Synthesis of magnetic crosslinked starch-graft-poly(acrylamide)-co-sodium xanthate and its application in removing heavy metal ions

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ABSTRACT
This paper describes the synthesis and characterisation of a magnetic crosslinked starch-graft-poly(acrylamide)-co-sodium xanthate (M-CSAX) nanocomposite based on magnetic starch (MCS), acrylamide (AM) and sodium xanthate that underwent heavy metal ions removal in response to an external magnetic field. The material was prepared using magnetic particle Fe₃O₄ nano flakes (NFs) together with vinylated starch and poly(acrylamide)-co-sodium xanthate via an ultrasound-assisted radical crosslinking/polymerisation reaction. MCS was synthesised by a direct compounding method using Fe₃O₄ NFs as nuclear and vinylated starch as shell. The obtained M-CSAX has a saturation magnetisation value of 19.21 emu·g⁻¹. Flocculation experiment results showed that the composites have functions of removing both turbidity and heavy metal ions from aqueous solution, and can adsorb 78.3% of Pb²⁺ and 63% of Cu²⁺ from the corresponding salt solutions. The findings of the present work highlight the potential for using M-CSAX as an effective and recyclable adsorbent for wastewater treatment.

1. Introduction
Exposure to heavy metals such as Cd(II), Pb(II), Co(II) and Ni(II), even at trace level, has been linked with risk for human developmental disturbance, kidney damage, various cancers, and death in some cases [1]. Considerable efforts have been made to develop effective treatment techniques for removing heavy metal ions from water. Flocculation is a process that makes finely divided particles aggregate and form large flocs which can then be settled and separated from water [2].

The adsorption technique is the most frequently studied and industrially adopted technique [3], an efficient strategy of designing a magnetic-separable flocculant absorbent has been highly demanded. At present, magnetic separation as a promising strategy has attracted much attention, because it can be used for easy separation under an applied magnetic field. The application of magnetic nanoparticles as adsorbent materials in
solving environmental problems has received great attention due to their unique physical and chemical properties, which make them superior to traditional adsorbents [4,5]. Nano-sized magnetic particles are considered as potential adsorbents for aqueous heavy metals due to their high surface area and the unique advantage of easy separation under external magnetic fields [6]. To further facilitate the adsorption affinity, surface modification, including physical coating and covalent binding, has often been explored to enable specific metal complexation [7,8]. For example, amino-functionalised Fe₃O₄@SiO₂ magnetic nanomaterial with a core–shell structure was developed by Tang et al., aiming to remove heavy metal ions from aqueous media [9]. Humic-acid-coated Fe₃O₄ nanoparticles synthesised using a coprecipitation method were found to effectively adsorb Hg(II), Pb(II), Cd(II), and Cu(II) ions from water [10].

The functionalisation and organisation of magnetic nanoparticles into complex mesostructured assemblies has generated considerable interest as a novel approach to materials’ syntheses. Encapsulation of magnetic particles with preformed natural or synthetic polymers is a simple and classical method to prepare magnetic polymeric particles. Starch is a natural polymer with important applications in biotechnology. It is obtained from renewable sources and offers important advantages such as low cost and the ability to replace some synthetic polymers [11]. Crosslinking starch with epichlorohydrin (EPI) is the most common method used in the preparation of polysaccharide-based derivatives. A synergetically acting new flocculant on the basis of starch-graft-poly(acrylamide)-co-sodium xanthate (CSAX) has been synthesised by our group. It was formed by grafting copolymerisation of crosslinked corn starch, acrylamide (AM), and sodium xanthate, using EPI as crosslinking agent and ceric ammonium nitrate (CAN) as polymerisation initiator in aqueous solution. Therefore, the combination of starch with magnetic particles which further creates a smart hydrogel is an excellent alternative in the production of new materials that may be used in the release of more sophisticated pollution.

To the best of our knowledge, CSAX has never been introduced to any magnetic adsorbents for the removal of heavy metals. Therefore, the objectives of this study are to synthesise and characterise a novel magnetic crosslinked starch-graft-poly(acrylamide)-co-sodium xanthate (M-CSAX) and to compare the adsorption abilities of heavy metals before and after modification by using batch techniques.

