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Functionalization of magnetic beads with chelating surfactants for metal ions extraction

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ABSTRACT

Divalent amino acid-based surfactants were utilized in the preparation and functionalization of polystyrene/superparamagnetic iron oxide nanoparticle (SPION) beads. These surfactants were derived from aminomalonic acid, aspartic acid, and glutamic acid, all containing two carboxylic groups and differing only in the spacer size between these groups, coupled with a fatty acid moiety, resulting in N-acyl amino acid surfactants. In the process of beads formation, the surfactant played a dual role as a stabilizer and a chelating agent towards the targeted metal. The beads were obtained using an emulsion solvent evaporation method. In this process, an oil-in-water emulsion was formed, containing polystyrene and iron nanoparticles. By concentrating the oil and evaporating it, solid nanoparticles were obtained. The morphology of these particles was characterized using atomic force microscopy (AFM), dynamic light scattering (DLS), while streaming potential measurements were used to determine their charge density. The surfactant's capability to extract divalent ions, specifically Zn^{2+} and Ni^{2+}, was assessed both in its pure form and when they were attached to the particles. The aspartate-based surfactant showed the best chelating performance for divalent ions, and the combination of surfactant-functionalized particles with magnetic responsiveness led to highly efficient extraction (up to 90 %) results. Additionally, the recyclability of the beads was also assessed, highlighting their practical utility.

1. Introduction

Waste water is released from a variety of sources, including municipal and household effluents, agricultural effluents, and industrial effluents [1]. As a result, their composition varies based on the source of formation, but in general, it consists of pathogens, suspended and dissolved organic and inorganic pollutants, and so on [2]. Recycling wastewater is essential to satisfy the demands of the current, rapidly expanding population [3]. Recycled water may be utilized for a variety of purposes, including industrial cooling, agriculture, flushing toilets, watering parks, aquaculture, creating animal habitats, etc. [4]. However, heavy metal ions are a potent impurity present in the industrial wastewater. Heavy metal ions are toxic and can be carcinogenic even in trace amounts [5]. Hence their accumulation in the ecosystem directly or indirectly hampers the metabolic processes and leads to the formation of toxic chemicals [6]. Frequently detected heavy metals in wastewater include As, Cu, Cr, Pb, Ni, and Zn. So removal of the heavy metals from the recycled wastewater before reuse is necessary [7]. As a result, numerous physical, chemical, and biological methods have been used for removal, which is quite expensive, time-demanding, and produces secondary pollutants [8]. Various studies have been conducted to overcome the restrictions of the traditional approaches.

Currently, adsorption presents advantages over membrane separation, electrochemical, and photochemical extraction methods in terms of low operating costs, easy implementation, low removal costs, high efficiency, and enhanced recyclability [9,10]. The adsorption-based methods employs the physiochemical interaction between the adsorbent material and the heavy metal [11]. There is a wide range for the choice of an adsorbent such as carbon-based, mineral-based, magnetic-based, MOFs, and biosorbents which have been previously used in heavy metal extraction [12,13]. Magnetic sorbents have been preferred amongst all the mentioned due to their easy recovery and high separation efficiency [14]. Thus functionalized magnetic beads based on iron oxide have gained signification attention from the scientific community for purifying wastewater from the heavy metal ions due to their low cost and easy availability [15,16a]. These are particles with magnetic activity with size ranging from micrometers to nanometers and that have a particular functional group attached [17]. Additionally, the

