Preparation and Adsorption Performance of Nano-hydroxyapatite-Enhanced Acrylamide Hydrogel Adsorbent

Zhi-Ke Wang · Ting-Ting Li · Hao-Kai Peng · Hai-Tao Ren · Ching-Wen Lou · Jia-Horng Lin

Accepted: 22 December 2021 / Published online: 24 February 2022
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
In this study, a hydrogel adsorbent was successfully synthesized using hydroxyapatite/acrylamide/β-cyclodextrin to adsorb heavy metal ions and dyes in water. In the study, different contents of hydroxyapatite were added to the hydrogel, and the mechanical properties and adsorption properties of the material were studied. Results showed that the compressive strength of the hydrogel added with hydroxyapatite increased by 37.1%. The adsorption isotherm model demonstrated that the maximum adsorption capacity was 300 mg/g. In addition, the preparation process of the composite hydrogel was simple and could be used at a low pH for multiple times. Therefore, the material is of great significance to the treatment of pollutants.

Keywords Adsorption · Hydrogel · Mechanical properties · Composites · Kinetics

Introduction
Currently, heavy metals and industrial wastes are major pollutants of water resources in many parts of the world. Industrial activities cause large amounts of organic and inorganic printing and dyeing wastewater. These pollutants can cause genetic and physiological problems in living organisms [1, 2]. Currently, many methods can be used to treat toxic substances, such as chemical precipitation, ion exchange, electrochemical removal, adsorption, coagulation, flocculation, and membrane separation [3–7]. The adsorption method is superior to other methods because of its low cost, simple design, and high efficiency. It is widely used due to its simplicity and high efficiency. However, conventional adsorbents are difficult to use to treat toxic substances in wastewater to safe levels [8–10].

Hydrogels are the most recent adsorbents to be utilized to remove pollutants [11, 12]. They are easy to use and reuse and have outstanding mechanical characteristics [13]. As a result, hydrogels have found a special place in the field of wastewater treatment [14]. Synthetic hydrogels are now made mostly of natural or synthetic polymers, such as inorganic clay, cellulose, acrylic acid, and graphene oxide [15–17]. Previous research used both natural polymer and synthetic materials to make hydrogel adsorbents. For example, Rui Xu et al. employed graphene oxide and sodium acrylate to make a hydrogel by initiating polymerization. The hydrogel can successfully remove Cd2+ ions from water by utilizing a high number of materials containing amino groups [6]. Lin Chu et al. created a recyclable hydrogel with polyvinyl alcohol and acrylic acid and discovered that it has a high adsorption capacity for Cd2+ and Pb2+ and can be reused numerous times after treatment [15]. Jie Ma et al. synthesized a three-network hydrogel that can effectively remove antibiotics in aqueous solutions using...
carbon nanotubes, graphene oxide, sodium alginate, and other materials [18]. We previously employed cyclodextrin and acrylamide to make a hydrogel adsorbent with improved strength and adsorption performance that can successfully remove heavy metal ions from water [19]. Hydroxyapatite is the natural mineral of calcium apatite (Ca₅(PO₄)₃(OH)) [20, 21]. It is abundant in nature and is employed in the medical profession because of its unique compatibility [22–24]. Furthermore, given that hydroxyapatite has a significant number of active groups that may adsorb harmful compounds in medium via ion exchange, coordination, and hydrogen bonds, it is utilized as an adsorbent [25, 26]. However, when utilized as an adsorbent, hydroxyapatite is a particulate material, which may make recovery difficult [27, 28].

In this study, acrylamide/cyclodextrin/polyvinyl alcohol hydrogel was used as a nano-hydroxyapatite carrier to synthesize composite hydrogel adsorbent. Composite hydrogel solves the problem of difficult recovery of hydroxyapatite adsorbent. A large number of oxygen-containing groups in hydroxyapatite can provide numerous adsorption sites for hydrogels and enhance the mechanical strength of hydrogels. The study maximizes the respective properties of hydroxyapatite and organic hydrogel, and the composite of the two materials has strong properties. The mechanical and adsorption properties of composite hydrogels were characterized and tested, and the adsorption mechanism was explained by adsorption kinetics and the adsorption isotherm model. Nano-hydroxyapatite hydrogel is of great significance for the combination and development of inorganic and organic adsorption materials.

