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Bioresource Technology

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https://doi.org/10.1016/j.biortech.2024.131205

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Bioresource Technology 410 (2024) 131205

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Nutrient removal in floating and vertical flow constructed wetlands using aluminium dross: An innovative approach to mitigate eutrophication

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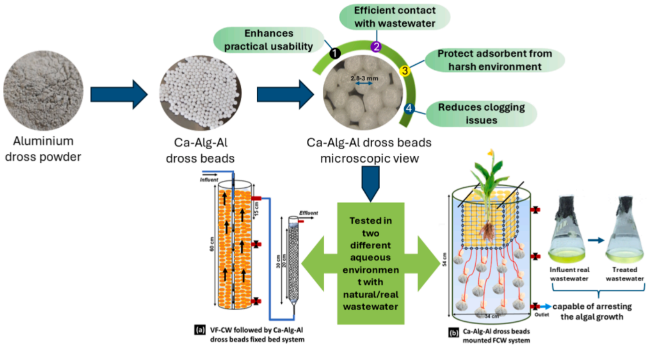
HIGHLIGHTS

- Aluminium dross beads enhance practical utility of raw aluminium dross.
- Efficiently removes pollutants from both flowing and stagnant water environments.
- Maximum phosphate and ammonium removal achieved were 85 % and 93 %, respectively.
- Treated water can prevent algal growth, ensuring safe water discharge.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
P recovery
Nature-based wastewater treatment
Eutrophication
Ca-Alg-Al dross beads development
Constructed wetlands
Adsorption
Lentic ecosystem remediation

ABSTRACT

On global scale, eutrophication is one of the most prevalent environmental threats to water quality, primarily caused by elevated concentration of nutrients in wastewater. This study utilizes aluminum dross (AD), an industrial waste, to create a value-added material by improving its operational feasibility and application for removing phosphate and ammonium from water. The operational challenges of AD such as its powdered nature and effective operation under only extreme pH conditions were addressed by immobilizing in calcium alginate to form calcium alginate aluminium dross (Ca-Alg-Al dross) beads. These Ca-Alg-Al dross beads were further tested for phosphate and ammonium removal from natural wastewater in two different aqueous environment systems: (*i*) vertical flow constructed wetlands (VF-CWs) followed by Ca-Alg-Al dross beads fixed bed system and (*ii*) Ca-Alg-Al dross beads mounted floating constructed wetlands (FCW) for remediating polluted lentic ecosystems. Our results show maximum phosphate and ammonium removal of 85 ± 0.41 % and 93.44 %, respectively, in VF-CWs followed by Ca-Alg-Al dross beads fixed bed system. The Ca-Alg-Al dross beads mounted FCW system achieved

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https://doi.org/10.1016/j.biortech.2024.131205
Received 27 March 2024; Received in revised form 21 June 2024; Accepted 31 July 2024

maximum phosphate removal of 79.18 ± 8.56 % and ammonium removal of 65.45 ± 21.04 %. Furthermore, the treated water from the FCW system was assessed for its potential to inhibit algal growth by artificially inoculating treated water with natural algae to simulate eutrophic conditions. Interestingly, treated water from the FCW system was found capable of arresting the algal growth. Besides, scanning electron microscopy with energy dispersive X-ray (SEM-EDX) and Fourier transform infrared (FTIR) spectroscopy confirmed the functional groups and surface properties and probable participation of multiple mechanisms including ion exchange, electrostatic attraction, and ligand complexation for phosphate and ammonium removal. Overall, these results offer a promising way to utilize AD for high-end applications in wastewater treatment.

1. Introduction

Eutrophication is a significant environmental concern impacting aquatic ecosystems worldwide, primarily triggered by excess phosphorus (in the form of orthophosphate, PO_4^{3-}) and ammonium (NH_4^+) (Yin and Kong, 2014a; Yin et al., 2018). The rise in the contribution of phosphate and ammonium nutrient levels in the water bodies is mainly owing to a rapid increase in human activities, including the runoff of agricultural, domestic, industrial, and municipal wastewater into water bodies. On the other hand, phosphorus is a critical resource that is essential for global food supply but is depleting at an alarming rate, with predictions estimating depletion of global reserves within a century (Li et al., 2019). Thus, to mitigate the imbalance of the global phosphorous cycle, phosphorous recycling from wastewater or eutrophic water bodies could be an environmentally sustainable approach, securing both water and food for the growing population (Kim et al., 2018). Consequently, combined management of phosphate and ammonium input in water bodies is advocated by many researchers.

