



Original Research

Magnetic poly(acrylic acid)-based hydrogels for rapid ammonium sorption and efficient sorbent separation from sewage

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ABSTRACT

Ammonium sorption and recovery processes typically take place in conventional packed columns, with a configuration that enables maximum sorption by the sorbents. However, batch or semi-continuous operations in packed columns have associated issues such as scaling and frequent backwashing requirements, which are economically prohibitive. As an alternative, ammonium sorption could occur in well-mixed continuously stirred tanks, which would allow for the ammonium sorption process to be retrofitted in existing wastewater treatment plants, provided that efficient sorbent separation can be achieved. This study demonstrates, for the first time, the preparation of magnetic poly(acrylic acid)-based (PAA) ammonium sorbents through the incorporation of magnetic (Fe₃O₄) nanoparticles (MNP) produced via scalable and cost-effective electrochemical synthesis. The MNP and PAA hydrogels were synthesized independently and the MNPs subsequently integrated into the PAA hydrogel network by particle diffusion and physical entrapment. No adverse effects on swelling and ammonium sorption following immersion in either synthetic or real sewage were observed after MNPs were incorporated into the hydrogels. Importantly, PAA-MNP hydrogels demonstrated high ammonium sorption efficiencies (80–93%) in real sewage and achieved rapid ammonium recovery of 73 ± 1.1% within 15 min of mild acid washing (pH 4) 15 min at a maximum recovery.

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1. Introduction

Sewage comprises 20 million tons of ammonium annually [1]. As a means to create a more sustainable society for the 21st century, ammonium recovery technologies are being developed to move away from the traditional biological conversion of ammonium to inert N₂ gas and shift toward the circular use of ammonium as a valuable resource. In addition to recovering a valuable resource, recovering ammonium potentially avoids N₂O emissions, environmental externalities, and technological limitations associated with existing biological ammonium conversion processes, as discussed in our previous study [2].

Adsorption is one of the most suitable techniques to recover ammonium from diluted streams (30–50 mg/L) such as sewage. Ammonium sorbents such as zeolites and ion-exchange resins have been tested in both lab- and full-scale, reporting excellent results in terms of ammonium removal (>98%) and reducing ammonium concentrations to below 1 mg/L [3–5]. Ammonium recovery using zeolites and ion-exchange resins typically takes place in packed columns [3,6–11]. However, ammonium recovery in packed columns is limited to either batch or semi-continuous mode which disqualifies it as an option for existing wastewater infrastructures since it cannot be retrofitted into the mainline operation of most treatment plants. An alternative strategy would be to introduce a suitable sorbent into mainstream wastewater treatment line in stirred tanks (and also in carousels and activated sludge tanks). This would eliminate the need for backwashing and allow for sorption in a simple configuration that can easily be incorporated into

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existing wastewater treatment plants [12]. An important requirement for such a configuration is a means to separate the sorbents from the liquid stream efficiently once the process is complete. While filtration and centrifuge-based techniques are suitable, they are relatively energy-intensive and have a high maintenance requirement due to filter fouling and caking [13]. Moreover, centrifuge-based separation methods would incur enhanced attrition of the sorbents, thus reducing their overall service life.

In our previous study, PAA-based hydrogel sorbents were shown to achieve rapid ammonium sorption from sewage at a very short retention time (~10 min) [14]. PAA hydrogels also demonstrated reusability with minimal decrease in sorption capacity after five sorption-desorption cycles using 1 M HCl as desorbing agent and regenerant. The promising properties of PAA hydrogels as ammonium sorbents, coupled with their low density (1 g/mL), would make them suitable for use in continuously stirred tanks, provided that a practical sorbent separation method is available. The other advantage of PAA hydrogels, and hydrogels in general, is their expandable polymer network [15–17]. This allows the hydrogels to take up inorganic components as long as their size is smaller than the hydrogel network. In theory, magnetic nanoparticles could be entrapped within the hydrogel network thereby opening up opportunities for solid-liquid separation by magnetic pulldown [18–21]. Indeed, solid-liquid separation by magnetic pulldown is being implemented as a pre-treatment for dissolved organic carbon removal in 37 full-scale drinking water production plants using macro-porous resin beads incorporated with magnetic iron oxide nanoparticles (MIEX®) [22–24]. We, therefore, hypothesized that it would be possible to produce magnetic ammonium sorbents from PAA with magnetic nanoparticles, which could be used for mainstream ammonium sorption followed by in-line sorbent separation using magnetic pulldown. This would eliminate the need for filtration systems and other complex separation techniques for recovering the sorbents from mixing tanks [25–32].

A recent study demonstrated a cost-effective and scalable, electrochemical method to produce magnetic nanoparticles (MNPs) in the form of hexagonal platelet-like Fe_3O_4 particles at industrially relevant concentrations (e.g. 10 g MNP-Fe/L) [33]. These MNPs could be incorporated into the PAA hydrogels in two ways. First, the MNPs could be added during the free-radical polymerization and crosslinking of acrylic acid with a crosslinking agent of choice. The MNPs can also be chemically reacted to the polymer matrix leading to a stable and even dispersion of MNPs inside the polymer beads, the latter being similar to the patented synthesis design for MIEX® resins [34]. However, such an approach is not suitable for synthesizing PAA hydrogels as MNPs could potentially disrupt the polymerization and gelation process of PAA, which may result in unpredictable properties such as brittleness, incomplete crosslinking, and inhomogeneous hydrogel structure [20,35]. The second method would be to incorporate MNPs into pre-formed PAA hydrogels. This preparation method is a common practice and the preferred approach when loading nano-sized drug compounds inside hydrogels for biomedical applications because it does not require chemical alteration to entrap drug compounds [36,37].

