.

Based on the previous work, simpler raw materials – polyacrylic acid (PAA), PVA and laponite, and simple method could be used to prepare a nano-composite hydrogel that has various excellent properties while adapting to a wide range of pH changes. Herein, we report a new type of hydrogel prepared by mixing 2APBA-conjugated PAA and PVA, as well as the introduction of laponite to form a nano-composite hydrogel (NC gel). The hydrogel is versatile, biocompatible, injectable, and self-healable, which could gel at a wide range of pH and could efficiently remove the organic dyes and heavy metal ions in model waste water. With these build-in properties, such type of hydrogel would have great potential application values in the field of waste water treatment.

Results And Discussion

2.1 Polymer Synthesis and Hydrogel preparation.

Polyvinyl alcohol (PVA) has good biocompatibility, and the cis-dihydroxy group within PVA chain can react quickly with phenylboronic acid to form hydrogels (Deng, Brooks et al. 2015, Deng, Attalla et al. 2018, Smithmyer, Deng et al. 2018). However, these traditional borate-based hydrogels are performed under neutral or alkaline conditions. In this project, a modified PAA (PAA-2APBA) was synthesized by using an amide bond reaction between -COOH on PAA and -NH₂ on 2APBA (Scheme 1a and Figure S1). In this way, 2APBA acts as a "bridge" which connects to PAA through an amide bond and combines with PVA through the reversible covalent bond of B-O (Scheme 1a). 2APBA can change its own conformation to accommodate a wider pH range (Scheme S1), which enables it to adapt to more complex environments (Cambre, Roy et al. 2011, Cambre, Roy et al. 2011, Deng, Brooks et al. 2015).

Nano-composite hydrogels were subsequently formed by simple mixing of PAA-2APBA + laponite and PVA solutions at neutral, acidic, or alkaline pH via coextrusion through a double-barrel syringe (Scheme 1b). PAA-2APBA/PVA + laponite gelation was assessed using a vial inversion test (Fig. 1a). Solutions of

either PVA or PAA-2APBA + laponite did not gel, while gelation occurred quickly (about 1 minute) after mixing of PAA-2APBA + laponite and PVA solutions, confirming that boronate-PVA cross-linking occurred. When the volume ratio of laponite solution increased to 40% v/v (PAA-2APBA precursor solution 60% v/v), the transparency of the hydrogel decreased significantly (Figure S2). In addition, the high grafting rate of precursor1 (see Supplementary Information) performed high crosslinking density in the hydrogel. Therefore, subsequent experiments are performed based on laponite 20% v/v (NCgel1) unless otherwise specified.

2.2 Characterization of nano-composite hydrogel

Wide pH adaptability of hydrogels

Due to the unique structure of 2APBA, it can break through the constraints between the environmental pH and the pKa of PBA, and act as a "bridge" in a wider pH range (Deng, Brooks et al. 2015, Deng, Attalla et al. 2018). At each of pH 2.5, 3.5, 5.5, 7.0, 8.0 and 9.0 of the precursor solutions, gelation occurred within 1 min after simple mixing the polymer solutions (NCgel1, Fig. 1). At the pH of about 2.5, mixing PAA-2APBA + laponite and PVA would generate precipitation of some white solids, since the PAA becomes less soluble at low pH (Scheme S2) (Michaeli and Katchalsky 1957, Tanaka, Fillmore et al. 1980). While for the modified PAA (PAA-2APBA), some of the carboxyl group were substituted, so it can still crosslink with PVA through borate linkage to form a gel at low pH.

Scanning electron microscopy

The hydrogels formed at room temperature were then freeze-dried to obtain a SEM specimen. Figure 2 showed the morphology of the hydrogels and nano-composite hydrogels, namely gel5, NCgel5, gel2.5, NCgel2.5, and gel1, NCgel1 respectively (see Supporting Information for the details of naming). The three-dimensional network structure of the NCgel5 appears loose, and the diameter of its pores is also large. Compared with NCgel5, the network structure of NCgel2.5 is denser, and the hole diameter is relatively small. The network structure of NCgel1 is much denser, and the hole diameter is the smallest than the first two nano hydrogels. With same laponite content, the network structure of the hydrogel became denser and the internal pore size was smaller with the increase of the 2APBA grafting rate (Fig. 2b, 2d, 2f). More 2APBA side chains appeared in the PAA polymer, more borate ester bond would form between PAA and PVA polymer chains, so the crosslinking density was greater. In addition, the hydrogels containing laponite had a better network structure compactness (Fig. 2), which indicated that laponite might act as a cross-linking point and promote the intertwining of polymer networks (Xiang, Peng et al. 2006, Shen, Li et al. 2015, Liu, Niu et al. 2020).