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functional groups attached to the bead surface can be tailored to target specific contaminants, making magnetic beads a highly selective and efficient method of water purification [18]. To date, many different kinds of functional magnetic particles have been employed for the removal of heavy metals. The functionalities commonly employed include -OH, -NH_2, -SH and -COOH. For example Liu et al. [19] studied the functionalized Ni and Fe hollow and porous magnetic beads for the adsorption of Cd, Cr, Cu, Co and Zn. In similar way, C. Zhang et al. [20] studied thiol functionalized CNT containing magnetic particles for Hg and Pb adsorption. Additionally, S. Villa et al. [21] used silane derivative to functionalize iron oxide magnetic particles with thiol group for the adsorption of Pb and S. Jin et al. [22] functionalized iron oxide particles for Cu adsorption.Various biomolecules such as amino acid functionalized (arginine for Cu, Co, and Ni [23], glycine functionalized for Pb [24] and Cu [25], asparagine functionalized for Ni [26], polysaccharide functionalized (alginate along with β-Cyclodextrin based magnetic biopolymer based hydrogel for the adsorption of Pb , Ni , Cu , and Cd [27], carboxymethyl chitosan-based magnetic sorbents for the detection of Cu, Cd, and Pb [28], magnetic alginate bead for the Pb adsorption [29]. Even chelating agents such as EDTA functionalized magnetic particles for adsorption of Pb, Hg, Cd, and Cu [30,31], diethylenetriamine functionalized mangnetic particles for Cu and Cr [32] have been previously studied. Even biofunctional magnetic beads have been employed for the adsorption of Cr [33]. Therefore, it shows that combination of magnetism along with varied functionalities enables to increase in the specificity of the bead towards the analyte.

These properties of magnetic beads have helped in the removal of heavy metal ions from the wastewater. The functionalized magnetic beads chelate the metal ions from the solution through chemical adsorption [34], and sequestration. The behavior of the functionalities under different pH conditions describes the chelating properties towards the different metal ions sequestration. These interactions of the functionalities and the metal ions are governed by the HSAB principle [35], which states that a hard acid has a strong affinity for a hard base while a soft acid has a higher affinity with a soft base (-COO^-pairs with a hard acid while -NH_3^+ pairs with a soft acid). Furthermore, the magnetic beads can then be separated from the water by applying a magnetic field, effectively concentrating the heavy metals in a small volume for disposal or further treatment. In addition to the benefits of magnetic separation and chemical specificity, functionalized magnetic beads are also reusable and can be easily regenerated [36]. This makes them a cost-effective and environmentally friendly alternative to traditional methods of wastewater treatment. Herein, we have described the role of dicarboxyl-functionalized amino acid surfactants in functionalizing polymeric magnetic beads for the removal of Ni^{2+} and Zn^{2+} ions, as well as their recyclability, demonstrating the practical utility of the system.

2. Materials and methods

2.1. Materials

Aminomalonic acid (≥ 98 %), Aspartic acid (≥ 99 %), glumatic acid (≥ 99 %), Dodecanoyl chloride (≥ 97.5 %), polystyrene (Molecular weight: 192,000), $ZnCl_2$ (≥ 98 %), $NiCl_2$ (≥ 98 %) and all solvents were purchased from Sigma Aldrich. Millipore water was used in all experiments. The amino acid-based surfactants with chelating groups were synthesized following the earlier reported procedure [16b]. The iron oxide nanoparticles used in this study were synthesized according to the method described by Sommertune et al. [37].

2.2. Preparation of oil-in-water emulsions by amino acid surfactants

Amino acid-based surfactants were initially used to prepare oil-in-water emulsions. In these tests, the oil phase, consisting of an organic solvent (2 wt% cyclohexane or chloroform or ethyl acetate), was emulsified with an aqueous surfactant solution (1 wt%). We observed that the cyclohexane-water and chloroform-water emulsions remained stable over time.

2.3. Preparation of polymeric functionalized dispersions

To prepare these dispersions, the oil phase (chloroform) containing polystyrene (2.5 wt%) was emulsified using an aqueous surfactant solution (1 wt%) through ultrasonication for 2 min with a Sonics Vibracell at 40 % amplitude in an ice bath. The resulting emulsion was stirred at room temperature for 6–8 h in an open glass vial to allow the chloroform to evaporate completely. The removal of the solvent was monitored by weighing the sample. Ultimately, we obtained a dispersion (0.625 wt% polystyrene and 1 wt% surfactant) with good stability, as indicated by its visual appearance.