Constructed wetlands (CWs) are widely adopted for nutrient removal due to their cost-efficiency, minimal operational requirements, and no sludge generation (Ji et al., 2022). Different types of CWs, such as subsurface and floating CWs (FCWs), are noted for their effectiveness in nutrient removal through various mechanisms, including plant and microbial uptake, and adsorption onto substrate (Ayaz et al., 2012; Srivastava et al., 2022; Vymazal, 2011; West et al., 2017). Although, if harvesting is not done on time, accumulated ammonium and phosphate in plants could be released back to the environment, making it only a temporary sink. Nevertheless, phosphate is typically stored in roots of the plants rather than leaves and can readily be released upon storage exhaustion, changes in water chemistry, or when adsorbed phosphate is loosely bound to plant roots (Ayaz et al., 2012; Kadlec, 2005; Martín et al., 2013). Thus, there is a need for selectively targeted additional treatment followed by CWs along with it to decrease the phosphate and ammonium concentration to desired levels to restrict eutrophication stimulation in treated waters (Preisner et al., 2020).

Adsorption is highlighted as an effective method for nutrient removal due to its flexibility, low cost, and high selectivity (He et al., 2017; Loganathan et al., 2014). Various adsorbents are explored, including natural materials (Ahmed et al., 2019; Yin and Kong, 2014a), industrial by-products (Ren et al., 2016; Sellner et al., 2019), and synthetic materials (Chitrakar et al., 2006; Rajan and Perrott, 1975), with aluminium-containing adsorbents showing high affinity for phosphate and concurrent ammonium recovery. For example, biochar has been modified with Mg-Al nanocomposites and displayed a concurrent maximum adsorption capacity of 74.47 mg/g (phosphate) and 0.70 mg/g (ammonium) at pH 6 with adsorbent pH_{pzc} of 9.7 (Yin et al., 2018). Further, natural zeolite modified with aluminium oxide was investigated for simultaneous phosphate and ammonium removal and reported 7 mg/g and 30 mg/g of adsorption, respectively at a pH of 4.2 ± 0.2 (Guaya et al., 2015a). Likewise, naturally rich attapulgite ($(Mg,Al)_2Si_4O_{10}(OH).4H_2O$) was modified with thermal treatments, revealing maximum ammonium and phosphate removal of 2.02 mg N/g and 3.32 mg P/g, respectively at pH value of 7 (Yin and Kong, 2014b). The developed adsorbents were also investigated with CWs such as iron modified aluminium sludge substrate was used in tidal flow CWs for simultaneous ammonium and phosphate removal and revealed total phosphorous and total nitrogen removal of 95 % and 47 %, respectively (Zhou et al., 2022). Further, to enhance the phosphate removal efficiency several adsorbents were used as filler in CWs including attapulgite (Xu et al., 2022), aluminium based water treatment residual (Yang et al., 2006), solidified lanthanum/aluminum amended attapulgite/biochar composite (Yin and Kong, 2014b) and drinking water treatment sludge on zeolite (Zhao et al., 2022). While many of these adsorbents have shown effective simultaneous phosphate and ammonium recovery potential individually and as substrate/filler in CWs, challenges still handicap their practical operation ability such as (*i*) clogging in the filtration material, (*ii*) inefficient phosphorous removal at extreme pH values, (*iii*) high pH of treated effluent, (*iv*) difficult recovery of adsorbent from treated water (*v*) ineffective contact of adsorbent due to density difference, (*vi*) unavailability of adsorbent in bulk amount, (*vii*) cost intensive (*viii*) lack of information on reuse/recycling of recovered adsorbent, and most importantly (*ix*) barely any implementation with natural wastewater (Dotto and McKay, 2020; Wu and Vaneeckhaute, 2022; Zhao et al., 2022). Thus, taking literature studies into account, aluminium industrial waste/by-product *i.e.* aluminium dross (AD), was chosen for its affinity for nutrient removal, bulk availability (annual production ~75,000 tons in India) and low cost (Das et al., 2007). Multiple studies reported efficient phosphate adsorption by raw AD under extreme pH conditions of 12 or 3 thus constraining its utility in natural waters (b Zakaria et al., 2017; Ren et al., 2016). Additionally, raw AD's powdered form complicates its recovery from water and can cause clogging along with its substantial density difference limiting its effective contact with water.

In this study, we propose a new strategy to manage phosphate and ammonium removal and recovery. We hypothesize that developing unique material through immobilizing AD inside calcium alginate beads can help overcome these challenges encountered by raw AD and improve its practical usability. The encapsulating agent *i.e.*, Calcium alginate ($(C_{12}H_{14}CaO_{12})_n$) is a biological organic substrate owing to its abundance in nature and its benign properties (Russo et al., 2007). Calcium alginate encapsulation enhances the practical usability of aluminum dross (AD) in several significant ways. Firstly, the encapsulated beads achieve better distribution in polluted water ensuring efficient contact with wastewater and overcoming the density differences that hindered raw AD powder. Secondly, the beads facilitate easier post-treatment recovery, allowing them to be readily separated from water using screens or simple sedimentation process unlike raw AD powder which required fine micron filtration. Additionally, this encapsulation method reduces clogging issues, protects adsorbents from harsh conditions, minimises contaminant release, and improves handling and scalability for large-scale water treatment applications (Xu et al., 2020).