This work aims at preparing a starch-based magnetic flocculant that undergoes heavy metal adsorption in response to an applied magnetic field, which could be separated quickly after absorbing heavy metal ions with a magnet. Fe₃O₄ nanoflakes (NFS) were synthesised using a magnetic field-induced method, where starch was vinyl-modified with a methacrylate compound and subsequently crosslinked and polymerised outside of Fe₃O₄ NFSs. Then, the magnetic crosslinked starch (M-CS) was further vinyl-modified to magnetic crosslinked starch-graft-polyacrylamide (M-CSA) and subsequently to M-CSAX.

2. Experimental

2.1. Materials and equipment

Pure Fe plate (99.6% purity) was supplied by Shanghai Zhongyu Co., Ltd., and corn starch (Food grade) was supplied by packinghouse. α-Amylase was from Xiasheng Corp.
Acrylamide (AM, AR, Shanghai Chemical Reagent Factory) and ceric ammonium nitrate (AR, Beijing Chemical Reagent Corp.) were used as graft monomer and initiator, respectively. Kaolin, EPI, acetone (AR, Tientsin Chemical Reagent Factory, Tientsin), and other compounds were used as purchased. All solutions were prepared with deionised (DI) water. Transmission electron microscopy (TEM) was performed with a JEOL100CX model transmission electron microscope at 100 kV accelerated voltage and the observations were carried out after retrieving the slices onto Cu grids. Fourier transforms infrared (FT-IR) spectra of the composites in KBr pellets were recorded on an EQUINOX55 FT-IR spectrometer (Bruker). Nitrogen adsorption/desorption analysis was measured at a liquid nitrogen temperature (77 K) using a micromeritics ASAP 2010 M instrument. X-ray diffraction studies were performed by using D/max-2400 diffraction X-ray diffractometer (Rigaku) with CuKa radiation (λ = 0.154 nm) operated at 40 kV and 30 mA. The weight loss temperature of the nanocomposites was determined with a Perkin-Elmer thermogravimetric analyzer (TG-DTA; model SSC-5200) from 20 to 800 °C under nitrogen atmosphere (10 °C/min). The rate of turbidity removal and the rate of Cu²⁺/Pb²⁺ removal of a water sample were measured by the turbidity meter (Hanna instruments, Italy) and 220 FS atomic absorption spectrometer (made in corp. Varian, USA), respectively.

2.2. Synthesis section

2.2.1. Preparation of magnetic crosslinked starch (M-CS)
Fe₃O₄ NFs were synthesised using a magnetic field-induced method improved from former research [12]. In a typical procedure, 8 g of pure iron powder was dissolved in 100 mL of 3.0 M nitric acid in a quartz reactor under vigorous stirring, the reactor was moved into a heating mantle of 50 °C for 20 min, at the bottom of which was fixed a cylindrical magnet with an intensity of about 6000 Gs. Then, the pH value of the reaction system was adjusted to about 10 by ventilation of NH₃ and air (the ratio of ammonia:air was about 10:1), respectively. After that, the system was heated to 80 °C and kept for 4 h. The obtained black powder was repeatedly washed with DI water and absolute ethanol, followed by drying at 40 °C under vacuum for 6 h.

Twelve gram of the obtained Fe₃O₄ NFs was ultrasonically treated for 5 min with 50 mL 0.02 mol/L HCl aqueous solution, separated and washed with DI water, and then homogeneously dispersed in the mixture of starch (5 g) and sodium chloride solution (15 mL, 0.2 M). To prepare the hydrogel nanocomposite, starch was vinyl-modified for the introduction of covalent crosslinks and subsequently crosslinked/polymerised with vinyl monomers. The slurry was heated to 30 °C and kept at a constant temperature in water bath. Fifteen minutes later, KOH solution (6 mL, 2.5 M) was added and then EPI was added dropwise for about 5 min. After 8 h, the suspension slurry was adjusted to pH 7.0 with 0.5 M HCl solution, and then washed with water and ethanol several times, dried in vacuum at 60 °C for 12 h, and the M-CS was obtained.