Based on the above, it was hypothesized that MNPs can be loaded into the pre-formed PAA hydrogels by particle diffusion in water and at room temperature and then be physically entrapped by the hydrogel network. To prove this concept, MNPs were integrated into the PAA hydrogel network using a simple, chemical-free, heat-free, and diffusion-driven method, whereby the MNPs and PAA hydrogels were synthesized independently. To the best of our knowledge, the feasibility of such a straightforward approach in the preparation of magnetic hydrogel sorbents for wastewater applications has not been demonstrated before. This study also explored the effect of MNPs on the magnetic response behaviour of

the hydrogels, swelling properties, ammonium sorption performance, and recoverability of ammonium from the hydrogels through mild acid washing at pH 4.

2. Materials and methods

A complete set of detailed materials, experiments, spectral data, and sorption experiments are available in the Supplementary Information.

2.1. Materials

Acrylic acid (AA) containing 200 mg/L monomethyl ethyl hydroquinone inhibitor (Sigma Aldrich, Australia) was used as the monomer. The initiator, ammonium persulfate (APS) and crosslinker, *N,N'*-methylenebisacrylamide (MBA) were purchased from Sigma Aldrich. For synthetic wastewater preparation, reagent grade calcium chloride dehydrate was purchased from Sigma Aldrich, Australia; potassium dihydrogen orthophosphate and magnesium sulfate heptahydrate from Chem Supply, Australia; sodium chloride and ammonium chloride were purchased from Merck, Australia. Sulfuric acid (98 w/w%) from Merck (Australia) was used as the regenerant. All materials were used as received.

2.2. Synthesis and characterization of PAA-MNP hydrogels

PAA hydrogels and MNPs were synthesized separately following the procedures detailed in the sections below.

2.2.1. Synthesis of PAA hydrogels

The PAA hydrogels were synthesized by free radical polymerization using solution polymerization [38]. A 20 g monomer solution containing 6.87 g AA, 0.011 g APS, 0.71 g MBA and 12.42 g distilled water was mixed thoroughly using a magnetic stirrer at room temperature. Once dissolved, the monomer solution was deoxidized by bubbling with N_2 gas for 20 min, and then the solution was poured into silicone-coated test tubes with 15 mm internal diameter and 125 mm length. The glass tubes were then capped and placed in an oil bath at 60 °C for 2 h to allow polymerization. After polymerization, the hydrogels were cut into 3 mm-thick discs and then immersed in 200 mL 100% w/v ethanol for 8 h, then 500 mL distilled water for 8 h. This washing procedure was repeated three times. After final washing with 200 mL ethanol, the hydrogels were filtered using a Büchner funnel with 120 μm Whatman filter paper and dried for 24 h at 60 °C. The dried hydrogel discs were crushed into small particles using mortar and pestle. The hydrogels were then immersed in 1 M NaOH solution (20 g dry hydrogel per L of NaOH solution) for 1 h at room temperature. Finally, the hydrogels were filtered using a Büchner funnel with a Whatman filter paper (120 μm) and soaked in 500 mL distilled water for 4 h to remove residual NaOH and then dried for 24 h at 60 °C.

2.2.2. Electrochemical production of magnetite (Fe_3O_4) nanoparticles

Magnetite nanoparticles (MNPs) were synthesized using an electrochemical-based production method, according to the procedures described in detail elsewhere [33]. In summary, MNPs were synthesized via electrochemical oxidation of sacrificial iron electrodes. The two iron plates used as both anode and cathode were submerged in 250 mL of 2 g/L NaCl solution in tap water as the electrolyte, with an applied current density fixed at 8 mA/cm² for 24 h. At the end of the experiment, a suspension of 10 g Fe_3O_4 -Fe/L in NaCl solution was obtained as a product. The electrolyte was discarded and the obtained MNPs were subsequently washed with

distilled water three times and dried in the oven at 50 °C for 12 h to obtain dried MNP powder.

2.2.3. Preparation of PAA-MNP hydrogels

Fig. 1a illustrates the preparation of PAA-MNP hydrogels. Aqueous suspensions of MNPs (0.06%, 0.12%, and 0.24% w/w) were prepared by dispersing dried MNP powder in 50 mL deionised water using an ultrasonic bath for 5 min. 3 g of dried PAA hydrogels were immersed in each dispersed MNP suspension immediately after sonication. The MNP particles were allowed to migrate into the PAA hydrogels via osmosis for 30 min, which was marked by a rapid change of colour in the PAA hydrogels from transparent to black and the solution turning from pitch black to grey. Lastly, the PAA-MNP hydrogels were dried in an oven at 60 °C for 48 h.

2.2.4. Characterization

Solid-State NMR was performed to characterize the PAA hydrogels (Bruker Avance III). X-ray diffraction (XRD) (qualitative and semi-quantitative) analysis of dried PAA-MNP hydrogels was performed to confirm the presence of Fe₃O₄ and to quantify the corresponding concentration of bound MNPs inside the PAA-MNP hydrogels. The XRD patterns were recorded in Bruker D8 diffractometer equipped with a (θ , 2θ) goniometer and a position-sensitive detector (Cu K α 1 radiation at $\lambda = 1.55$ Å). Reflections were collected within the [5–80°] 2θ range, with a step width of 0.02 and 1.2 s/step of collecting time. The resultant 2θ peaks were analysed with the embedded XRD software Diffrac.Eva (version 4) and matched with the ICDD PDF4+ 2019 database. Additionally,

semi-quantitative XRD analysis was conducted to determine the concentration (%) of MNPs bound inside the hydrogels as a result of PAA-MNP synthesis. Corundum (α -Al₂O₃, an internal standard) was used for all semi-quantitative measurements following a procedure described elsewhere [39].