With these advantages in mind, the study aimed to investigate the potential and applicability of AD-immobilized calcium alginate beads, *viz.* Ca-Alg-Al dross beads for simultaneous phosphate and ammonium management in different aqueous environments. The developed Ca-Alg-Al dross beads were tested for two different aqueous environment systems (i) vertical flow constructed wetlands (VF-CWs) followed by Ca-Alg-Al dross beads fixed bed system in continuous mode operation for real municipal wastewater treatment, and (ii) Ca-Alg-Al dross beads mounted floating constructed wetlands (FCW) imitating lentic ecosystems like lakes or ponds which are polluted (eutrophic water bodies). Further, algal growth tests were conducted to assess the treated water's ability to inhibit algal growth. Our experimental results will validate whether: (i) the coupling of VF-CWs and Ca-Alg-Al dross beads fixed bed system is safe for discharge and will not stimulate eutrophication in river bodies and (ii) the Ca-Alg-Al dross beads have enough potential to treat pollutants in lentic ecosystems efficiently. As per the authors' knowledge, this is a first ever detailed investigation of material for simultaneous remediation and recovery of phosphate and ammonium from natural water streams in two different aqueous environment situations, along with an assessment of the treated water for its capability of stimulating algal growth.

2. Material and methods

2.1. Preparation and characterization of calcium-alginate-aluminium dross beads

Ca-Alg-Al dross beads were prepared using sodium alginate powder ($C_6H_9NaO_7$), $CaCl_2$ solution, and industrial waste AD powder. This study utilized analytical-grade chemicals obtained from HI Media Pvt. Ltd, India. The bead preparation process involves blending 0.2 g of sodium alginate powder in 20 mL double distilled water (DDW) and heating until achieving homogenized mixing at 100 °C. Promptly, 0.4 g of ground AD powder was introduced into the viscous sodium alginate solution and thoroughly mixed using a magnetic stirrer at room temperature. The 0.4 g AD loading in Ca-Alg-Al dross beads was selected based on our previous study, where this amount was optimized for efficient phosphate removal from a 10 mg/L synthetic phosphate solution (Mittal et al., 2024). Consequently, the same loading was used in the current study. Alongside, 0.2 M $CaCl_2$ solution was prepared. Further, for preparation of the Ca-Alg-Al dross beads, sodium alginate AD solution was filled into the burette and continuously dropped into the $CaCl_2$ solution at a fixed rate. The beads, once prepared, were immersed in a $CaCl_2$ solution for 24 h at 4 °C to facilitate hardening and crosslinking. Subsequently, the beads were thoroughly washed with double-distilled water multiple times the following day. The same procedure was adopted for control bead preparation *i.e.,* Ca-Alg without AD entrapment.

The morphology, elemental composition, and mapping of Ca-Alg beads and Ca-Alg-Al dross beads were characterized using a scanning electron microscope (SEM) system (Zeiss EVO 18, Germany) equipped with an energy-dispersive X-ray spectroscope (EDS) (Octane elect, USA). Additionally, surface functional groups of Ca-Alg-Al dross beads before and after treatment were analyzed using a Fourier transform infrared (FTIR) spectrometer (ATIR-FTIR Alpha Bruker II) to provide further insights.

2.2. Applications of Ca-Alg-Al dross beads in different aqueous environment situations

The performance of Ca-Alg-Al dross beads was investigated for the treatment of real wastewater in two different aqueous environment systems (*i*) VF-CW followed by Ca-Alg-Al dross beads fixed bed system in continuous mode operation for real municipal wastewater treatment, and (*ii*) Ca-Alg-Al dross beads mounted FCW system imitating lentic ecosystems like lakes or ponds in batch mode operation for contaminated (eutrophic water bodies) water treatment.