2.4. Preparation of polymeric functionalized magnetic beads

Polymeric functionalized magnetic beads were synthesized using a two-step methodology. First, the oil phase, consisting of 2 mL of chloroform containing 2 wt% SPIONs, was used to dissolve 2.5 wt% polystyrene. This oil phase was then transferred to an aqueous solution (8 mL) containing 1.0 wt% dicarboxylic surfactant, and the mixture was emulsified using ultrasonication for 2 min with a Sonics Vibracell at 40 % amplitude in an ice bath. The resulting emulsion was stirred at room temperature for 6–8 h in an open glass vial, allowing the chloroform to evaporate completely, with the removal of the solvent monitored by weighing the sample. This process ultimately produced a magnetic dispersion containing 0.5 wt% SPIONs, 0.625 wt% polystyrene, and 1 wt % surfactant.

2.5. Instrumentation

Surface tension measurements were conducted using a Sigma 70 tensiometer (KSV) with the du Noüy ring method. The temperature was maintained at 25 ± 0.01 °C using a Neslab RTE-200 cryostat. The glassware was cleaned with chromosulfuric acid, and the ring was flamed before use. Particle charge density measurements of both magnetic and non-magnetic emulsions were carried out using a PCD 02 particle charge detector (Mütek) connected to a Mettler DL21 titrator (Mettler Toledo). This setup enabled monitoring of the streaming potential, which is directly related to the electrokinetic surface charge of the sample during the addition of an oppositely charged titrant [38]. Dynamic light scattering measurements were conducted using a N4 Plus submicron particle analyzer (Beckman Coulter). The emulsions were diluted with ultra-pure water to a concentration of 0.05 wt% and sonicated for 5 min. Measurements were taken at an angle of 90° for 300 s. The resulting autocorrelation functions were analyzed using the Kohlrausch-Williams-Watts (KWW) fitting function and the CONTIN inverse Laplace fitting routine [39]. Atomic force microscopy (AFM) imaging of emulsions was carried out using an NTEGRA Prima (NTMDT, Russia) operating in tapping mode. The samples were prepared by drop-casting 0.01 wt% dispersions onto a clean silicon wafer. The raw data was processed using Gwyddion software. Inductive coupled plasma mass spectrometry (Agilent 7800 Q-ICP-MS), was used to analyze the extraction efficacy of pure surfactants and functionalized particles respectively.

3. Results and discussion

3.1. Chelation assessment of amino acid surfactants by surface tension measurements

Previous research by Bordes et al. established the chelation behavior of amino acid-based surfactants towards calcium ions [16b]. In this study, we have focused on the extraction efficacy of these surfactants towards Zn^{2+} and Ni^{2+} ions. To this end, we have monitored the surface

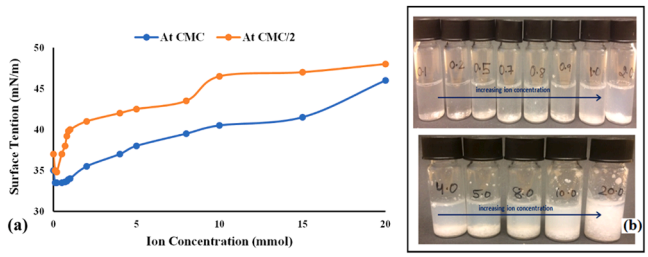

Fig. 1. (a) Surface tension of malonate surfactant (at cmc/2 & cmc) with respect to increasing $ZnCl_2$ concentration. (b) Picture of the samples that shows that precipitation increases in surfactant (malonate) solution at cmc with increasing Zn^{2+} concentration (0.1 - 20.0 mM).

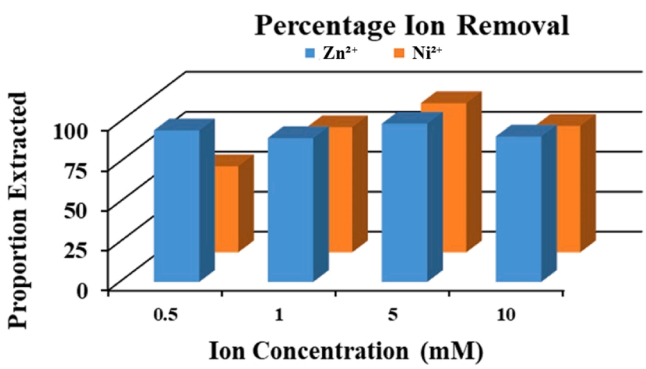

Fig. 2. ICP-MS results showing the efficient extraction of Zn^{2+} and Ni^{2+} ions using aspartate based surfactants.

tension of the surfactant solutions at their critical micelle concentration (cmc) and at half of the critical micelle concentration (cmc/2) while gradually increasing the concentration of zinc and nickel ions.