The equilibrium swelling ratios of PAA-MNP hydrogels were evaluated in the following media: (i) distilled water, (ii) aqueous NH₄Cl solution (40 mg/L NH₄-N), (iii) synthetic wastewater, and (iv) sewage. The hydrogels were placed in a drying oven at 60 °C for 12 h before all swelling experiments. Dry PAA-MNP hydrogels (100 mg) were immersed in a 50 mL solution for 24 h and then separated using a vacuum-assisted filter unit with a 120 μ m Whatman filter paper. The swelling degree of the hydrogels was determined from the average of three measurements as the ratio of the mass of swollen hydrogel over dry hydrogel [40].

2.3. Batch sorption studies

2.3.1. Synthetic wastewater and sewage preparation

Synthetic wastewater was prepared using reagent grade calcium chloride dihydrate, potassium dihydrogen orthophosphate, magnesium sulfate heptahydrate, sodium chloride, and ammonium chloride. Characterizations of the synthetic wastewater used in the experiments are summarized in Table S1.

Sewage was collected from a local wet well in a residential zone in Brisbane, Australia. The collected sewage was immediately stored at 4 °C and used within seven days of collection. Before each sorption experiment, the wastewater was warmed up to ambient

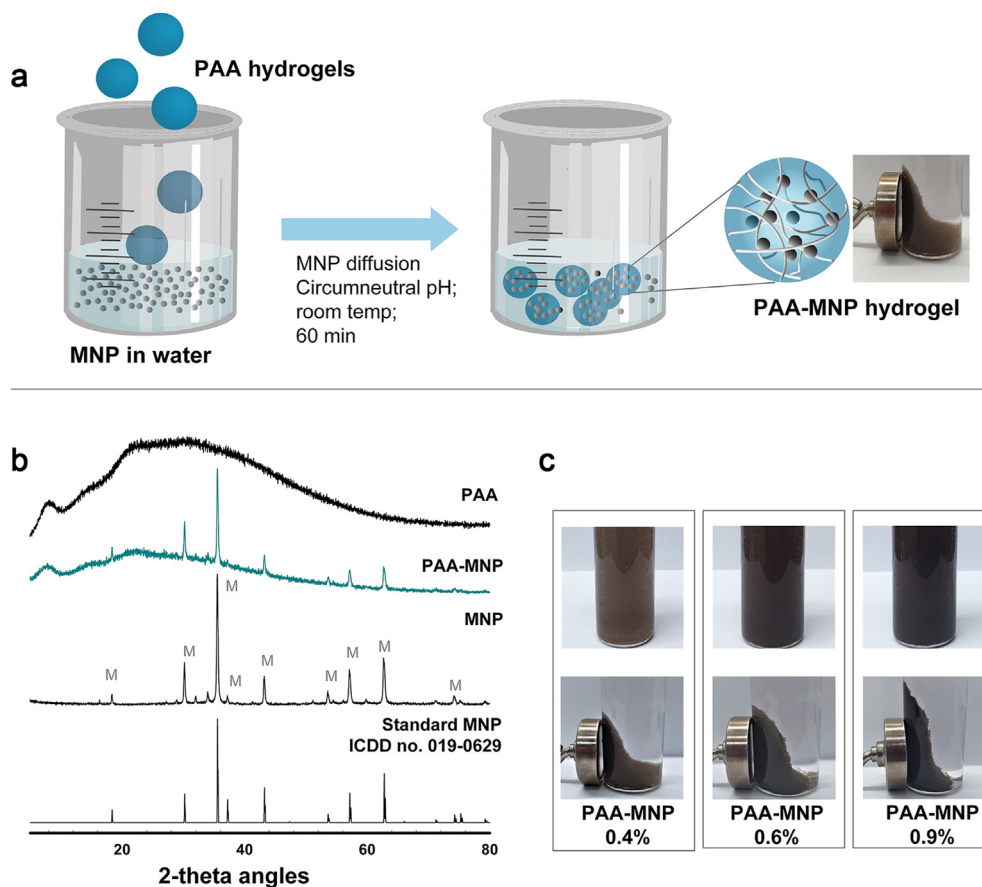


Fig. 1. (a) Schematic presentation of PAA-MNP hydrogel preparation (b) X-ray diffractograms of bare PAA hydrogels, PAA-MNP hydrogels, magnetic nanoparticles (MNPs) used in this study, and standard MNP from ICDD 2019 database (c) Demonstration of magnetic separation of PAA-MNP hydrogels from a 1.5% w/w aqueous suspension using a 25 mm neodymium magnet.

temperatures (22–24 °C). Table S2 shows the composition of the sewage used in the experiments.

2.3.2. Sorption experiments

Three sets of ammonium sorption experiments were performed in three media: (i) aqueous NH_4Cl solution (40 mg/L $\text{NH}_4\text{-N}$), (ii) synthetic wastewater (40 mg/L $\text{NH}_4\text{-N}$) and other competing cations, and (iii) real sewage. The pH of both synthetic wastewater and sewage were kept at circumneutral $\text{pH } 7 \pm 0.2$ during all sorption experiments since our previous study demonstrated that varying the initial pH did not impact the ammonium sorption performance of PAA hydrogels [14]. Furthermore, for this study, the duration of sorption was maintained at 60 min, owing to the rapid kinetics of the hydrogels in reaching equilibrium (<30 min), as previously demonstrated in our preceding studies [14,38].

PAA-MNP hydrogels (250 mg) were placed in 70 mL gamma sterile polypropylene cylindrical containers together with 50 mL of influent, corresponding to a hydrogel loading of 5 g/L. The mixture was gently stirred using an overhead stirrer at 90 rpm for 60 min. After sorption, the magnetic hydrogels were immediately pulled down using a 25 mm diameter neodymium-based disc magnet with a 22 kg pull force (Supplementary video). Subsequently, samples were taken from the supernatant via a syringe and filtered immediately using a 0.45 μm filter to measure the ammonium concentration. The filtration of the remaining supernatant using a 120 μm Whatman filter paper confirmed that all hydrogel particles were pulled down by the magnet (data not shown).