2.2.1. VF-CW followed by Ca-Alg-Al dross beads fixed bed system

A system was designed with VF-CW followed by Ca-Alg-Al dross beads fixed bed system, represented in Fig. 1(a). CW column was constructed with a polyvinyl chloride (PVC) tube of 60.0 cm × 11.0 cm (height × diameter) with ports at 10.0 cm, 33.0 cm, and 54.0 cm from top. The column was capped at the base with a circular base of PVC. Column was packed with siliceous garden gravels of ~5.0–8.0 mm diameter taken up from a functional CWs facility at CSIR-IMMT, Bhubaneswar, India, and fed with real municipal wastewater from the same facility daily. Wastewater was collected weekly and stored at 4.0 °C and 2.0 L was fed to column daily using a peristaltic pump (Watson Marlow Pvt. Ltd., UK) with help of PVC pipe (2.0 cm diameter) that is placed at the centre of the column allowing hydrological up flow in the column (Fig. 1). CW was planted with *Canna indica* species, which were collected from the CWs facility at CSIR-IMMT and positioned at 15.0 cm from the top of the CW column. The uprooted *Canna indica* had a root length of 18.4 cm, shoot length of 69.5 cm, and weight of 78.0 g. Fig. 1(a) shows a general layout of a filled vertical up flow CW column.

The outlet of the CW column was connected with the bottom of the Ca-Alg-Al dross beads glass column (length × diameter: 20.0 cm × 3.0 cm), as shown in Fig. 1(a). The column was packed with Ca-Alg-Al dross beads, reaching a height of 20.0 cm (2.0 g. of total AD mass inside the beads) and samples were collected at the top (Fig. 1) after completion of empty bed contact time (EBCT) for further analyses. The EBCT was calculated as 19.42 min by dividing the void volume of the Ca-Alg-Al dross column (77.7 ml) by the flow rate (4 ml/min). For further analysis, three different types of wastewater samples were collected as follows: (i) initial wastewater (0 h), (ii) VF-CW treated sample from the top of CW column (*i.e.,* after 24 h of HRT), and (iii) Ca-Alg-Al dross beads

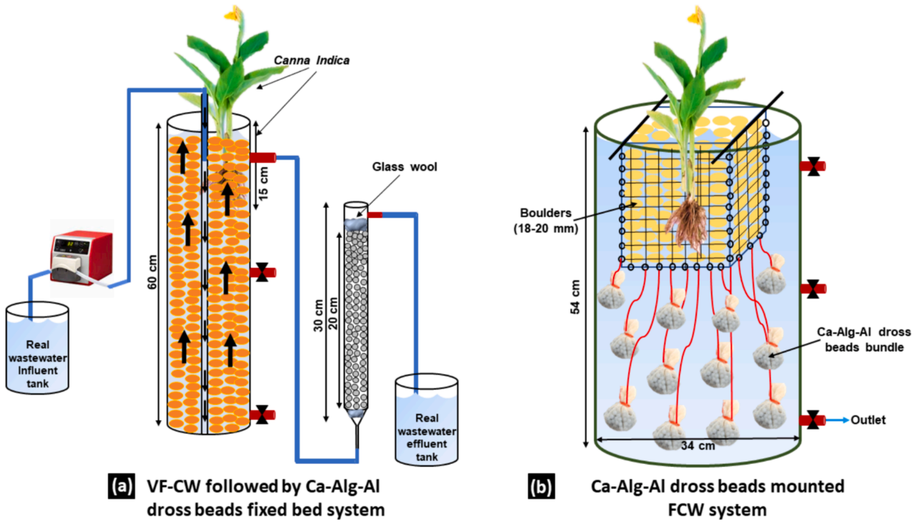

Fig. 1. Schematic diagram of (a) VF-CW followed by Ca-Alg-Al dross beads fixed bed system and (b) Ca-Alg-Al dross beads mounted FCW system.

fixed bed column treated sample collected after 24.19 h. All the samples were tested for phosphate, ammonium, and chemical oxygen demand (COD). All experiments were carried out at ambient temperature of 30 ± 2 °C.

To further study the potential of Ca-Alg-Al dross beads fixed bed column, the used beads from the column were regenerated with 0.5 M NaOH solution. In this experiment, NaOH solution was employed for regeneration instead of an acidic HCl solution because an acidic solution regenerated adsorbent tends to lose its regeneration capacity more quickly, can damage the exhausted adsorbent even at low concentrations, and mostly high regeneration capacity are observed with NaOH (Patel, 2021). To regenerate the Ca-Alg-Al dross column, it was disconnected from the CW column and NaOH solution was pumped in continuous mode (with peristaltic pump) to the Ca-Alg-Al dross beads fixed bed column at a flow rate of 4 mL/min for one day to achieve regeneration. After that, DDW was pumped for 2 days through the column at a flow rate of 4 mL/min to wash off the retained NaOH in the column. After regeneration, the CW column was reconnected with the Ca-Alg-Al dross column and examined for ammonium, phosphate, and COD removal. Table 1 presents a range of column parameters for the VF-CW and Ca-Alg-Al dross beads column.