Materials and Methods

Materials

Acrylic acid, acrylamide, melamine, and paraformaldehyde were purchased from Tianjin Kairuisi Fine Chemical Co., Ltd. (Tianjin China). Polyvinyl alcohol (PVA) and dimethyl sulfoxide (DMSO) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). N,N’-Methylene bisacrylamide (MBA), potassium peroxodisulfate (KPS), Ni(NO₃)₂, Pb (NO₃)₂, β-cyclodextrin, epichlorohydrin (ECH), and NaOH were all purchased from Tianjin Jiangtian Chemical (Tianjin, China). Hydroxyapatite was purchased from Shengan Biotechnology (China), with a particle size of 10 μm±1 μm. The physical diagrams of the three clays are shown in Fig. 1.

Hydrogel Preparation

First, about 90 mL of deionized water was heated to 90 °C, slowly added with 10 g of polyvinyl alcohol particles, and stirred. After the solution became transparent, it was left to stand to cool. Subsequently, 1%, 3%, and 5% of its mass of hydroxyapatite were added to the PVA solution. About 2 g of β-cyclodextrin, 2 mL of acrylic acid, 2 g of acrylamide, and 30 mg of MBA were dissolved in 5 mL of deionized water. The mixed solution was added to 20 mL of PVA solution containing hydroxyapatite, stirred evenly, and added to 15 mg of KPS. Nitrogen protection was used during the preparation process, and the mixed solution was placed in a vacuum drying oven at 60 °C for 2 h. Finally, using 20 mL of DMSO as the solvent, 4 mL of epichlorohydrin was dissolved in DMSO and 2 g of sodium hydroxide was added. The hydrogel was impregnated in the mixed solution and kept at 60 °C for 1 h to obtain the hydroxyapatite composite hydrogel. The physical diagram of the sample is shown in Fig. 2.

Characterizations

The thermal stability of the hydrogel was tested with a thermogravimetric analyzer (TG 209F3, NETZSCH, Bavaria, Germany). The samples were analyzed with a Fourier infrared spectrometer (Thermo Scientific Nicolet 380 FT-IR Fourier spectrometer). Instron 5969 (Instron, USA) was used to compress the hydrogel, and the compression rate was 300 mm/min. A flame atomic absorption spectrometer (PerkinElmer AA900) was used to test the ion concentration of lead ions and nickel ions. A UV spectrophotometer (UV-2600) was used to measure the concentration of methylene blue. X-ray photoelectron spectroscopy (Thermo Fisher Scientific ESCALAB 250Xi) was performed to measure the changes in atomic energy before and after adsorption of the material. The swelling experiment of the hydrogel was measured by the gravity method. Under certain conditions (pH 7 at 25 °C), it swelled from the absolute dry state to the swelling equilibrium state. All samples were measured three times, and the average value was obtained. The swelling rate (SR) of the hydrogel was calculated using Eq. 1:

\[ SR = \left( \frac{W_t - W_d}{W_d} \right) \times 100\% \]

where \( W_t \) is the weight of the swollen hydrogel and \( W_d \) is the weight of the dry hydrogel.
Where $W_t$ is the mass of the hydrogel for swelling time $t$, and $W_d$ is the mass of the absolutely dry hydrogel.

Sorption Experiments

For the adsorption performance of the hydrogel materials for pollutants, this study conducted a series of adsorption experiments using two heavy metal ions and methylene blue. An Ni(II) and Pb(II) solution with a concentration of 1 g/L was prepared for standby. Methylene blue solution (1 g/L) was prepared for standby. The removal efficiency of the three pollutants by the hydrogel was continuously recorded within 5 h. Different concentrations of heavy metal ions and methylene blue solutions were used to test the removal efficiency of the hydrogel, and the adsorption capacity of the hydrogel at different concentrations was calculated. The adsorption capacity ($Q_e$) of the material for ions can be expressed as Eq. (2) as follows:

$$Q_e = \frac{(C_0 - C_e) \times V}{m}$$

where $C_0$ and $C_e$ are the initial and final concentrations (mg/L) of Pb(II) and Ni(II), $V$ is the volume of the solution (mL), and $m$ is the weight of the adsorbent (mg).