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.ese.2021.100097>

2.4. Ammonium recovery and material regeneration

Further experiments were performed to determine the regeneration ability of PAA-MNP hydrogels. A small volume of 1 M H_2SO_4 (250 g dry hydrogel per L of regenerant) was dropped on the ammonium-loaded hydrogels from the synthetic wastewater sorption experiment above. The hydrogels were slowly stirred with the regenerant by hand until they released the absorbed liquid, as signalled by a significant collapse of the hydrogel volume shortly after stirring. Subsequently, the released liquid from the hydrogels and the regenerant reached pH 4. After 15 min, the samples were collected from the liquid to determine the concentration of the recovered ammonium.

2.5. Chemical analysis and calculations

Flow injection analysis (FIA) was used to determine the concentrations of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, and $\text{PO}_4\text{-P}$ (QuickChem 8000, Lachat Instruments, USA). Soluble COD concentrations were determined using COD cuvette tests (Merck, range 25–1500 mg/L). Elements (e.g. Na^+ , Ca^{2+} , K^+ , Mg^{2+} , total Fe) were measured using inductively coupled plasma optical emission spectrometry (Optima 7300DV, PerkinElmer, USA).

The statistical difference in the swelling and sorption capacities between different PAA-MNP hydrogels was determined using one-way ANOVA at a 95% confidence level.

3. Results and discussion

3.1. PAA-MNP hydrogels characterization

Electrochemically-synthesized MNPs were integrated inside post-polymerized PAA hydrogels by osmosis to add magnetic responsiveness to the PAA hydrogels [20,41,42]. As shown in Fig. 1b, the XRD spectrum of pure PAA hydrogel is broad and lacks sharp

peaks, indicating that the PAA hydrogel has an amorphous structure. In contrast, the XRD spectrum of MNPs has clearly defined and sharp peaks, which is consistent with a highly crystalline structure [43,44]. The PAA-MNP hydrogel spectrum displays features of both amorphous and MNP crystalline structures, indicating that the MNPs have been successfully loaded into the PAA hydrogel.

Quantitative XRD analysis showed that loadings of 0.4–0.9 g MNP were entrapped per 100 g PAA hydrogel (Table S3). The low loadings may be due to the poor diffusion of MNPs into the PAA hydrogels [41], as well as the presence of larger size or aggregated MNPs [45,46] that are larger than the hydrogel matrix. The latter could not be confirmed with the experimental procedures performed in this study. Nevertheless, the MNP loadings achieved in this study were sufficient to impart strong magnetic properties to enable hydrogels to be separated efficiently and rapidly from the liquid stream using a simple setup using a standard neodymium magnet, as visualized in Fig. 1c. Lastly, the swelling experiments confirmed that the incorporation of MNP did not affect the swelling ratios of the hydrogels when submerged in synthetic wastewater ($p = 0.8$) and real sewage ($p = 0.6$) (Figure S2, Supplementary Information).

3.2. Ammonium sorption performance of PAA-MNP hydrogels

Fig. 2 shows the ammonium sorption performance of PAA-MNP hydrogels in NH_4Cl solution and synthetic and real sewage at a hydrogel loading of 5 g/L. Findings show that the ammonium sorption of the PAA-MNP hydrogels was the highest in the NH_4Cl solution (89–93%) and decreased to 80–83% range in synthetic and real sewage. Our findings are in agreement with previous studies on PAA hydrogels, attributing the satisfactory sorption ammonium performance of PAA hydrogels to electrostatic interactions between COO^- groups and NH_4^+ and other cations [14,47]. Due to this mechanism, other cations in sewage (Mg^{2+} , Ca^{2+} and K^+) can also compete with COO^- sorption sites in the hydrogel, which resulted in lower sorption performance in sewage than in pure ammonium chloride solution [14,47]. Despite this, the ammonium sorption performance of PAA-MNP hydrogels in sewage (80–83%) within 30 min, is already well within the range of the sorption performance of existing polymer sorbents, as detailed elsewhere [48].

The inclusion of MNP, regardless of loading concentration, did not significantly impact the ammonium sorption performance of PAA-MNP hydrogels in synthetic wastewater ($p = 0.8$) and real sewage ($p = 0.6$). The average sorption capacities in synthetic wastewater and sewage were 6.6 ± 0.02 and 6.5 ± 0.02 mg $\text{NH}_4\text{-N}$ per g hydrogel, respectively (Figure S3, Supplementary Information). In comparison, the sorption performance of bare PAA hydrogels from our preceding study was reported to be 6.3 ± 0.1 mg/g in real sewage [38], suggesting that MNP added magnetic property without compensating the ammonium sorption properties of the sorbents. Equally important, the ammonium sorption capacities and removal efficiencies achieved in this paper were within the range of the sorption capacities of various natural zeolite-based ammonium sorbents (1.5–30.6 mg $\text{NH}_4\text{-N/g}$) [48].