Self-healing and injectable properties

We used gel1 and NCgel1 to investigate their self-healing characteristics. After healing for three minutes without external pressure, the healed gel could be handled with a tweezer to indicate its mechanical integrity (Fig. 3a). The healed gel could bear its own weight, and the macroscopic size can be restored to

the initial state. As for NCgel1, the broken hydrogels could also heal without any external stimulus, restore size, and bear its own weight (Fig. 3b). As mentioned above, the reversible covalent bonds between 2APBA and the cis-diols in PVA is a dynamic equilibrium. The broken hydrogel will generate a key rearrangement at the fracture interface by B-O, and spontaneously repair into a whole structure.

Mechanical testing demonstrated the shear storage modulus (G') is higher than shear loss modulus (G''), which meant gel1 and NCgel1 behaving as gels (Figure S3). The rheological results showed the self-healing properties of both gel1 and NCgel1. As shown in Fig. 3c, G' is higher than G'' from 0s to 120s at a low oscillation displacement (0.02 rad, 1.468Hz), which indicated that the materials behaved as gels. From 120s to 240s, a higher oscillation displacement (0.5 rad, 1.468Hz) was exerted to damage the structure of hydrogels (G' decreased from ~ 600 to 50 Pa). At this time, the materials tended to be fluid rather than gels ($G'' > G'$). After the destroyed hydrogels were allowed to heal for 180s, the gel showed mechanical recovery at a low oscillation displacement (0.02 rad, 1.468Hz).

NCgel1 also showed gel behavior and reversibility of self-healing. The G' of NCgel1 was about 1500 Pa, as compared with 600 Pa of gel1, indicating that laponite could significantly improve the mechanical properties of the hydrogel (Fig. 3d). After the hydrogel structure was destroyed, NCgel1 can still recover to $\sim 90\%$ of the initial state within 3 minutes, ensuring that the mechanical properties of the hydrogel could be recovered.

In addition, we tried to inject the already-formed NCgel1 through the syringe, and allowed the squeezed-out gel fractures to form integral gel again. In order to facilitate the distinction, the gels were stained with a red dye (left, sulforhodamine B solution) and blue (right, methylene blue solution) (Fig. 3e). The NCgel1 could be easily extruded through a 0.5 mm diameter needle (Supplementary Video 1). Such nano-composite hydrogels were used to write 'NPU' through the syringe, and the different line segments of the 'NPU' could heal together into a whole structure through the self-healing performance (Fig. 3f).

Stability and degradation of the hydrogels

The stability and degradation tests of hydrogels were showed in figure S4 and S5. The introduction of laponite significantly improved the stability of the hydrogels, and the stability of the hydrogel also increases with the grafting rate of modified PAA. In addition, NCgel1 showed glucose-responsiveness. The NCgel1 was completely dissociated after 40 min immersion in a 2 mg/mL glucose solution, this means that these NC gels have a good application in the biomedical field (Figure S4c). According to the experimental data, NCgel1 has the best stability. In the following process of adsorbing pollutants by the hydrogel, it is necessary to ensure that the hydrogel can exist stably to avoid secondary pollution to the environment. So only NCgel1 was used to adsorb cationic organic dyes and metal ions.

2.3 Adsorption of organic dyes

The adsorption of methylene blue and malachite green is determined by measuring the absorbance of the solution against time (Fig. 4a, 4b and S6). After putting NCgel1 into the dye solution for 4 h, 63% of

methylene blue and 49% of malachite green was quickly removed from the solution phase according to the absorbance value respectively. After 28 h treatment, 71% of methylene blue and 81% of malachite green was removed and trapped into the gel.

Laponite is a silicate with disc-like structure when dispersed in water (Scheme 1b). Typically, more negative charges exist on both bottom surfaces of laponite than positive charges on the side. Therefore, laponite generally contains a large number of permanent negative net charges (Liu and Thomas 1991, Mourchid and Levitz 1998, Herrera, Letoffe et al. 2004). Both the free carboxyl group in PAA chains and laponite contain negative charges accompanying with good 3D network, which lead to its strong adsorption capacity for cationic dyes through positive and negative charge interactions (Hajjaji, Alami et al. 2006, Zhang, Zhou et al. 2006).