Surfactants adsorbs at the air-water interface, forming ordered arrangements that results from their surface activity. In the presence of metal ions, the chelating surfactants tend to form precipitates, resulting in a reduction in their surface activity. This phenomenon is illustrated by the surface tension isotherms in Fig. 1. Specifically, the surface tension of the malonate surfactant solution increases with rising ion concentration, indicating a decrease in the availability of surfactant molecules at the interface. This decrease is attributed to the formation of complexes between the surfactant molecules and the ions, which affects their adsorption behavior and surface activity when exposed to zinc and nickel ions.

With the exception of aspartate, all the investigated amino acid-based surfactants exhibited similar behavior as the ion concentration increased. Notably, the aspartate surfactant system displayed gelation when exposed to zinc ions at concentrations above 0.5 mM, which posed challenges in measuring the surface tension of the solution (supporting information; Fig. S1). Yet, precipitation took eventually place as well, indicating a strong inteaction with the metal cations. According to the tensiometry measurements, all the investigated surfactants demonstrated a notable ability to chelate divalent ions, showing effectiveness in chelating these ions over a range of concentrations. Among them, the aspartate surfactants exhibited the highest extraction efficacy.

The outcomes of surface tension mesaurements were further supported through mass spectrometry experiments using ICP-MS. Following the precipitation process, the supernatant solutions were subjected to mass spectroscopy analysis. The results indicated that the aspartate surfactant exhibited a remarkable extraction efficacy of 90 %- 99 % for zinc ions and 53 % - 94 % for nickel ions, as depicted in the provided Fig. 2. Consequently, these mass spectrometry results align-with and support the conclusions drawn from the surface tension measurements.

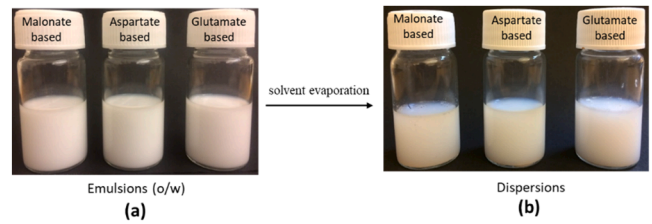

Fig. 3. (a) Emulsions stabilized by the amino acid based surfactants (2 mL $CHCl_3$ [2.5 wt% polystyrene] + 8 mL H_2O [1 wt% surfactant]) (b) Appearance of the suspensions after solvent evaporation.

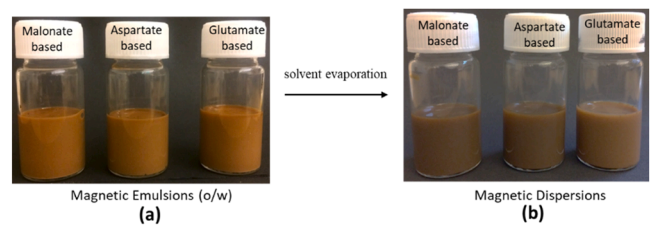

Fig. 4. (a) Magnetic emulsions stabilized by the amino acid based surfactants (2 mL $CHCl_3$ [2.5 wt% polystyrene + 2 wt% iron nanopartcles] + 8 mL H_2O [1 wt% surfactant]) (b) Appearance of the suspensions after solvent evaporation.

Table 1
DLS and PCD measurements of Emulsions (non-magnetic & magnetic).