The unaffected sorption performance of PAA hydrogels after the addition of MNPs could be attributed to the positive surface charge of MNPs at circumneutral pH, at which sewage is typically observed which makes the MNP ineffective for binding cations such as NH_4^+ [28,49]. For this reason, MNPs have been increasingly studied for their capability in removing anions such as phosphate and sulfate from sewage [30,33]. In theory, the positive surface charge of MNPs could also bind with the negatively charged COO^- groups in the PAA hydrogels. However, since the ammonium sorption performance of the hydrogels was unaffected by the addition of MNP, this suggests that the MNPs were only physically entrapped by the

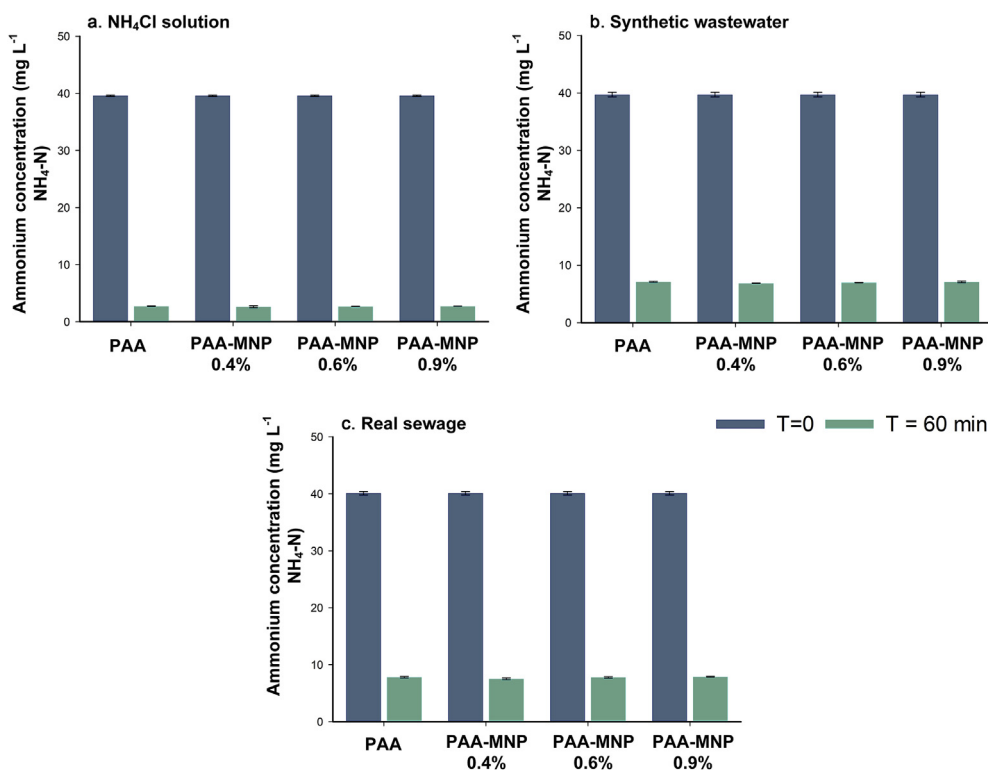


Fig. 2. Ammonium sorption performance of PAA-MNP hydrogels in various media. Hydrogel loading = 5 g/L, contact time = 60 min, room temperature, circumneutral pH. All experiments were conducted in triplicates. Error bars represent the standard deviation at a 95% confidence interval.

hydrogel matrix.

ICP analysis also revealed that the PAA-MNP hydrogels lost 0.7–2.0% of the initially loaded MNPs after one sorption experiment (Table S4, Supplementary Information). Lower MNP losses of 0.7% were observed in hydrogels with higher initial MNP loading (PAA-MNP 0.9%). This could be due to the mobility of MNP in the hydrogel network, in that at higher MNP loading, the nanoparticles have less mobility to leach out from the hydrogel matrix. However, this could not be confirmed with the experimental procedures performed in this study. Leaching of MNPs to a certain degree may be unavoidable due to the presence of physically unbound particles on the surface and around the pores.

3.3. Ammonium recovery performance

Preliminary recovery experiments show that ammonium can be effectively recovered from the PAA-MNP hydrogels with 1 M H₂SO₄ solution within 15 min (Fig. 3). Ammonium streams with concentrations of 450–689 mg/L NH₄-N were recovered, corresponding to recovery efficiencies ranging from 61.8 to 97.6%, respectively. Unlike the sorption process, the PAA-MNP hydrogels exhibited lower recovery efficiencies in comparison to bare PAA hydrogels. The highest ammonium recovery at 97.6 ± 0.9% was achieved with bare PAA hydrogels, while the ammonium recovery efficiencies of the PAA-MNP hydrogels were 61.8 ± 0.5%, 73.0 ± 1.1%, and 72.5 ± 1.4%, increasing in proportion to MNP loading (0.4%, 0.6%, and 0.9%, respectively). This could be due to the physical obstruction of NH₄⁺ ions by the nanoparticles within the hydrogel network. Since ammonium recovery was conducted using acid washing at very short contact times and mild conditions (pH 4; 15 min), the release of NH₄⁺ ions from the hydrogel matrix might have been restricted by the nanoparticles, which might lead to a slower release of NH₄⁺ ions into the regenerant.

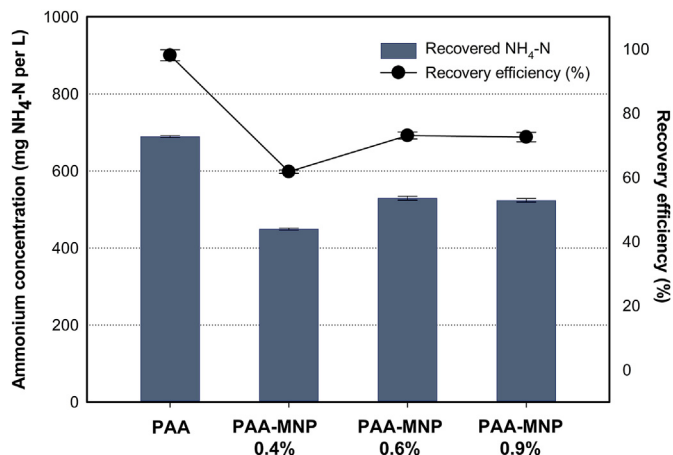


Fig. 3. Ammonium recovery performance of PAA-MNP hydrogels after sorption experiments from synthetic wastewater. Regenerant: 1 M H₂SO₄, contact time = 15 min, room temperature. All experiments were conducted in triplicates. Error bars represent the standard deviation at a 95% confidence interval.