2.2.2. Preparation of magnetic crosslinked starch-graft-polyacrylamide (M-CSA)
M-CSA samples were prepared according to the following procedure: M-CS (5 g) was treated with 20 mL distilled water to prepare a uniform slurry, then 40 mL 0.9 M AM solution was added. The mixture was placed in a 250 mL three-necked flask and heated to 45 °C. Nitrogen gas was passed through the reaction mixture for 5 min to remove
dissolved oxygen. A predetermined volume of $6.7 \times 10^{-4}$ M CAN solution was added. The polymerisation was continued under constant stirring and in a nitrogen atmosphere for 3 h. The polymer was precipitated in acetone and the crude products dried in a vacuum oven at 60 °C.

### 2.2.3. Preparation of M-CSAX

M-CSA (4.0 g) was placed in a sealed conical flask at 30 °C and xanthated by the dropwise addition of 40 mL 2 M NaOH and 3 mL CS$_2$ (0.05 M). The mixture was stirred with a mechanical stirrer for 2 h and then dispersed by ultrasonic until it turned saffron yellow. The product (M-CSAX) was cooled to room temperature, precipitated, filtered, and washed with 50% aqueous acetone and distilled water, respectively, then dried at 25 °C to constant weight.

### 2.3. Turbidity and heavy metal ion removal of CSAX

CSAX (10 g/L), 5% (w/v) kaolin suspension, and 0.0625 mol/L CuSO$_4$ solution were prepared as stock solutions. For each test, 1 L water, 1 mL kaolin suspension, and 3 mL CuSO$_4$ solution were added to a 1.5 L jar. The jars were placed on the six-joint-stirrers and agitated by stirring blades in the suspension. The different dosage of CSAX solution was added into different jars, which were stirred at uniform speed of 140 rpm for 2 min, and then at 40 rpm for 10 min. Then, the precipitates were allowed to settle for 10 min and the supernatant removed. The removal of Pb$^{2+}$ was tested as comparison using Pb(NO$_3$)$_2$ with the same concentration as CuSO$_4$. The rates of turbidity removal and the rate of heavy metal ions (Cu$^{2+}$ and Pb$^{2+}$) removal of a water sample was measured and calculated as

$$ T\% = 100 \left( \frac{T_0 - T_1}{T_0} \right) $$

and

$$ R\% = 100 \left( \frac{R_0 - R_1}{R_0} \right) $$

where $T_0$ and $T_1$ are the turbidity of initial suspension and supernatant, respectively. $R_0$ and $R_1$ are the concentration of the metal ions initial suspension and supernatant, respectively.

### 3. Results and discussion

The preparation of the M-CSAX microstructure involves the coating of starch in the presence of Fe$_3$O$_4$ NFs and the further chemical polymerisation. To clarify the relationship between the Fe$_3$O$_4$ and starch during the formation of the M-CSAX, we analysed the vibrating sample magnetometer (VSM) and Brunauer-Emmett-Teller (BET) of products with different content of starch while the amount of Fe$_3$O$_4$ NFs remained unchanged, from which we could see that the optimum mass ratio of Fe$_3$O$_4$ NFs to starch was 12:5. Please refer to Table 1 for the detailed preparation conditions for typical samples.

| Sample no. | Fe$_3$O$_4$ NFs (g) | Starch (g) | VSM (emu g$^{-1}$) | BET (m$^2$ g$^{-1}$) |
|------------|---------------------|------------|-------------------|---------------------|
| S1         | 12                  | 3          | 24.3              | 88.4                |
| S2         | 12                  | 4          | 22.9              | 90.9                |
| S3         | 12                  | 5          | 19.6              | 104.2               |
| S4         | 12                  | 6          | 16.1              | 92.6                |
| S5         | 12                  | 7          | 14.3              | 89.8                |
The synthetic pathway and morphologies of M-CSAX are depicted in Figure 1. When starch was added into the preparation system dispersed with Fe₃O₄ NFs, flower-like structural M-CS were formed and further grew into flakes inlaid with polymer bump after polymerised with AM. The obtained M-CSA were xanthated to obtain the M-CSAX composite, which is magnetic Fe₃O₄ flakes coated by CSAX.