Furthermore, an additional batch experiment was carried out to comprehend the simultaneous removal of ammonium in a Ca-Alg-Al dross beads fixed bed system. In this experiment, both Ca-Alg-Al dross beads and control Ca-Alg beads were exposed separately with 50 mL of 13 mg/L ammonium solution and with a mixture of 25 mL of 13 mg/L ammonium solution + 25 mL of 10 mg/L phosphate solution in a separate conical flask and kept at rotatory shaker (Spinix Orbital shaker MC-02, Tarson, India) at 100 rpm. All samples were analysed after 60 min of contact time for total phosphate and ammonium concentrations.

Table 1
Characterization parameters of VF-CW and Ca-Alg-Al dross fixed bed column.

VF-CW		Ca-Alg-Al dross fixed bed	
Flow rate	4 ml/min		
Void volume	2.0 L	Void volume	77.7 ml
Hydraulic retention time (HRT)	1.0 day	Adsorbent bed height	20.0 cm
Working height	50.0 cm	Adsorbent mass	2.0 g
Void volume	4749 mL	Empty bed contact time	19.42 min

2.2.2. Ca-Alg-Al dross beads mounted floating constructed wetlands (FCW)

Ca-Alg-Al dross beads mounted FCW was built in a PVC container of height 54.0 cm with a diameter of 34.0 cm and volume of 46.0 L. The PVC container had three ports at a height of 3.0 cm, 27.0 cm, and 51.0 cm from the bottom. Within the container, a basket (length × breadth × height: 23.0 cm × 23.0 cm × 20.0 cm) with 8–10 mm holes was suspended using a steel rod, as illustrated in Fig. 1(b). The holes were made in the outer container with the help of a soldering machine to support the basket on steel rods. Inside the basket, 12.0 kg siliceous gravels of 12–15 mm diameter were filled that provided support for the planted *Canna indica*. The uprooted *Canna indica* had a root length of 21.5 cm, shoot length of 64.5 cm, and weight of 78.0 g. With the help of a basket, 25.0 bundles of Ca-Alg-Al dross beads were suspended containing a total of 11.0 g. of AD in calcium alginate beads. These bundles were made up of synthetic netting (1.2 mm diameter) and suspended with 1 mm insulated wire, as shown in Fig. 1(b). In addition, these bundles were suspended at variable depths to maintain homogeneity of the Ca-Alg-Al dross beads in the system, as depicted in Fig. 1(b). Ca-Alg-Al dross beads mounted FCW system was fed with wastewater collected from the local facility, containing nutrient pollutants and organics that trigger eutrophication in water bodies. The collected water was also tested without any treatment with Ca-Alg-Al dross beads and showed massive algal growth within two weeks. The sample was collected from Ca-Alg-Al dross beads mounted FCW system every alternate day (*i.e.,* 2nd day (S-2), 4th day (S-4), 6th day (S-6)), and the wastewater was changed every 6 days from the time of influent filling. Based on the same sampling and inoculation method, 15 experiment cycles were performed. To ensure homogeneous sample collection, sampling was carried out by decanting water in a bucket through bottom most port of the container and mixing thoroughly before sample collection. All the samples were tested for phosphate, ammonium, and chemical oxygen demand (COD). All experiments were carried out at ambient temperature of 30 ± 2 °C.

2.3. Algal growth assessment in treated wastewater

The objective of this study was to assess post treatment scenario when treated water was discharged. This was achieved by artificial inoculation of treated water with natural algae to simulate eutrophic conditions. For this experiment, at first, to attain mother culture, 5 mL of algae containing water was collected from local facility and mixed with 500 mL of BG11 solution (BG11 algal growth solution preparation utilized 0.075 g; $MgSO_4{\cdot}7H_2O$, 0.02 g; Na_2CO_3, 0.036 g; $CaCl_2{\cdot}2H_2O$, 0.001 g; EDTA, 0.006 g; $C_6H_8O_7$, 0.006 $(NH_4)[Fe_5(C_6H_4O_7)_2]$, 0.006 g; $K_2HPO_4{\cdot}3H_2O$ and 0.6 g $NaNO_3$) (Mittal et al., 2020). Further, to produce mother culture, algae were intentionally adopted from natural wastewater to mimic the natural/practical system. After attainment of exponential phase in algal growth *i.e.*, 10–12 days in BG-11 solution, UV–Vis spectra (Cary 100, Agilent Technologies, USA) of algal culture were repeatedly observed to ensure the attainment of absorbance value as 0.9 by the algal culture at 689 nm of wavelength. This absorbance level of 0.9 is crucial to ensure the optimal growth of the algae. After, 50 mL of mother culture was centrifuged and the supernatant was removed to attain a pellet of algae. This pellet was washed several times with DDW and mixed with 75 mL of Ca-Alg-Al dross mounted FCW system treated water in a conical flask. Further, the formation of the algal pellet process was repeated several times to create flasks in triplicates for the initial (I-0), 2nd day (S-2), 4th day (S-4), 6th day (S-6), and negative control (NC-DDW *i.e.,* algal pellet dissolved in 75 mL of DDW). The above process allowed the inoculation of each sample with similar amounts of algae. All experimental conical flasks and mother culture were kept on a rotatory shaker at 140 rpm for proper mixing and algal growth. The experiment set up was equipped with a light source (85 W, Spiral, Crompton Greaves Ltd.) at an illumination period of 12 h (6 a.m. to 6 p.m.) each day. The on and off cycles were maintained using an automatic on–off timer (HPA digital timer, Australia). Thereafter, the absorbance of each algal conical flask was observed at 689 nm up to 25 days from the start of the experiment using a UV Vis spectrophotometer (Cary 100 UV–Vis, Agilent Technologies, USA).