Type	Size (in nm) DLS measurements		Charge (μeq\g) PCD measurements
	Before evaporation of oil phase	After evaporation of oil phase	
	Non-magnetic functionalized beads		
Malonate based emulsion	148.8 ± 1.93	155.2 ± 1.85	−291.4 ± 0.50
Aspartate based emulsion	156.0 ± 1.55	158.4 ± 1.67	−170.2 ± 1.05
Glutamate based emulsion	115.6 ± 1.45	145.8 ± 1.75	−255.0 ± 0.90
Magnetic functionalized beads			
Malonate based dispersion	93.3 ± 1.87		−283.4 ± 1.20
Aspartate based dispersion	177.7 ± 1.90		−141.8 ± 0.80
Glutamate based dispersion	94.5 ± 1.75		−226.8 ± 0.95

3.2. Evaluation of polymeric functionalized dispersions (non-magnetic and magnetic)

The emulsion solvent-evaporation process was employed to prepare dispersions, starting with the preparation of an oil-in-water emulsion stabilized by a chelating surfactant. Amino acid surfactants also introduce COOH groups to the polymer matrix, providing effective coordination sites for metal ion binding. The oil phase contained both the magnetic particles and a solvent in which the polymer was dissolved. Once the solvent was removed, the polymer matrix trapped the magnetic cores.

Initially, non-magnetic polymer dispersions were prepared using chloroform as the oil phase, containing 2.5 wt% polystyrene. This oil phase was emulsified with a 1 wt% aqueous surfactant solution. After solvent evaporation, the size and charge of dispersions were measured Fig. 3.

Similarly, magnetic dispersions (Fig. 4) were prepared, with $CHCl_3$

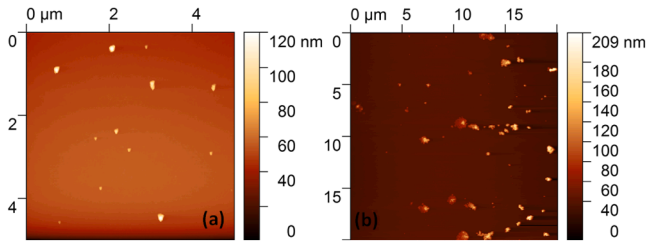

Fig. 5. AFM micrographs (a) & (b) shows the size distribution of aspartate based non-magnetic emulsion & magnetic dispersion respectively.

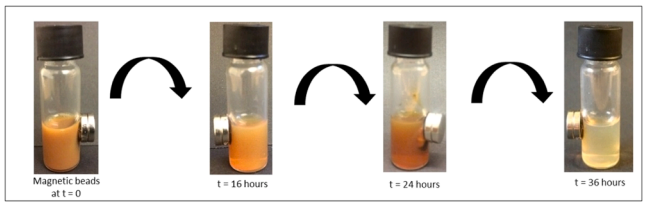

Fig. 6. Magnetic response of magnetic beads functionnalized with the aspartate-based surfactant with time.

acting as the oil phase containing 2.5 wt% polystyrene and 2 wt% iron nanoparticles. This mixture was emulsified with a 1 wt% aqueous surfactant solution. After removal of solvent, the dispersions were characterized for their magnetic response, size and charge.

DLS, AFM and PCD experiments were conducted to investigate the size and charge density trends of both non-magnetic and magnetic dispersions, respectively. The DLS measurements revealed that the dispersion sizes ranged from 90 to 180 nm (Table 1). Surprisingly, after the evaporation of the oil phase, the expected size reduction did not occur, and instead, a reverse trend was observed. Among the dispersions, those based on aspartate surfactants were found to be larger in size compared to dispersions containing malonate and glutamate surfactants.

The PCD measurements demonstrated that all dispersions exhibited a negative charge, indicating the presence of adsorbed or embedded amino acid-based surfactants at the surface or within the matrix of polystyrene, respectively. The dispersions containing malonate and glutamate surfactants showed higher negative values ranging from 220 to 300 µeq\g, whereas the aspartate-appended dispersions exhibited a lower charge ranging from 141 to 170 µeq\g, as determined by PCD measurements (Table 1).

The morphology of the investigated dispersions were evaluated with AFM measurements. Both the magnetic and non-magnetic dispersions were found to be polydisperse, exhibiting a size range of 80–200 nm. Fig. 5a displays the AFM graph of the non-magnetic emulsion based on aspartate surfactants, while Fig. 5b shows the AFM graph of the magnetic dispersion utilizing aspartate surfactants.