To investigate the morphology, particle size and structure of the synthesised samples, SEM images of Fe₃O₄ NFs, M-CS, M-CSA and M-CSAX together with the corresponding TEM (Fe₃O₄ NPs and M-CSAX) images are shown in Figure 2. Figure 2(a) shows the SEM and TEM micrographs of the Fe₃O₄ NFs, respectively, from which one can see hierarchically nanostructured flakes self-assembled into clusters with a thickness of approximately 20 nm (Figure 2(a,b)). To further demonstrate the nucleating roles the Fe₃O₄ NFs played and the coating roles the crosslinked starch (CS) played, the morphology of M-CS and M-CSA were tested using SEM, as shown in Figure 2(c,d). First, Fe₃O₄ NFs were wrapped into the core–shell structure by the uniformly deposited CS molecules (Figure 2(c)). Second, after AM and CAN were added respectively, the strong static interactions between the –NH₂ group in AM molecules and the –NH₂ group in M-CS, AM molecules were absorbed on the surface of M-CS NFs and polymerised with the initiation of CAN (Figure 2(d)). Then, the CSA molecules on the surface of Fe₃O₄ NFs have a good chance to be xanthated by CS₂ under alkaline environment, forming a magnetic porous structure, M-CSAX (Figure 2(e,f)). Figure 2(g) shows the EDX pattern of the M-CSAX. The atomic ratio of Fe:O is 1:1.26, which is very close to the desired ratio of 1:1.33 for Fe₃O₄. The signals of C and Cu should come from the carbon-coated copper grids and the signals of S should come from CS₂. The selected area electron diffraction (SAED) pattern from a region marked in Figure 2(f) by a square is shown in Figure 2(h). The concentric rings consisting of distinct spots are a result of many small single crystals and suggest the crystalline nature of Fe₃O₄ NFs. The diffraction samples were also consistent with XRD result.

The prepared Fe₃O₄, M-CSAX and pure CSAX (for the synthetic process, see our previous work [13]) sample were characterised by FTIR technique, as shown in Figure 3. The strong IR band at 576 cm⁻¹ is characteristic of the Fe–O vibrations. The peaks at 1623 and 2931 cm⁻¹ were attributed to C=C and C–H vibrations, respectively, 1015 and 1154 cm⁻¹ to C–OH stretching and –CO stretching vibration, respectively [14], and 1431 cm⁻¹ was due to the –CH₂ scissoring vibration. The bands at 917 and 765 cm⁻¹ resulted from the pyranose ring vibrations. The peak at 3435 cm⁻¹ implied the existence of hydroxyl groups and the absorbed H₂O molecules [15]. The FTIR spectra of M-CSAX shows the composites containing both the characteristic spectral absorption peaks of
Figure 2. SEM images of Fe$_3$O$_4$ NFs (a), M-CS (c), M-CSA(d) and M-CSAX (e, arrows show the coated Fe$_3$O$_4$ NFs), TEM images of Fe$_3$O$_4$ (b) and M-CSAX (f). (g) The EDX spectra of the obtained M-CSAX. (h) SAED of the M-CSAX.
Fe₃O₄ and CSAX; combining the results of SEM and TEM images, we can confirm that the binary compound finally obtained were Fe₃O₄@CSAX composites. Besides, for the spectra of Fe₃O₄@CSAX, we could see that some changes took place compared to CSAX and Fe₃O₄; this is due to the presence of ferrite which destroyed the intramolecular –OH orderly arrangement in the crosslinking starch.

Figure 4 shows the magnetisation hysteresis loops of the obtained Fe₃O₄ NFs, M-CSA and M-CSAX at room temperature. The samples exhibit typically superparamagnetic features with a negligible coercivity and remanence. These results indicated that the particles are superparamagnetic at room temperature, meaning that the thermal energy could overcome the anisotropy energy barrier of a single particle, and the net magnetisation of the particle assemblies in the absence of an external field was zero. With the organic coating process, the saturation magnetisation (Ms) values decreased from 52.77 emu·g⁻¹ (Fe₃O₄ NFs) to 27.12 emu·g⁻¹ (M-CSA) and further to 19.21 emu·g⁻¹ (M-CSAX), decreasing with the content of the organic substances. It has a relatively high value as an absorbent material compared to the results in the literature [16,17]. For example, magnetic hydroxamic acid-modified polyacrylamide/Fe₃O₄ adsorbents synthesised by Zhao have saturation magnetisation values of 15.93 emu/g (magnetic polyacrylamide/Fe₃O₄ adsorbent) [18].