4. Implications for practice

This proof-of-concept describes a practical and effective method for preparing magnetic ammonium sorbents by physically entrapping MNPs. By combining MNPs and PAA hydrogels in water, the MNPs were successfully integrated into the hydrogel matrix to form magnetic hydrogels that can be readily separated from liquid streams such as sewage using a compact magnet.

While successful in proving the concept, the stability of MNPs in the hydrogels needs to be improved and investigated further. Leaching is a critical issue that needs to be addressed for the

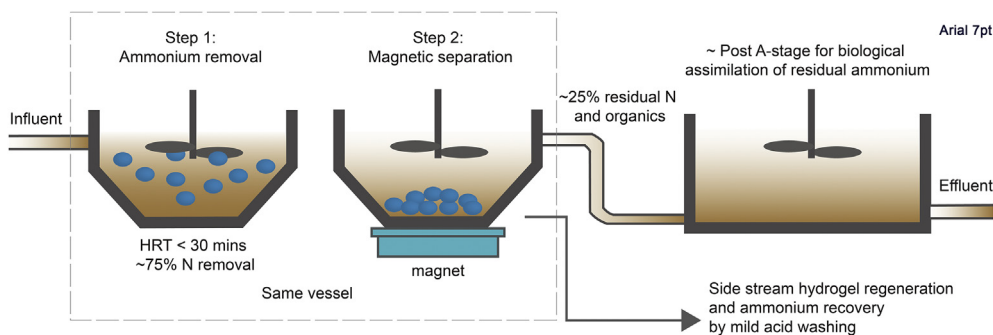


Fig. 4. Schematic illustration of ammonium removal coupled with magnetic separation of PAA-MNP hydrogels in mainline wastewater treatment.

hydrogels to be fully reusable for multiple cycles. Approaches such as adjusting the crosslinking density of the hydrogels to prevent the leaching of MNPs from the hydrogels could be an interesting investigation [47,50,51]. The introduction of a copolymer with a higher affinity to MNPs could also be explored to increase the stability of the MNPs within the hydrogels. Equally important to fully understand the stability of the PAA-MNPs, a detailed characterization of the magnetic properties of the hydrogels depending on MNP loading, sorption cycles, and regeneration conditions should also be performed.

The significance of the use of magnetic ammonium sorbents lies in their versatility. PAA-MNP hydrogels can be mixed with raw wastewater suspended in a completely mixed reactor where a significant fraction of the incoming ammonium load can be sorbed (~75%) before conventional activated sludge processes to treat organics and residual ammonium. After the sorption process, PAA-MNP hydrogels will be separated magnetically from the resin in the upper section of the vessel, as described in Fig. 4 below. This configuration is similar to the MIEX® process, which has been successfully implemented at full-scale for the removal of natural organic matter during the production of drinking water [52]. The captured magnetic hydrogels that settle in the reactor can be regenerated in a completely independent process from the mainstream. Such a concept allows for a continuous ammonium sorption process in which the PAA-MNP hydrogels only have a very short contact time with the sewage (~10mins) followed by a prolonged regeneration process to enable efficient regeneration.

5. Conclusions

This paper demonstrated the simple and effective preparation of magnetic poly(acrylic acid)-based ammonium adsorbents through the incorporation of MNP produced from scalable and cost-effective electrochemical synthesis method. This study builds on previous research demonstrating that the properties of PAA hydrogels can be tailored as effective ammonium sorbents for wastewater treatment applications [14,47]. The outcomes of the study are:

- The inclusion of MNP in the hydrogels, regardless of loading concentration, did not significantly impact the ammonium sorption performance of PAA-MNP hydrogels in synthetic wastewater and sewage ($p > 0.5$).
- The incorporation of MNP in the hydrogels did not affect the swelling of the PAA-MNP hydrogels when tested in synthetic and real sewage.
- Ammonium streams with concentrations of 450–689 mg/L $\text{NH}_4\text{-N}$ were recovered, corresponding to recovery efficiencies

ranging from 61.8 to 97.6%, respectively by washing the hydrogels with 1 M H_2SO_4 .

- The confinement of MNPs inside the hydrogels needs further improvement since 0.7–2.0% of the MNP loading leached from the hydrogels after 1 h of sorption.

Overall, this study can be seen as a step forward toward a circular economy through the development of approaches enabling mainstream recovery of ammonium from sewage.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ese.2021.100097>.

References

- [1] B.L. Bodirsky, A. Popp, H. Lotze-Campen, J.P. Dietrich, S. Rolinski, I. Weindl, C. Schmitz, C. Muller, M. Bonsch, F. Humpenoder, A. Biewald, M. Stevanovic, Reactive nitrogen requirements to feed the world in 2050 and potential to mitigate nitrogen pollution, *Nat. Commun.* 5 (2014) 3858.
- [2] H. Cruz, Y.Y. Law, J.S. Guest, K. Rabaey, D. Batstone, B. Laycock, W. Verstraete, I. Pikaar, Mainstream ammonium recovery to advance sustainable urban wastewater management, *Environ. Sci. Technol.* 53 (19) (2019) 11066–11079.
- [3] E. Cooney, G. Stevens, N. Booker, D. Shallcross, Ammonia removal from wastewaters using natural Australian zeolite. II. Pilot-scale study using continuous packed column process, *Separ. Sci. Technol.* 34 (14) (1999) 2741–2760.
- [4] E.L. Cooney, N.A. Booker, D.C. Shallcross, G.W. Stevens, Ammonia removal from wastewaters using natural Australian zeolite. I. Characterization of the zeolite, *Separ. Sci. Technol.* 34 (12) (1999) 2307–2327.
- [5] J.H. Koon, W.J. Kaufman, Ammonia removal from municipal wastewaters by ion exchange, *J. Water Pollut. Control Fed.* 47 (3) (1975) 448–465.
- [6] J.P. Soetardji, J.C. Claudia, Y.-H. Ju, J.A. Hriljac, T.-Y. Chen, F.E. Soetaredjo, S.P. Santoso, A. Kurniawan, S. Ismadji, Ammonia removal from water using