To study the effect of pH and sodium ions on the adsorption performance, HCl (1 M) or NaOH (1 M) was used to adjust the pH of the solution of the two ions to range from 2 to 7. The initial concentration of both ions was 50 mg/L. The adsorption properties of hydrogels were tested at different temperatures, and their adsorption models were fitted.

To evaluate the recyclable properties of hydrogels, the Pb(II) and Ni(II) adsorbents were eluted with 0.1 M HCl solution and then treated with 0.1 M NaOH solution. Methylene blue was desorbed by hydrochloric acid and anhydrous methanol solution with a concentration of 0.1 mol/L. Finally, deionized water was used to wash the adsorbents.

Results and Discussion

Characterizations

An SEM image of hydroxyapatite hydrogel is shown in Figure S1. After freeze-drying, the hydrogel was imaged; it had a porous structure that was favorable to pollutant adsorption. In addition, no agglomeration of nano-hydroxyapatite occurred and it was uniformly distributed in the hydrogel. The IR spectrum of the hydroxyapatite composite hydrogel is shown in Fig. 3a. The stretching vibration peaks of -C=O in the acrylic carboxyl group and acrylamide amide group were 1727 and 1649 cm$^{-1}$, respectively, whereas the bending vibration peak of -NH$_2$ was 1025 cm$^{-1}$ [29–31]. The peaks at 3100–3400 and 1090 cm$^{-1}$ were attributed to the -OH stretching vibration and -CO- stretching vibration of polyvinyl alcohol, respectively [32]. β-Cyclodextrin’s primary functional groups generally overlapped with PVA’s distinctive peaks. The amino characteristic peak of acrylamide and the characteristic peak of -OH around 3300 cm$^{-1}$ almost completely obscured the -PO$_4$ characteristic peak of hydroxyapatite at 1030 cm$^{-1}$ [21]. The binding of hydroxyapatite to the hydrogel did not affect the characteristic functional groups of the hydrogel. Figure 3b depicts the TGA findings of four hydrogels. The hydroxyapatite composite hydrogel appeared to be relatively stable below 200 °C. The SR of a hydrogel used in water treatment is an essential metric. Figure 3c shows the SR before and after adding hydroxyapatite to the hydrogel. The SR of the hydrogel dropped after adding hydroxyapatite (from 180 to 167%), as shown in Fig. 3b, and the SR decreased with the addition of clay. Given that hydroxyapatite can cling to long polymer chains, the pores of the 3D structure created by PVA and PAA decreased, and the space for filling free water was reduced, lowering the hydrogel’s SR progressively.
Figure 3d shows the compression resilience curves of three hydroxyapatite hydrogels at 50% strain. First, the addition of hydroxyapatite improved the compressive strength of the hydrogel. The integral area of the compression rebound curve represents internal friction dissipation during compression. The smaller the area, the better the elasticity of the hydrogel, so the introduction of hydroxyapatite reduced the elasticity of the hydrogel. Figure 3d shows the maximum compressive strength of the hydroxyapatite composite hydrogel. The strength of the hydrogel increased as the amount of hydroxyapatite added increased. According to the findings, hydroxyapatite boosted the hydrogel’s compressive strength the greatest (37.1%). The OH⁻ in hydroxyapatite may create hydrogen bonds with the hydroxyl group of PVA, and its nanoparticles can cling to the 3D framework of PVA and polyacrylic acid [21].