Nitrogen sorption measurements were conducted to further characterise the pore parameters of the products. The liquid nitrogen adsorption/desorption isotherms of M-CSAX are shown in Figure 5. The loops of the sample exhibit typical IV-type isotherms with broad H3-hysteresis according to the International Union of Pure and Applied Chemistry (IUPAC) classification, which is typical for mesoporous materials that exhibit capillary condensation and have mesoporous pore sizes with narrow size distributions [19]. The BET surface area and total pore volume of M-CSAX were calculated to be 104.2 m²/g and 0.37 cm³/g, respectively. The pore size distribution curves (inset in Figure 5)

Figure 3. FTIR spectra of Fe₃O₄, CSAX and M-CSAX sample.
further confirmed that the average pore size of M-CSAX was 54.6 nm. Information on macropores (>100 nm) cannot be obtained by N₂ adsorption–desorption analysis, but macroporous structures can be observed in the SEM images (Figure 1(e)). The larger surface areas provided more sites for pollution adsorption, making the adsorption process more efficient.

Figure 4. VSM patterns of the obtained M-CSAX, M-CSA and Fe₃O₄ NFs.

Figure 5. Nitrogen adsorption–desorption isotherm of the typical M-CSAX.
Thermogravimetrics (TG) were adopted to analyse the uptake of CSA or CSAX in the composites. Figure 6 shows the TG results of the M-CSA and M-CSAX heat-treated under N2 atmosphere. In the dehydration between 30 and 300 °C, the weight loss represents two different types of water molecules and any physically adsorbed species [20]. One represents dehydration of external water molecules while the second denotes those that escaped from organic compounds and crystal lattice [21]. From 300–650 °C, M-CSA and M-CSAX slowly lost about 37% and 47.5% weight, respectively, which were associated with the thermal degradation of polymers (decomposition of functional groups and carbonisation of main chains) [22]. Compared with M-CSA, the extra weight loss for M-CSAX can be attributed to the former coat of Fe3O4 NFs by polymer, meaning that the dehydrated CSA outside of Fe3O4 NFs was xanthated by NaOH and CS2. The magnetite nanoparticles weakened the interchain interactions and led to polymer decomposition at lower temperatures. Our explanation for this dependence is as follows: the perturbation that the particles introduced affected the three-dimensional (3-D) structure of the polymer. This perturbation weakened the van der Waals interactions in, and therefore the stability of, the polymer, which was reflected by the lowering of the decomposition temperature.

Since the molecular chain of CSAX includes a large number of hydroxyl groups, it can form hydrogen bond with the substances containing –NH2 and –COOH groups such as amino acid in water, which is able to absorb and sediment the substances so as to remove the organics and improve the removal rate of COD [23]. Depending on the larger number of polar groups contained by M-CSAX, removal Cu2+ can be obtained by several mechanisms such as physical adsorption, ion exchange, electric neutralisation, and chelation [24].

The crystallinity and phase purity of the as-prepared Fe3O4 nanoparticles were examined by XRD measurements. As shown in part (a) of Figure 7, the sample does not show any significant peaks, indicating that the materials might be still amorphous or the quantity of the crystalline particle is below the limit of detection. In parts (b) and (c) of Figure 7,
the strong and sharp reflection peaks suggest that the prepared samples during ultrasonic radiation were well crystallised. The diffraction peaks at 2 theta values of 31.11, 36.29, 44.08, 53.76, 57.35, and 62.76 can be ascribed to the reflection of (220), (311), (400), (422), (511), and (440) planes of the Fe₃O₄, respectively [25]. XRD of the CSAX are shown in Figure 7(d), indicating that no obvious peaks could be observed except for a wide peak at 2 theta = 18.92. Similar peaks to the CSAX sample and Fe₃O₄ NFs were observed in the XRD pattern of sample M-CSA and M-CSAX, indicating that after the coating process, the surface of Fe₃O₄ NFs was coated with polymer and the crystallite phase of Fe₃O₄ was well preserved during the reaction. We can also see from the XRD pattern of M-CSAX that after the drug-loading process, the peak of the amorphous structure became stronger while those of the Fe₃O₄ NF crystal became weaker, reflecting that the proportion of Fe₃O₄ NFs in the composition was decreased, which means that the M-CSA has been further xanthated under the experimental conditions.