At present, the adsorption of dyes by hydrogels is performed after lyophilization, in which the adsorption process is accompanied by the swelling of the hydrogel (Meng, Peng et al. 2018). The nano-composite hydrogel (NCgel1) does not need to undergo the lyophilization step before adsorption nor a shaking process during the adsorption process. After putting the gel into the solution, about 65% of the dye can be quickly absorbed into the gel at the bottom of the beaker within 4 hours (Fig. 4a and b). When the samples were kept in the tube for 24 h and centrifuged (1500 rpm, 5 min), the hydrogel sticks to the bottom of the centrifuge tube, and the waste water turned almost clear (Figure S6a). We also found that the NCgel1 could still adsorb methylene blue at acidic and basic conditions, especially when pH is 9.0, the adsorption efficiency is similar as pH 7.0 (Figure S6c).

2.4 Adsorption of metal ions

Due to the non-degradability of heavy metal ions, the common method for removing heavy metal ions is adsorption (Riederer, Belova et al. 2013, Zhang, Li et al. 2018). This method usually relies on the three-dimensional structure of porous materials for adsorption, which is simple and effective.

The heavy metal adsorption of NCgel1 was tested by directly immersing into the Cu^{2+} , Cd^{2+} , Pb^{2+} and Fe^{3+} solution. With time, the hydrogel turned blue gradually due to the adsorption of copper ions (Figure S7). Freshly prepared NCgel1 showed quick and obvious adsorption to Cu^{2+} , and the hydrogel can reach the adsorption equilibrium in about an hour (Fig. 4c). The maximum adsorption of Cu^{2+} , Cd^{2+} , Pb^{2+} and Fe^{3+} by NCgel1 at 60 min is as high as 259.1 mg/g, 243.4 mg/g, 217.4 mg/g and 166.2 mg/g respectively according to the tests taken with gels of about 0.2 g, which proves the application value in removing heavy metal ions from waste water. When the four ionic solutions are mixed, the hydrogel exhibits different adsorption effects. NCgel1 has the highest selective adsorption for Pb^{2+} and the lowest selective adsorption for Cd^{2+} . When methylene blue is mixed with metal ions, NCgel1 shows stronger adsorption to cationic organic dyes.

The PAA chain in the hydrogel mainly plays a role in the adsorption of heavy metal ions (Meng, Peng et al. 2018). Due to the large negative charge in the PAA chain, it has a strong adsorption effect on heavy

metal cations through electrostatic interactions. At the same time, the introduction of laponite nanoparticles greatly enhances the stability of the hydrogel and at the same time improves the negative charge of the hydrogel, so the hydrogel's ability to adsorb heavy metal ions can be further improved. This hypothesized model is illustrated in Scheme S3. In addition, we evaluated the biocompatibility of the hydrogel, please see the supplementary material for details (Figure S8, S9, and S10).

Conclusions

In summary, the PAA-2APBA/PVA hydrogel and PAA-2APBA/PVA + laponite nano-composite hydrogel were successfully prepared, which had good self-healing performance and injectability. At the same time, this hydrogel could hold the integrity in a relatively wide range of pH by employing dynamic cross-linking between PVA and 2APBA. In addition, the hydrogel had good biocompatibility, and it can quickly and effectively adsorb cationic organic dyes and heavy metal ions from model waste water. The raw materials of nano-composite hydrogel were cheap and the preparation process was simple. Therefore, this multifunctional nano-composite hydrogel which can adapt to complex pH environments has great application prospects in the fields of waste water treatment, as well as other environmental and biomedical engineering in the future.

Abbreviations

EDC, ethyl(dimethylaminopropyl) carbodiimide; PAA-2APBA, 2-aminophenylboronic acid modified polyacrylic acid; PVA, poly(vinyl alcohol); 293T, human renal epithelial cells; HT22, mouse hippocampal neuron cells.

Declarations

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Supplementary Materials

The Supplementary Information and Supplementary Video are available free of charge on the website at XXX

Notes

The authors declare no competing financial interest.