**Adsorption Study**

**Effect of Environmental Conditions**

Figure 4a–c show how changing the pH of the system affects the hydroxyapatite composite hydrogel’s ability to remove Pb(II) and Ni(II) ions, as well as MB. The elimination effectiveness of the hydrogel for contaminants steadily improved as the pH of the system rose from 2 to 6, and the adsorption equilibrium was ultimately established. When pH<2, the removal efficiency of the adsorbent for the two ions was low. Given the occurrence of protonation (i.e., -NH₂ + H⁺ → -NH₃⁺ or -COO⁻+H⁺→-COOH) [33], the removal efficiency was low. The adsorption of lead ions and nickel ions achieved equilibrium at pH 3, while the adsorption of MB reached equilibrium at pH 4.5, suggesting that the adsorption principles of metal ions and methylene blue were
distinct. Figure 3d shows that pH_{PZC} of the hydrogel was 8.12, and pH_{PZC} of the hydroxyapatite composite hydrogel was 7.43. After adding hydroxyapatite, the positive charge on the hydrogel’s surface was lowered, making cation adsorption easier [22]. At a low pH, the composite material had a higher removal efficiency for the two metal ions. The positive charges in the system made the adsorption of metal ions difficult. The high concentration of metal ions in the hydrogel might be the explanation. Heavy metal ions are coordinately adsorbed by the electron-rich group [15].

**Adsorption kinetics**

Figure 5 shows the time curve of the adsorption of two metal ions and methylene blue by the hydrogel. The removal efficiency of the two metal ions grew fast in the early stages of adsorption and achieved equilibrium during the following 50 min. The adsorption of metal ions reached equilibrium faster than the adsorption of methyl blue. In the initial stage of adsorption, the hydrogel contained a large number of adsorption sites provided by polar groups, such as hydroxyl, carboxyl, and amino groups, so the concentration of pollutants decreased rapidly. The pseudo-first-level model and the pseudo-second-level model were used to fit the kinetic data and examine the equilibrium time data to better understand the link between time and adsorption rate (supporting information, Eqs. 1 and 2) [34–36]. The adsorption kinetics are summarized in Table 1. The fitting correlation coefficient R^2 of the pseudo-second-order kinetic model was higher than 0.985 when compared with the pseudo-first-order kinetic model. The fitting results of Pb(II) and Ni(II) were more in line with the pseudo-second-order kinetic model, which could also explain the relationship between time and adsorption rate in the adsorption process, as shown in Fig. 5; Table 1. The findings demonstrated that chemical adsorption or coordination adsorption involving shared valence bonds through electron exchange may be the rate-limiting phase in adsorption. The pseudo-first-order kinetic model agreed with the fitting result of the composite hydrogel’s methylene blue adsorption data, indicating that the dye’s adsorption process differed from that of the metal ion. From the perspective of the adsorption rate constant, the crystal structure of hydroxyapatite will affect the adsorption of metal ions by the hydrogel. The adsorption rate depends not only on the content of functional groups but also on the structure of the material.

The internal diffusion model of the hydroxyapatite composite hydrogel is depicted in Figure S2 (supporting information, Eq. 3). The adsorption process could be divided into two parts, with the first step’s curve not passing through the origin. The adsorption of pollutants is thought to be two phases functioning at the same time if it passes through the origin, according to the model [37, 38].
Adsorption Isotherm and Thermodynamics

The Langmuir, Freundlich, and Dubini–Radushkevich (D-R) isotherm models are most commonly used in adsorption thermodynamics (supporting information, Eqs. 4 and 5). Figure S3 shows the Langmuir and Freundlich fitting models of hydroxyapatite composite hydrogel adsorption of the three pollutants. The adsorption capacity of the composites for the three pollutants increased with the increase in pollutant concentration. Even if the pollutant concentration (>200 mg/L) was high, the materials demonstrated high removal efficiency (>95%). In addition, when the hydroxyapatite content increased, the adsorption capacity of the hydrogel increased. At 313 K, the maximum adsorption capacity of the hydroxyapatite composite hydrogel (5%) was 337.68 (Pb), 226.26 (Ni), and 330.46 mg/g (MB). Figure S2 shows that the fitting result of the adsorption isotherm was more complicated with the Langmuir adsorption model ($R^2 > 0.98$), suggesting that the three pollutants were mostly absorbed by the material via single-layer adsorption [36, 39].