3.3. Evaluation of magnetic response of polymeric magnetic dispersions

The magnetic response of dispersions was evaluated by subjecting them to an external magnetic field. To conduct this evaluation, a magnet was attached to a solution containing the magnetic dispersion and observed over a period of time (Fig. 6). Remarkably, within 36 h, all magnetic beads were found to have migrated close to the magnet, demonstrating the remarkable magnetic behavior of the polymeric beads in response to the external magnetic field.

The above studies demonstrated that amino acid-based surfactants were effective in chelating metal ions and that the polymeric magnetic beads exhibited significant magnetic response over time. Following these observations, we evaluated the metal ion extraction capabilities of the polymeric magnetic beads as discussed below.

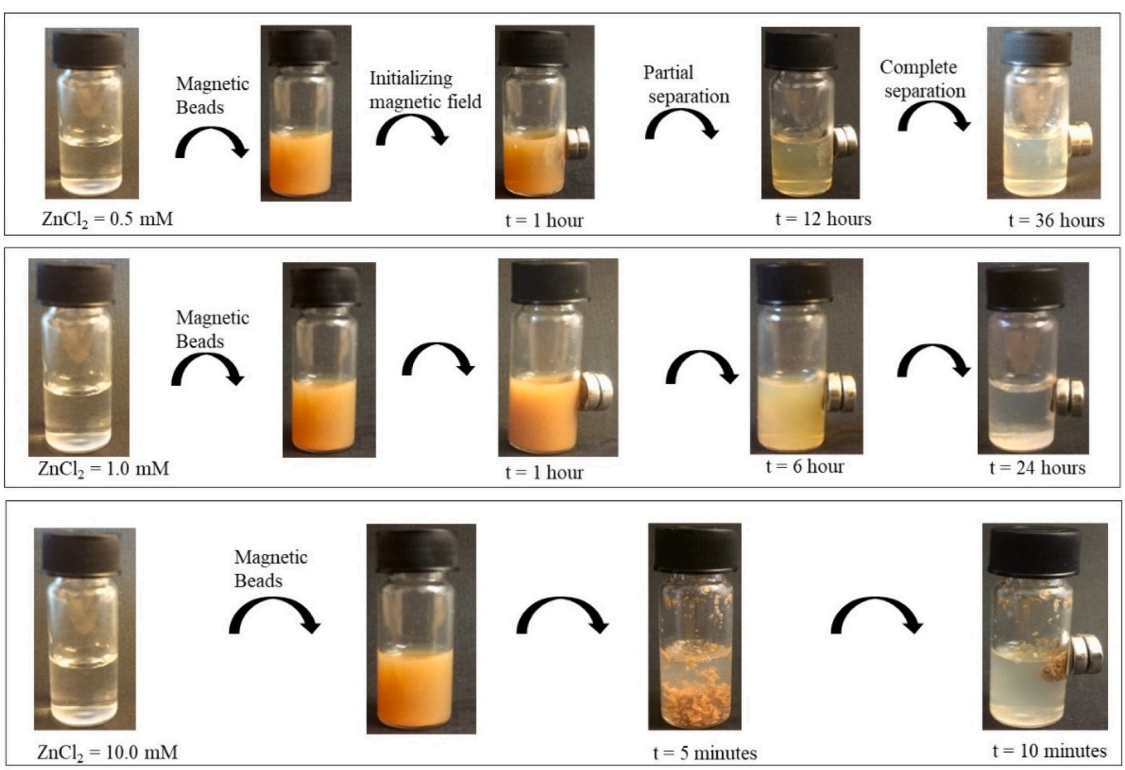

Fig. 7. Zn^{2+}ions extraction and magnetic separation by aspartate functionalized magnetic beads over time.