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Figures

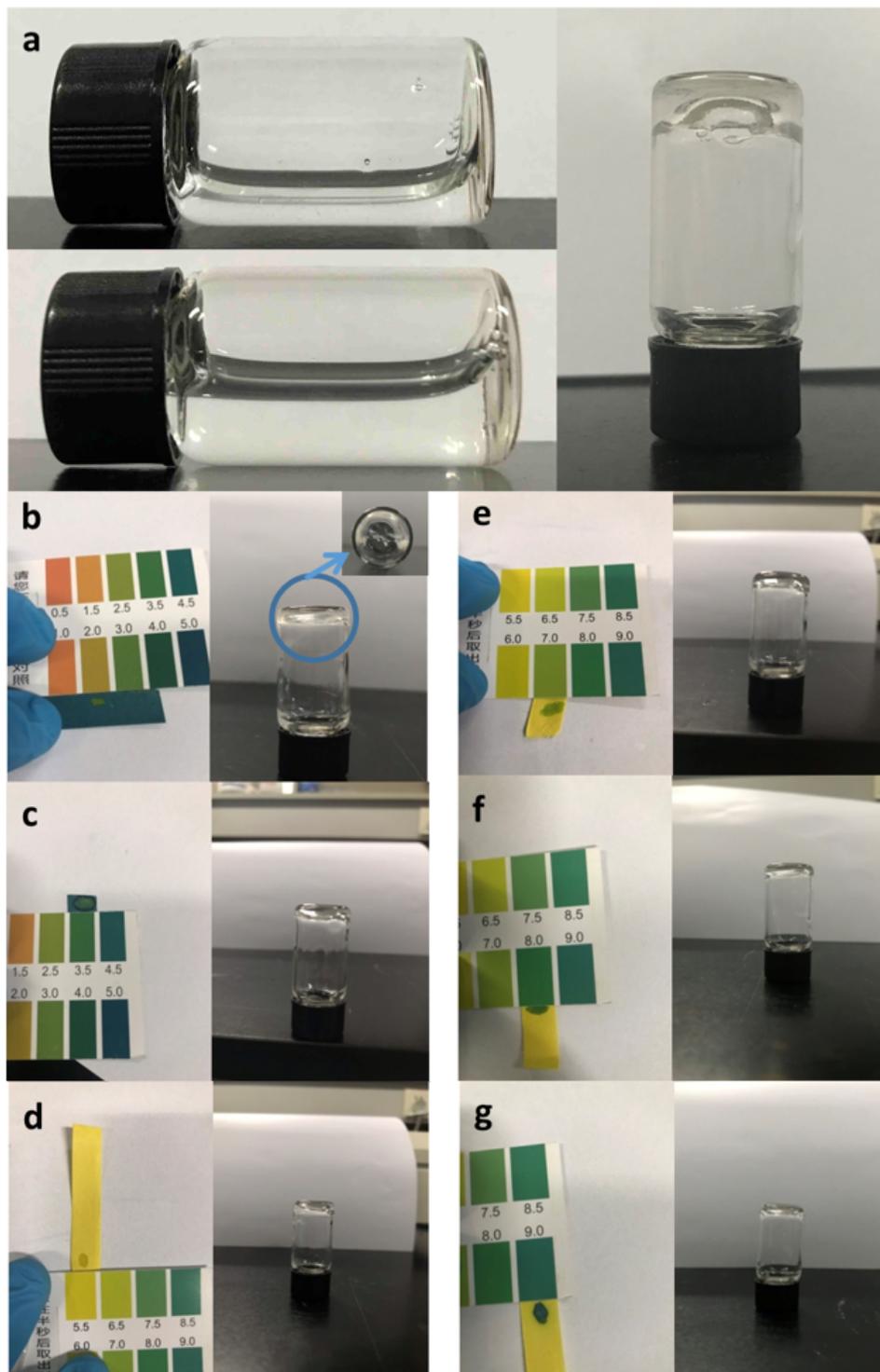


Figure 1

(a) Vial inversion tests of PVA solution (30 mg/mL, left top), PAA-2APBA + laponite solution (30 mg/mL, left bottom), and gelation after simple mixing of PAA-2APBA + laponite and PVA solutions (right). (b, c, d, e, f, g) PAA-2APBA/PVA + laponite hydrogel formation (containing 80% v/v of a 30 mg/mL PAA-2APBA stock solution well mixed with 20% v/v of a 30 mg/mL laponite stock solution, NCgel1) at different pH of the precursor solutions. (b) pH 2.5; (c) pH 3.5; (d) pH 5.5; (e) pH 7.0; (f) pH 8.0; (g) pH 9.0.