Tables S2 and S3 and Figure S4 show the fitting results of the adsorption thermodynamics and the D-R adsorption isotherm model [40]. In accordance with the Van’t Hoff equation, the adsorption process of hydroxyapatite hydrogel to the three pollutants was exothermic and spontaneous ($\Delta G < 0, \Delta S > 0$) [7]. According to the D-R adsorption isotherm model, $E(8.18–11.97)$ was calculated in the range of 8–16 kJ/mol. The main form of adsorption of the three pollutants by the material was through chemical adsorption [41].

Adsorption Mechanism

Different adsorbents have varying adsorption mechanisms, such as electrostatic interaction, ion exchange, and chelation [26, 42, 43]. The hydrogel’s polyvinyl alcohol and acrylamide include numerous electron-rich groups, such as carboxyl and amino groups, which can adsorb contaminants [44].

X-ray photoelectron spectroscopy was utilized to examine the alterations before and after the adsorption of lead ions by the hydrogel to further confirm the mechanism of this investigation (Fig. 6). First, from the full spectrum scan, a new peak of Pb$^{4+}$ appeared in the material, indicating that lead ions were adsorbed by the material (Fig. 7a). Figure 7b shows the precise scanning spectrum of Cl$^{-}$, which could be divided into three peaks: C-C, C-N, and C=O [45, 46]. The binding energies of these three peaks all rose to varying degrees when lead ions were adsorbed, demonstrating that nitrogen and oxygen near carbon were involved in the adsorption process. Figure 7c and d corresponded to the precise scanning spectra of O1s and N1s, respectively, corresponding to O=O and -NH$_3^+$ at 532.08 and 399.48 eV [47]. The binding energies of the matching peaks of O=O and -NH$_3^+$ all appeared to rise after adsorption, suggesting that the lone pair electrons in nitrogen form coordination bonds with lead ions, adsorbing lead ions [48].

Comparison with Other Adsorbents

Although hydroxyapatite hydrogel has a high adsorption capacity, the adsorption capacity of different adsorbents

---

Fig. 5  Sorption kinetics of Pb(II) and Ni(II) on hydroxyapatite composite hydrogel (a). Sorption kinetics of MB on hydroxyapatite composite hydrogel (b). $C_0$ = 50 mg/L or 100 mg/L, $T = 303$ K, $m/V = 1$ mg/mL, pH=5
cannot be directly compared due to varying application circumstances. Table S4 highlights the adsorption capacity of this study and other adsorbents in terms of capacity. Hydroxyapatite hydrogel has high potential in the pollution removal sector.

### Selective Adsorption Test and Adsorption Recyclability

In this study, the selective adsorption of materials was tested to deal with the diversity of pollutants in wastewater. The selective adsorption properties of hydrogels were tested by