2.4. Analysis and calculations

Collected liquid samples were either analysed on the day it was collected or stored overnight at 4 °C for measurement the following day. On the measurement day, all the samples were filtered through 0.45 μm Whatman filter paper (USA) and then analysed for total phosphorus, ammonium, and COD using procedure described in APHA (2005) (American Public Health Association, 2005) protocol with the colorimetric method using a UV–Vis spectrophotometer (Cary 100 UV–Vis, Agilent Technologies, USA). Eq. (1) was used to calculate the percentage removal of COD, ammonium, and phosphate. Likewise, an ion chromatograph (930 compact IC flex, Metrohm, Switzerland) was used to determine the concentration of cations and anions present in the wastewater.

$$\%\,removal = \frac{Influent\ concentration - Effluent\ concentration}{influent\ concentration} \times 100 \quad (1)$$

3. Results and discussion

3.1. Characterization studies

3.1.1. FTIR analysis

Fig. 2 shows FTIR spectra of Ca-Alg-Al dross beads and ammonium and phosphate loaded Ca-Alg-Al dross beads. Data shows several Fourier transform peaks representing various functional groups in these samples. Nonetheless, when delving deeper into the FTIR analysis discussion, our emphasis remains exclusively on the removal of phosphate. This is because, during adsorption from natural wastewater, the pH is lower than the pHpzc of Ca-Alg-Al dross beads, resulting in a positively charged surface and thus encouraging a preferential interaction with phosphate rather than ammonium. In Fig. 2, the Fourier transform peak at 1594 cm^{-1} is associated with the ester group (–COO) present in the sodium and calcium alginate structure (Zhou et al., 2018). Similarly, interactions resembling those observed at the 1421 cm^{-1} peak can be attributed to the asymmetric stretching vibration of the carboxyl (COO–) group. However, both peaks 1594 cm^{-1} and 1421 cm^{-1} disappear almost completely for phosphate and ammonium loaded Ca-Alg-Al dross beads which imply an interaction between COO^- groups and phosphate during adsorption/uptake (Luo et al., 2019). Further, the –OH vibration can reveal any transformation of the –OH group present on the Ca-Alg-Al dross beads. The bonding –OH vibration was detected at 3466 cm^{-1} (3200–3600 cm^{-1}) representing both antisymmetric and symmetric OH stretching modes (Yang et al., 2008). After adsorption, the peak at 3466 cm^{-1} weakens, thus, indicating that the –OH group was subjected to interference, possibly due to interaction with phosphate through electrostatic attraction. The band appearing at 2360 cm^{-1} corresponds to CO_2 (g) and was observed in all samples, although with variations in intensities (Mokhtari et al., 2019). The band at 1011 cm^{-1} in the Ca-Alg-Al dross bead was attributed to Si–O stretching vibration (Abukhadra et al., 2019). After phosphate and ammonium adsorption, a distinctive sharp peak emerged at 1021 cm^{-1}, likely attributable to the characteristic P–O asymmetric stretch vibration (He et al., 2016; Mittal et al., 2024). Thus, it can be inferred that the surface hydroxyl group was substituted with phosphate through ligand complexation. Similar new peaks were also observed after simultaneous phosphate and ammonium adsorption onto different adsorbents such as hydrated aluminium oxide modified natural zeolite (HAlO) and NaOH activated lanthanum impregnated zeolite (Guaya et al., 2015b; He et al., 2016). Our results agree with previous studies which indicated phosphate can be adsorbed over the surface of aluminium and magnesium ions through ligand complexation/exchange process at circumneutral pH through the formation of monodentate or bidentate species (Wu et al., 2019; Yang et al., 2006).