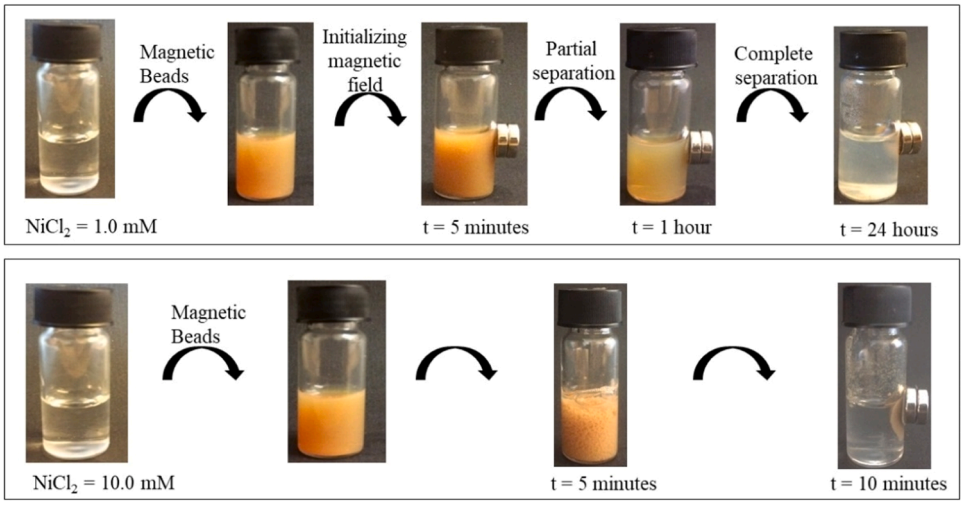

Fig. 8. Ni^{2+}ions extraction and magnetic separation by aspartate functionalized magnetic beads over time.

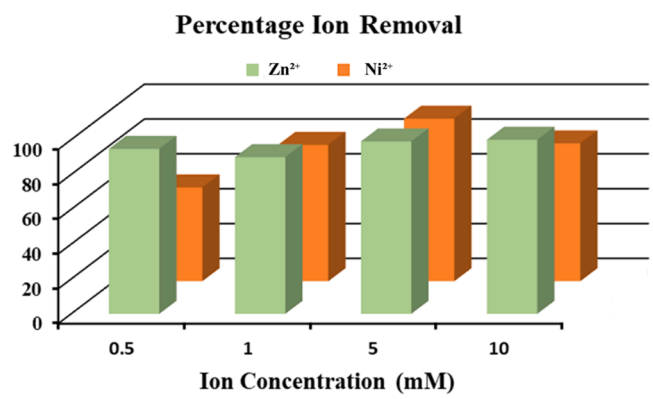

Fig. 9. ICP-MS results showing the efficient extraction of Zn^{2+} and Ni^{2+} ions using aspartate functionalized magnetic beads.

3.4. Chelation of metal ions by polymeric functionalized magnetic dispersions

To evaluate the ion chelation capability, the magnetic beads underwent a magnetic study, which was subsequently validated by experiments using coupled plasma mass spectrometry (ICP-MS). In these experiments, polymeric functionalized beads were immersed in metal ion solutions having concentrations of 0.5, 1.0, and 10.0 mM, and then subjected to magnetic separation. The results obtained from the Fig. 7 demonstrated that the aspartate functionalized beads exhibited remarkable efficacy in chelating Zn^{2+} ions, leading to the formation of precipitates in the solution. Moreover, it was observed that as the ion concentration increased, both the particles precipitation and magnetic separation processes were significantly enhanced.

Similar experiments were carried out to investigate the ion extraction and magnetic separation capabilities of the aspartate-based beads towards Ni^{2+} ions in an aqueous system (Fig. 8). The results showed that the aspartate-based beads demonstrated a behavior similar to that observed when extracting Zn^{2+} ions. This suggests that the beads have a broad range of applications in the extraction and separation of different metal ions from aqueous solutions.

In these experiments, the extraction behavior of polymeric functionalized beads towards divalent ions was assessed primarily through visual observations. Following the magnetic separation of the beads from the system, the respective solutions were subjected to mass spectrometry analysis (ICP-MS). This analytical technique was employed to accurately determine the actual ion concentration, providing additional quantification to support the findings obtained from the visual experiments.