#### Table 1 Hydroxyapatite-hydrogel adsorption kinetic model fitting parameters

|        | C₀ (mg/L) | Pseudo-first-order | Pseudo-second-order |
|--------|-----------|--------------------|--------------------|
|        |           | k₁ (L/min) | Qₑ (mg/g) | R² | k₂ (g/(mg h)) | Qₑ (mg/g) | R² |
| Pb     | 50        | 0.052    | 46.58    | 0.9639 | 0.090 | 46.58     | 0.9639 |
|        | 100       | 0.049    | 95.76    | 0.9716 | 0.041 | 95.76     | 0.9716 |
| 1% Ni  | 50        | 0.036    | 46.91    | 0.9773 | 0.050 | 53.87     | 0.9915 |
|        | 100       | 0.025    | 97.69    | 0.9828 | 0.016 | 115.26    | 0.9909 |
| MB     | 50        | 0.031    | 48.36    | 0.9944 | 0.037 | 56.66     | 0.9812 |
|        | 100       | 0.031    | 98.23    | 0.9978 | 0.019 | 114.74    | 0.9882 |
| 3% Pb  | 50        | 0.037    | 47.70    | 0.9742 | 0.052 | 54.36     | 0.9913 |
|        | 100       | 0.042    | 97.12    | 0.9746 | 0.030 | 109.48    | 0.9878 |
| Ni     | 50        | 0.056    | 46.84    | 0.9585 | 0.083 | 52.22     | 0.9831 |
|        | 100       | 0.026    | 99.15    | 0.9696 | 0.017 | 115.48    | 0.9826 |
| MB     | 50        | 0.033    | 48.53    | 0.9934 | 0.040 | 56.31     | 0.9818 |
|        | 100       | 0.033    | 97.91    | 0.9962 | 0.020 | 113.59    | 0.9875 |
| 5% Pb  | 50        | 0.059    | 47.46    | 0.9614 | 0.092 | 52.32     | 0.9856 |
|        | 100       | 0.049    | 95.76    | 0.9716 | 0.037 | 106.76    | 0.9884 |
| Ni     | 50        | 0.044    | 47.80    | 0.9853 | 0.063 | 53.90     | 0.9940 |
|        | 100       | 0.026    | 99.66    | 0.9927 | 0.016 | 117.77    | 0.9938 |
| MB     | 50        | 0.033    | 49.21    | 0.9925 | 0.040 | 57.18     | 0.9753 |
|        | 100       | 0.032    | 99.17    | 0.9960 | 0.019 | 115.53    | 0.9825 |

---

**Fig. 6** XPS spectra of hydroxyapatite composite hydrogel before and after the adsorption of lead ions. **a** Full-spectrum scan; **b** C₁s peaks; **c** O₁s peaks; **d** N₁s peaks.
mixed solutions of four metal ions (Pb(II), Cu(II), Zn(II), and Ni(II)). The results are shown in Fig. 6. The removal efficiency of lead ions by hydroxyapatite hydrogel was higher than that of the other three (>80%), followed by copper ion, zinc ion, and nickel ion. Thus, the material can not only adsorb a variety of ions in the mixed solution but also preferentially remove lead ions.

Recyclability is a requirement of the adsorbent. The study conducted five adsorption–desorption experiments on hydroxyapatite hydrogel, as shown in Fig. 8. After five cycles of adsorption–desorption experiments, the removal efficiency of the hydroxyapatite hydrogel for both ions and dyes exceeded 81%. The result meets the requirements of the adsorbent, and the decrease in removal efficiency may be caused by the quality loss of the material, but this does not affect the reusability of the material.

Conclusions

In this study, a hydrogel adsorbent was successfully synthesized, and its adsorption and mechanical properties were studied. After adding hydroxyapatite to the hydrogel, the compressive strength increased (the maximum increase was 37.1%), the swelling performance decreased, and the maximum adsorption capacity of the hydrogel increased by about 10%. The hydrogel removes heavy metal ions and dyes in a high-quality environment and can be reused many times. The materials used in the research are low in cost and short in process flow, and they have great potential for the treatment of polluted wastewater.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10924-021-02370-5.