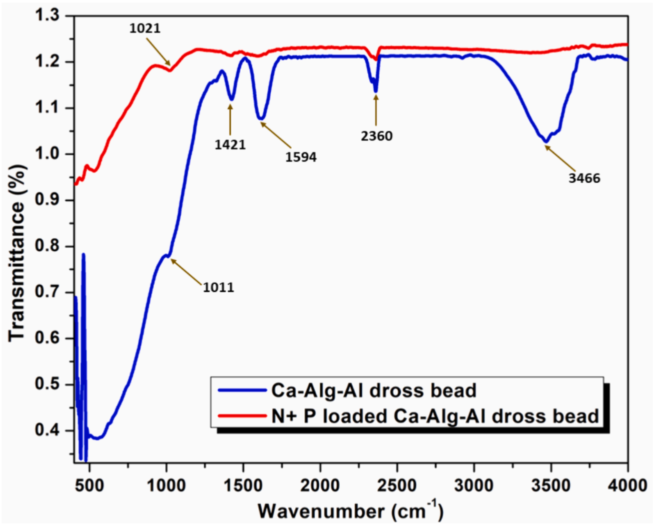

Fig. 2. FTIR spectra of Ca-Alg-Al dross bead before adsorption and Ca-Alg-Al dross bead after simultaneous N (ammonium) and P (phosphate) adsorption.

3.1.2. SEM-EDX analysis

The Ca-Alg-Al dross bead surface before and after the phosphate and ammonium removal was examined by SEM equipped with EDX as shown in Fig. 3. SEM images indicated that the surface morphology of the control bead was smooth, as shown in Fig. 3 (a). The control Ca-Alg beads contained Na, Ca, Cl, C, and O elements in EDX spectra as shown in Fig. 3(b), whereas Fig. 3(c) shows the distribution of detected elements on the beads surface. Similar SEM-EDX results of control Ca-Alg beads were also observed by Torres-Caban et al. (2019) and Bilici et al. (2019). SEM image after entrapment of AD inside Ca-Alg beads represents a much rough structure, as shown in Fig. 3(d). The EDX analysis of Ca-Alg-Al dross beads reveals the presence of additional elements like Mg, Al, and Si, attributed to entrapment by AD (Fig. 3(e)). Thus, the relative content of Cl, Ca, Na, C, and O decreased in Ca-Alg-Al dross beads in comparison to the bare Ca-Alg beads. Further, in Fig. 3(f) and (i), elemental mapping of Ca-Alg-Al dross beads certainly confirms the loading of Al in a high percentage (*i.e.,* 26.4 wt% by EDX data). After the adsorption of ammonium and phosphate, through closer observation and comparison, it was found that the surface of Ca-Alg-Al dross beads seemed coarser than the non-exposed Ca-Alg-Al dross beads. It appeared that the surface of Ca-Alg-Al dross was covered with several small particles after ammonium and phosphate adsorption experiment (Fig. 3(g)). These small particles were more likely due to newly formed precipitation after reactions. Our results are in agreement with Ren et al. (2016), investigating phosphate removal in aqueous solution by aluminium slat slag derived from scrap aluminium melting process. Adsorption of ammonium and phosphate was confirmed with the presence of N and P element in the EDX (Fig. 3(h)) and mapping in Fig. 3(i), (k) and (l), whereas individual mapping displayed that N (Fig. 3(k)) and P (Fig. 3(l)) was evenly adsorbed/uptake over the surface of Ca-Alg-Al dross bead (Fig. 3(i)). This finding was reinforced by the outcomes of experiments involving the exposure of Ca-Alg-Al dross beads to a simultaneous solution of ammonium and phosphate, as well as to a solution containing only ammonium. Notably, the removal of ammonium was significantly lower when Ca-Alg-Al dross beads were exposed solely to the ammonium solution. Conversely, a substantial removal of both ammonium and phosphate was observed when a mixture of ammonium and phosphate solutions was exposed to Ca-Alg-Al dross beads. Besides, the weight percentage of Na and Mg on Ca-Alg-Al dross beads was surprisingly decreased from 1.9 % to 0.7 % and 0.5 % to 0.1 % after the adsorption of ammonium and phosphate. This decrease in cation concentrations over Ca-Alg-Al dross beads was further confirmed by ion chromatography data of samples, which showed an increase in Na and Mg concentrations in the solution after treatment with ammonium and phosphate. This is detailed in Supplementary File Table S1 and Fig. S1. The decrease in Na and Mg and the appearance of the N peak in EDX data seem to indicate the exchange of Na with ammonium as the main process involved in ammonium removal. In addition, a decrease in weight % of Cl^- ion from 1 % to 0.2 % was observed after adsorption, this could be due to the exchange of phosphate ion present in the solution with Cl^- ion present in the Ca-Alg-Al dross bead interlayer. Ion chromatography data further confirmed this by showing an increase in Cl^- anion concentrations in the solution after ammonium and phosphate adsorption, as detailed in Supplementary File Table S1 and Fig. S1. Similar results were also demonstrated by He et al. (2016) and Yin and Kong (2014a), investigating the simultaneous removal of ammonium and phosphate with lanthanum impregnated zeolite and calcium rich attapulgite, respectively.