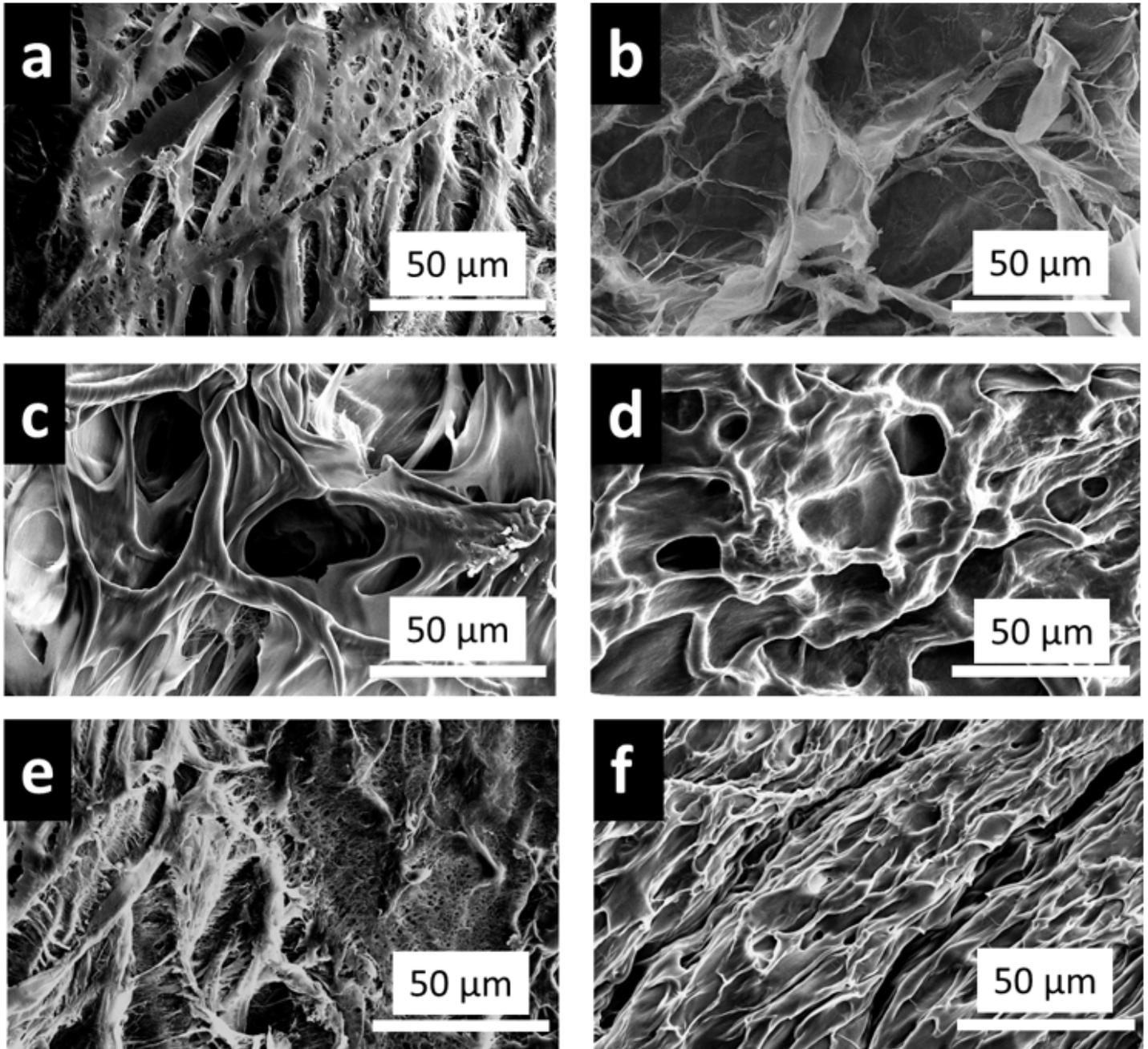


Figure 2

SEM picture of the three-dimensional network structure of hydrogels. (a) gel5; (b) NCgel5; (c) gel2.5; (d) NCgel2.5; (e) gel1; (f) NCgel1.

initiated at low oscillation displacement (0.02 rad, 120s) followed by high oscillation displacement (0.5 rad, 120s), then hydrogels healed 180 s and returned to low oscillation displacement (0.02 rad, 600s); (e, f) The injectable properties of nano-composite hydrogel (NCgel1, labeled with red or blue dye).