References

1. Macías-García A, Corzo MG, Domínguez MA, Franco MA, Naharro JM (2017) Study of the adsorption and electroadsorption process of Cu (II) ions within thermally and chemically modified activated carbon. J Hazard Mater 328:46–55
2. Zhu F, Li L, Xing J (2017) Selective adsorption behavior of Cd (II) ion imprinted polymers synthesized by microwave-assisted inverse emulsion polymerization: Adsorption performance and mechanism. J Hazard Mater 321:103–110
3. Al-Rashdi B, Johnson D, Hilal N (2013) Removal of heavy metal ions by nanofiltration. Desalination 315:2–17
4. Anitha K, Namsani S, Singh JK (2015) Removal of heavy metal ions using a functionalized single-walled carbon nanotube: a molecular dynamics study. The Journal of Physical Chemistry A 119(30):8349–8358
5. Gogoni N, Barooah M, Majumdar G, Chowdhury D (2015) Carbon dots rooted agarose hydrogel hybrid platform for optical detection and separation of heavy metal ions. ACS Appl Mater Interfaces 7(5):3058–3067
6. Xu B, Wang X, Huang Y, Liu J, Wang D, Feng S et al (2020) Electrospinning preparation of PAN/TiO2/PANI hybrid fiber membrane with highly selective adsorption and photocatalytic regeneration properties. Chem Eng J 399:125749
7. Xu R, Zhou G, Tang Y, Chu L, Liu C, Zeng Z et al (2015) New double network hydrogel adsorbent: Highly efficient removal of Cd (II) and Mn (II) ions in aqueous solution. Chem Eng J 275:179–188
8. Phetphaisit CW, Yuanyang S, Chaiyasith WC (2016) Polyacrylamido-2-methyl-1-propane sulfonic acid-grafted-natural rubber as bio-adsorbent for heavy metal removal from aqueous standard solution and industrial wastewater. J Hazard Mater 301:163–171
9. Repo E, Warchot JK, Bhatnagar A, Mudhoo A, Sillanpää M (2013) Aminopolycarboxylic acid functionalized adsorbents for heavy metals removal from water. Water Res 47(14):4812–4832
10. Tan L, Wang S, Du W, Hu T (2016) Effect of water chemistries on adsorption of Cs (I) onto graphene oxide investigated by batch and modeling techniques. Chem Eng J 292:92–97
11. Echeverria C, Fernandes SN, Godinho MH, Borges JP, Soares PI (2018) Functional stimuli-responsive gels: Hydrogels and microgels. Gels 4(2):54
12. Liao H, Liu Y, Wang Q, Duan W (2019) Preparation and properties of a poly (vinyl alcohol) hydrogel-melamine formaldehyde foam composite. Polym Compos 40(5):2067–2075
13. Anjum S, Gurave P, Badiger MV, Torris A, Tiwari N, Gupta B (2017) Design and development of trivalent aluminium ions induced self-healing polycrylic acid novel hydrogels. Polymer 126:196–205
14. Martín C, Merino S, González-Dominguez JM, Rauti R, Ballerini L, Prato M et al (2017) Graphene improves the biocompatibility of polycrylamide hydrogels: 3D polymeric scaffolds for neuronal growth. Sci Rep 7(1):1–12

15. Chu L, Liu C, Zhou G, Xu R, Tang Y, Zeng Z et al (2015) A double network gel as low cost and easy recycle adsorbent: highly efficient removal of Cd (II) and Pb (II) pollutants from wastewater. J Hazard Mater 300:153–160

16. Ma J, Liu Y, Ali O, Wei Y, Zhang S, Zhang Y et al (2018) Fast adsorption of heavy metal ions by waste cotton fabrics based double network hydrogel and influencing factors insight. J Hazard Mater 344:1034–1042

17. Zhou G, Liu C, Chu L, Tang Y, Luo S (2016) Rapid and efficient treatment of wastewater with high-concentration heavy metals using a new type of hydrogel-based adsorption process. Bioresour Technol 219:451–457

18. Ma J, Jiang Z, Cao J, Yu F (2020) Enhanced adsorption for the removal of antibiotics by carbon nanotubes/graphene oxide/sodium alginate triple-network nanocomposite hydrogels in aqueous solutions. Chemosphere 242:125188

19. Wang Z, Li T-T, Peng H-K, Ren H-T, Lou C-W, Lin J-H (2021) Low-cost hydrogel adsorbent enhanced by triethylamine and β-cyclodextrin for the removal of Pb (II) and Ni (II) in water. J Hazard Mater 411:125029

20. Li T-T, Xing M, Gao B, Ren H-T, Peng H-K, Zhang X et al (2021) Multiscale synergistic toughened pluronic/PMEA/hydroxyapatite hydrogel laminated aramid soft composites: Puncture resistance and self-healing properties. Composites Part B: Engineering 216:108856