Based on the above characterisation (SEM, TEM, FTIR, BET and XRD), we can say that a M-CSAX nanocomposite with a structure of Fe₃O₄ NPs core and porous CSAX shell has been successfully synthesised. The decontamination mechanism of M-CSAX can be seen in Figure 8. The adsorption of pollutants in wastewater may include two ways: pollutants can be adsorbed easily by the porous structure on the one hand, and those heavy metal ions can form complexes with CSAX shell on the other. Furthermore, the composite carrying pollutants can be quickly separated by applying a magnetic field.

In order to compare the similarities and differences between CSAX and M-CSAX in removing the turbidity, we carried out the test under the same experimental conditions. When CSAX reached the highest rate of turbidity removal (79%), the rate of M-CSAX was only 51%. This was because the M-CSAX has a higher density for the introduction of Fe₃O₄ NPs core (Figure 9). The M-CSAX was utilised for the removal of toxic Pb²⁺ and
Cu$^{2+}$ metal ions from aqueous solutions (Figure 10). The effect of the polymer dose on the percentage adsorption of the metal ions was examined at various polymer doses varying from 20 to 60 mg. At the beginning, it was observed that the metal ions uptake increased with increasing polymer dosage until the maximum percent adsorption was reached. The M-CSAX was found to adsorb 78.3% of Pb$^{2+}$ and 63% of Cu$^{2+}$ from the corresponding salt solutions at doses of 20 and 45 mg, respectively. This increase in the percentage adsorption was due to the availability of more adsorption sites and increased surface area with increasing adsorbent dose. No noticeable increase in the percentage adsorption was observed with further increase in the dose of adsorbent. This was due to the fact that, after maximum adsorption, the concentration of metal ions became limiting in the system.

The pH values of the wastewater samples containing 20 mg/L copper ions were adjusted to various values from 3.0 to 6.0 by using hydrochloric acid, and then different
dosages of CSAX were added. The results are shown in Figure 11. It can be concluded that the removal rate of copper ions increases with the increasing of pH. When the pH is raised, more xanthogenic acid groups of macromolecules ionise to negative xanthogenic acid radical groups, so that the chelation between xanthogenic acid radicals and copper ions increases.

Figure 10. Adsorption of Pb$^{2+}$ and Cu$^{2+}$ using the M-CSAX.

Figure 11. Effect of pH on removal of copper ions.
Figure 12 shows the digital photographs of M-CSAX and CSAX after adsorbing the heavy metals. The separation of M-CSAX from suspension under an external magnetic field needs only 5 s, while the same bottle of CSAX sample still has flocs floating after 90 s. From this obvious contrast, we can see that M-CSAX has the advantage that it could be separated quickly by a magnet and significantly shorten the time of removing pollutants.

4. Conclusions

An efficient eco-friendly magnetic flocculant, M-CSAX, with a unique porous structure was designed and successfully prepared by coating and further polymerisation reaction outside of Fe₃O₄ NPs, providing a new approach to synthesis of magnetic composites using the cheap biomaterials as basic source. The performances of M-CSAX in wastewater treatment were evaluated by flocculation experiment. The results show that the M-CSAX not only acts as a floculant but also has the capacity to trap heavy metal ions. The high turbidity removals in the kaolin suspension as well as the magnetic properties make the M-CSAX an excellent candidate as efficient adsorbent for the treatment of industrial wastewater.
Disclosure statement

No potential conflict of interest was reported by the authors.

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