- sodium hydroxide modified zeolite mordenite, *RSC Adv.* 5 (102) (2015) 83689–83699.
- [7] A. Hedstrom, Ion exchange of ammonium in zeolites: a literature review, *J. Environ. Eng.* 127 (2001) 673–681.
 - [8] L. Ćurković, Š. Cerjan-Stefanović, T. Filipan, Metal ion exchange by natural and modified zeolites, *Water Res.* 31 (6) (1997) 1379–1382.
 - [9] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, *Chem. Eng. J.* 156 (1) (2010) 11–24.
 - [10] N.A. Booker, E.L. Cooney, A.J. Priestley, Ammonia removal from sewage using natural australian zeolite, *Water Sci. Technol.* 34 (9) (1996) 17–24.
 - [11] S. Guida, C. Potter, B. Jefferson, A. Soares, Preparation and evaluation of zeolites for ammonium removal from municipal wastewater through ion exchange process, *Sci. Rep.* 10 (1) (2020) 12426.
 - [12] H. Patel, Fixed-bed column adsorption study: a comprehensive review, *Appl. Water Sci.* 9 (3) (2019) 45.
 - [13] A. Rushton, Batch filtration of solid–liquid suspensions, in: P.N. Sharratt (Ed.), *Handbook of Batch Process Design*, Springer Netherlands, Dordrecht, 1997, pp. 153–192.
 - [14] H. Cruz, P. Luckman, T. Seviour, W. Verstraete, B. Laycock, I. Pikaar, Rapid removal of ammonium from domestic wastewater using polymer hydrogels, *Sci. Rep.* 8 (1) (2018) 2912.
 - [15] E.M. Ahmed, Hydrogel: preparation, characterization, and applications: a review, *J. Adv. Res.* 6 (2) (2015) 105–121.
 - [16] M. Bahram, N. Mohseni, M. Moghtader, An introduction to hydrogels and some recent applications, in: S.B. Majee (Ed.), *Emerging Concepts in Analysis and Applications of Hydrogels*, InTech, Rijeka, 2016. Ch. 02.
 - [17] S.B. Majee, Introductory chapter: an overview of hydrogels, in: S.B. Majee (Ed.), *Emerging Concepts in Analysis and Applications of Hydrogels*, InTech, Rijeka, 2016. Ch. 01.
 - [18] H. Wang, X. Ji, M. Ahmed, F. Huang, J.L. Sessler, Hydrogels for anion removal from water, *J. Mater. Chem., A* 7 (4) (2019) 1394–1403.
 - [19] S. Naficy, S. Kawakami, S. Sadegholvaad, M. Wakisaka, G.M. Spinks, Mechanical properties of interpenetrating polymer network hydrogels based on hybrid ionically and covalently crosslinked networks, *J. Appl. Polym. Sci.* 130 (4) (2013) 2504–2513.
 - [20] C. Dannert, B.T. Stokke, R.S. Dias, Nanoparticle-hydrogel composites: from molecular interactions to macroscopic behavior, *Polymers* 11 (2) (2019) 275.
 - [21] G. Jing, L. Wang, H. Yu, W.A. Amer, L. Zhang, Recent progress on study of hybrid hydrogels for water treatment, *Colloid. Surface. Physicochem. Eng. Aspect.* 416 (2013) 86–94.
 - [22] M. Slunjski, K. Cadee, J. Tattersall, MIEEX® resin water treatment process, *Proc. Aquatech* (2000) 26–29.
 - [23] T.H. Boyer, Removal of dissolved organic matter by magnetic ion exchange resin, *Curr. Pollut. Rep.* 1 (3) (2015) 142–154.
 - [24] M. Slunjski, H. Nguyen, M. Ballard, R. Eldridge, J. Morran, M. Drikas, P. Smith, MIEEX®-GOOD RESEARCH COMMERCIALISED, 2002.
 - [25] B. Wu, D.Y.S. Yan, M. Khan, Z. Zhang, I.M.C. Lo, Application of magnetic hydrogel for anionic pollutants removal from wastewater with adsorbent regeneration and reuse, *J. Hazard. Toxic Radioactive Waste* 21 (1) (2017).
 - [26] T.H. Boyer, P.C. Singer, Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors, *Water Res.* 39 (7) (2005) 1265–1276.
 - [27] J. Zhang, Z. Lu, M. Wu, Q. Wu, J. Yang, Large-scale synthesis and characterization of magnetic poly(acrylic acid) nanogels via miniemulsion polymerization, *RSC Adv.* 5 (72) (2015) 58889–58894.
 - [28] S. Rajput, C.U. Pittman, D. Mohan, Magnetic magnetite (Fe₃O₄) nanoparticle synthesis and applications for lead (Pb²⁺) and chromium (Cr⁶⁺) removal from water, *J. Colloid Interface Sci.* 468 (2016) 334–346.
 - [29] Z. Sekhavat Pour, M. Ghaemy, Removal of dyes and heavy metal ions from water by magnetic hydrogel beads based on poly(vinyl alcohol)/carboxymethyl starch-g-poly(vinyl imidazole), *RSC Adv.* 5 (79) (2015) 64106–64118.
 - [30] E. Rott, M. Nouri, C. Meyer, R. Minke, M. Schneider, K. Mandel, A. Drenkova-Tuhtan, Removal of phosphonates from synthetic and industrial wastewater with reusable magnetic adsorbent particles, *Water Res.* 145 (2018) 608–617.
 - [31] O. Ozay, S. Ekici, Y. Baran, N. Aktas, N. Sahiner, Removal of toxic metal ions with magnetic hydrogels, *Water Res.* 43 (17) (2009) 4403–4411.