21. Li T-T, Zhang Y, Ren H-T, Peng H-K, Lou C-W, Lin J-H (2021) Two-step strategy for constructing hierarchical pore structured chitosan–hydroxyapatite composite scaffolds for bone tissue engineering. Carbohydr Polym 260:117765

22. Chen Y, Peng J, Xiao H, Peng H, Bu L, Pan Z et al (2017) Adsorption behavior of hydrotalcite-like modified bentonite for Pb2+, Cu2+ and methyl orange removal from water. Appl Surf Sci 420:773–781

23. Liu X, Cheng C, Xiao C, Shao D, Xu Z, Wang J et al (2017) Poly-aniline (PANI) modified bentonite by plasma technique for U (VI) removal from aqueous solution. Appl Surf Sci 411:331–337

24. Nayak AK (2010) Hydroxyapatite synthesis methodologies: an overview. International Journal of ChemTech Research 2(2):903–907

25. Abollino O, Giacomino A, Malandrino M, Mentasti E (2008) Inter-reaction of metals ions with montmorillonite and vermiculite. Appl Clay Sci 38(3-4):227–236

26. Sellaoui L, Soetaredjo FE, Ismadji S, Bonilla-Petriciolet A, Belver L, Prato M et al (2017) Novel insights into the adsorption mechanism of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chemistry–A European Journal 7(6):1281–1288

27. Bergaoui M, Nakhlia A, Benguerra Y, Khalfaoui M, Ertorh Y, Trains M (2014) Cysteine-grafted nanowoven geotextile: A new and efficient material for heavy metals sorption–Part B. Journal of environmental management 143:99–105

28. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156(1):2–10

29. Dada A, Olatekun A, Olutunya A, Dada O, Langmuir (2012) Frendlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry 3(1):38–45

30. Liu Y, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chem Soc Trans 45(8):3202–3209

31. Jiang M-q, Wang Q-p, Jin X-y, Chen Z-l (2009) Removal of Pb (II) from aqueous solution using modified and unmodified kaolinite clay. J Hazard Mater 170(1):332–339

32. Lui J, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chemistry–A European Journal 7(6):1281–1288

33. Jiang M-q, Wang Q-p, Jin X-y, Chen Z-l (2009) Removal of Pb (II) from aqueous solution using modified and unmodified kaolinite clay. J Hazard Mater 170(1):332–339

34. Dada A, Olatekun A, Olutunya A, Dada O, Langmuir (2012) Frendlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry 3(1):38–45

35. Liu Y, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chem Soc Trans 45(8):3202–3209

36. Lui J, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chemistry–A European Journal 7(6):1281–1288

37. Bergaoui M, Nakhlia A, Benguerra Y, Khalfaoui M, Ertorh Y, Trains M (2014) Cysteine-grafted nanowoven geotextile: A new and efficient material for heavy metals sorption–Part B. Journal of environmental management 143:99–105

38. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156(1):2–10

39. Dada A, Olatekun A, Olutunya A, Dada O, Langmuir (2012) Frendlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry 3(1):38–45

40. Lui J, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chem Soc Trans 45(8):3202–3209

41. Lui J, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chemistry–A European Journal 7(6):1281–1288

42. Bergaoui M, Nakhlia A, Benguerra Y, Khalfaoui M, Ertorh Y, Trains M (2014) Cysteine-grafted nanowoven geotextile: A new and efficient material for heavy metals sorption–Part B. Journal of environmental management 143:99–105

43. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. Chem Eng J 156(1):2–10

44. Dada A, Olatekun A, Olutunya A, Dada O, Langmuir (2012) Frendlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry 3(1):38–45

45. Liu Y, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chem Soc Trans 45(8):3202–3209

46. Lui J, You CC, Li B (2001) Synthesis and molecular recognition of novel oligo (ethyleneamidino) bridged bis (β-cyclodextrin) and their copper (II) complexes: enhanced molecular binding ability and selectivity by multiple recognition. Chemistry–A European Journal 7(6):1281–1288

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.