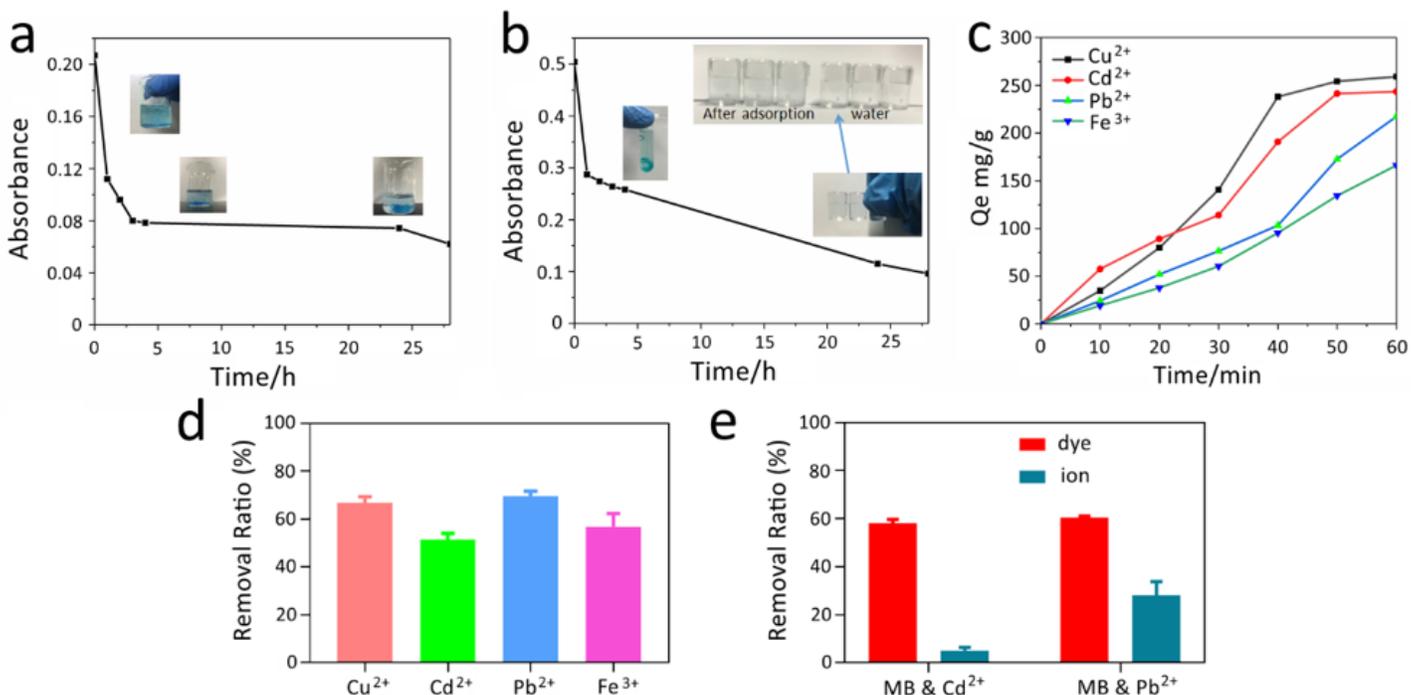


Figure 4

(a, b) Nano-composite hydrogels (NCgel1) adsorption test on organic dyes. (a) the absorbance of the methylene blue (MB) solution at 665 nm during the adsorption by NCgel1; (b) the absorbance of malachite green (MG) solution at 625 nm during the adsorption of by NCgel1; (c) NCgel1's adsorption of Cu²⁺, Cd²⁺, Pb²⁺ and Fe³⁺ over time. The adsorption reaches equilibrium at around 60 minutes; (d) selective adsorption by hydrogel in the mixed solutions of four ions; (e) Selective adsorption by hydrogel in the solution of methylene blue (MB) mixed with different ions.

Supplementary Files

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