 - [32] A. Drenkova-Tuhtan, M. Schneider, M. Franzreb, C. Meyer, C. Gellermann, G. Sextl, K. Mandel, H. Steinmetz, Pilot-scale removal and recovery of dissolved phosphate from secondary wastewater effluents with reusable ZnFe₂Zr adsorbent @ Fe₃O₄/SiO₂ particles with magnetic harvesting, *Water Res.* 109 (2017) 77–87.
 - [33] H.W. Lin, K. Couvreur, B.C. Donose, K. Rabaey, Z. Yuan, I. Pikaar, Electrochemical production of magnetite nanoparticles for sulfide control in sewers, *Environ. Sci. Technol.* 51 (21) (2017) 12229–12234.
 - [34] M.J. Ballard, R.J. Eldridge, J.S. Bates, Polymer beads and method for preparation thereof, in: U.S. Patent (Ed.), ICI Australia Operations Proprietary Limited: Australia, vol. 6, 2001, pp. 171–489 B1. US.
 - [35] J. Li, D.J. Mooney, Designing hydrogels for controlled drug delivery, *Nat. Rev. Mater.* 1 (12) (2016) 16071.
 - [36] R.S.H. Wong, K. Dodou, Effect of drug loading method and drug physico-chemical properties on the material and drug release properties of poly(ethylene oxide) hydrogels for transdermal delivery, *Polymers* 9 (7) (2017) 286.
 - [37] Z. Liu, J. Liu, X. Cui, X. Wang, L. Zhang, P. Tang, Recent advances on magnetic sensitive hydrogels in tissue engineering, *Front. Chem.* 8 (2020) 124.
 - [38] H. Cruz, B. Laycock, E. Strounina, T. Seviour, A. Oehmen, I. Pikaar, Modified poly(acrylic acid)-based hydrogels for enhanced mainstream removal of ammonium from domestic wastewater, *Environ. Sci. Technol.* 54 (15) (2020) 9573–9583.
 - [39] S. Salehin, M. Rebosura, J. Keller, W. Gernjak, B.C. Donose, Z. Yuan, I. Pikaar, Recovery of in-sewer dosed iron from digested sludge at downstream treatment plants and its reuse potential, *Water Res.* 174 (2020), 115627.
 - [40] J. Ostroha, M. Pong, A. Lowman, N. Dan, Controlling the collapse/swelling transition in charged hydrogels, *Biomaterials* 25 (18) (2004) 4345–4353.
 - [41] D. Palioura, S.P. Armes, S.H. Anastasiadis, M. Vamvakaki, Metal nanocrystals incorporated within pH-responsive microgel particles, *Langmuir* 23 (10) (2007) 5761–5768.
 - [42] F. Wahid, C. Zhong, H.-S. Wang, X.-H. Hu, L.-Q. Chu, Recent advances in antimicrobial hydrogels containing metal ions and metals/metal oxide nanoparticles, *Polymers* 9 (12) (2017).
 - [43] M.I. Dar, S.A. Shivashankar, Single crystalline magnetite, maghemite, and hematite nanoparticles with rich coercivity, *RSC Adv.* 4 (8) (2014) 4105–4113.
 - [44] T. Liu, C. Jiao, X. Peng, Y.-N. Chen, Y. Chen, C. He, R. Liu, H. Wang, Super-strong and tough poly(vinyl alcohol)/poly(acrylic acid) hydrogels reinforced by hydrogen bonding, *J. Mater. Chem. B* 6 (48) (2018) 8105–8114.
 - [45] M. Baalousha, Aggregation and disaggregation of iron oxide nanoparticles: influence of particle concentration, pH and natural organic matter, *Sci. Total Environ.* 407 (6) (2009) 2093–2101.
 - [46] N. Pérez, C. Moya, P. Tartaj, A. Labarta, X. Batlle, Aggregation state and magnetic properties of magnetite nanoparticles controlled by an optimized silica coating, *J. Appl. Phys.* 121 (4) (2017), 044304.
 - [47] H. Cruz, B. Laycock, E. Strounina, T. Seviour, A. Oehmen, I. Pikaar, Modified poly(acrylic acid)-based hydrogels for enhanced mainstream removal of ammonium from domestic wastewater, *Environ. Sci. Technol.* 54 (15) (2020) 9573–9583, <https://doi.org/10.1021/acs.est.9b07032>.
 - [48] J. Huang, N.R. Kankanamge, C. Chow, D.T. Welsh, T. Li, P.R. Teasdale, Removing ammonium from water and wastewater using cost-effective adsorbents: a review, *J. Environ. Sci.* 63 (2018) 174–197.
 - [49] T.J. Daou, S. Begin-Colin, J.M. Grenèche, F. Thomas, A. Derory, P. Bernhardt, P. Legaré, G. Pourroy, Phosphate adsorption properties of magnetite-based nanoparticles, *Chem. Mater.* 19 (18) (2007) 4494–4505.
 - [50] M. Yu, L. Xu, F. Tian, Q. Su, N. Zheng, Y. Yang, J. Wang, A. Wang, C. Zhu, S. Guo, X. Zhang, Y. Gan, X. Shi, H. Gao, Rapid transport of deformation-tuned nanoparticles across biological hydrogels and cellular barriers, *Nat. Commun.* 9 (1) (2018) 2607.
 - [51] X. Zhang, J. Hansing, R.R. Netz, J.E. DeRouchey, Particle transport through hydrogels is charge asymmetric, *Biophys. J.* 108 (3) (2015) 530–539.
 - [52] P.C. Singer, T. Boyer, A. Holmquist, J. Morran, M. Bourke, Integrated analysis of NOM removal by magnetic ion exchange, *Am. Water Works Assoc.* 101 (1) (2009) 65–73.