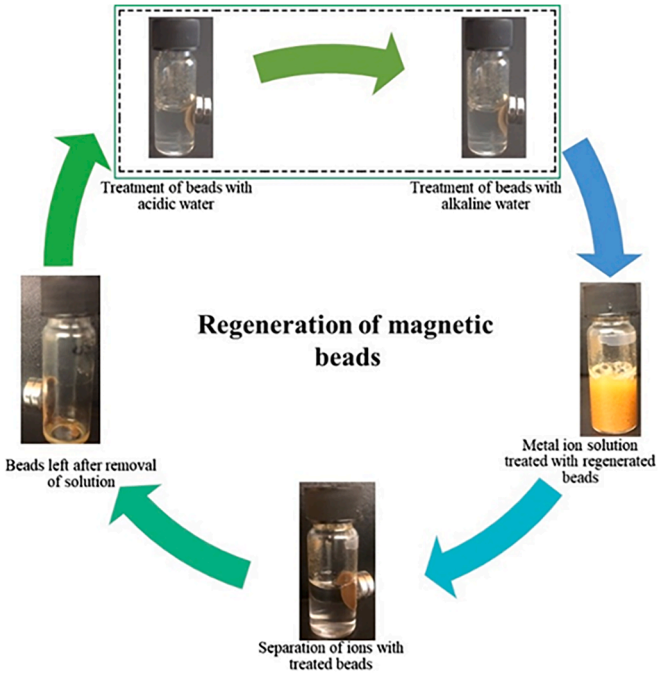

Fig. 10. Method used for regenerating magnetic beads under acidic (protonation) and alkaline conditions (deprotonation) conditions, followed by fresh ions extraction and magnetic separation.

The ICP experiments, as shown in Fig. 9, demonstrated that aspartate-functionnalized beads significantly reduced the concentration of Zn^{2+} ions. The results indicated that at ion concentrations of 0.5, 1.0, 5.0, and 10.0 mM, the aspartate-functionalized magnetic beads removed 90–99 % of zinc ions and 58–90 % of nickel ions.

To evaluate practical applicability, the recyclability of the magnetic beads was assessed (Fig. 10). After magnetic separation, the beads were treated under acidic conditions (pH 2.0–3.0) followed by alkaline conditions (pH 12.0–13.0). This treatment resulted in the protonation and deprotonation of the dicarboxylic groups of the amino acid surfactants, effectively removing the bound ions from the beads' surface. The treated aspartate-based beads were then reused in fresh solutions of zinc and

nickel chloride (concentration: 10 mM). ICP measurements revealed that the treated beads removed 67 % of Zn^{2+} and 81 % of Ni^{2+} from their respective solutions. However, the recyclability experiments indicated a 20–35 % decrease in the ion extraction ability of the treated beads. Despite this reduction in efficiency, the study confirmed the excellent ion extraction capabilities of the aspartate-functionalized magnetic beads, demonstrating their significant potential for practical applications in wastewater treatment and other relevant fields.

4. Conclusion

Magnetic beads functionalized by chelating groups containing amino acid surfactants were synthesized and have demonstrated notable effectiveness in the removal of Zn^{2+} and Ni^{2+} ions from aqueous solutions. The successful intregration of chelating surfactant over polymer matrix was confirmed by PCD measurements that demonstrated high negative surface charge values. The size of these beads were found to be 80–200 nm, as evaluated from DLS and AFM measurements. The tunning of polymer matrix with chelating surfactant introduces carboxylate groups that acted as effective coordination sites for binding of metal ions. The extraction behaviour of pure amino acid surfactants and functionalized magnetic beads was confirmed with ICP mass experiments, with a maximum 99 % ions removal rate was achieved with aspartate-based system. Additionally, these magnetic beads showed potential for reuse and could be easily regenerated through a magnetic separation process followed by acid-base treatment. These findings demonstrate that this system is highly efficient in extracting targeted meatal divalent ions, achieving an impressive removal rate as confirmed by ICP experiments. The implications extend beyond simply improving metal ion removal; this approach could be adapted for broader environmental remediation efforts, addressing heavy metal contamination in various industrial processes. Future applications may include the development of tailored functionalized beads for specific contaminants, enhancing their utility in diverse settings, from industrial effluents to municipal wastewater treatment. This functionalized magnetic bead system thus represents a significant advancement in eco-friendly wastewater treatment technologies, offering a sustainable solution to environmental challenges.

CRediT authorship contribution statement

Vinay Chauhan: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology. **Romain Bordes:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Methodology, Investigation.

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 review article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2024.140716.

Data availability

Data will be made available on request.

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