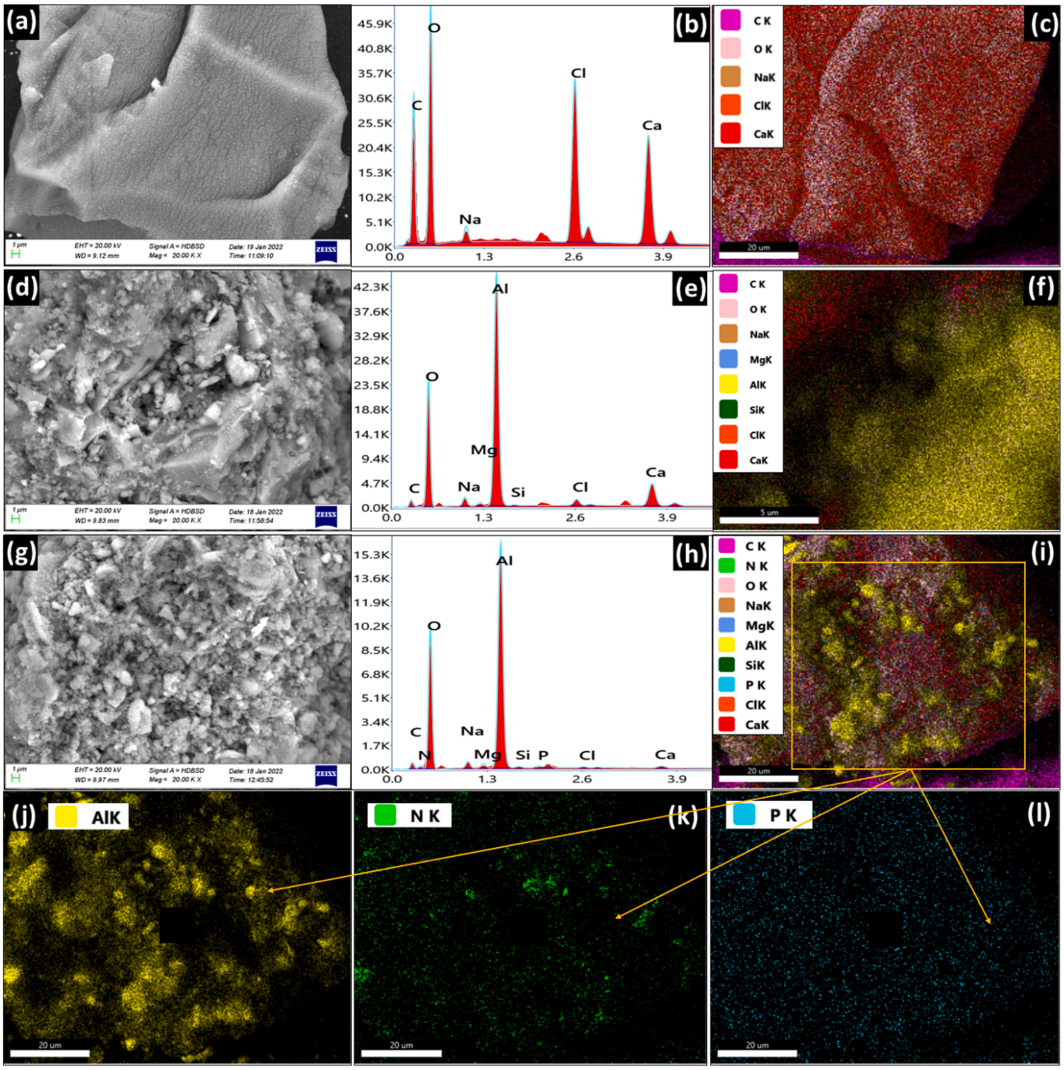

Fig. 3. SEM morphology, EDX spectra, and elemental mapping of raw AD (a–c); Ca-Alg-Al dross beads (d–f) and (N + P) loaded Ca-Alg-Al dross beads (g–i), respectively. Further, (j–l) shows the elemental mapping and distribution of Al, N, and P.

3.2. Performance of Ca-Alg-Al dross beads in different aqueous environments

These studies utilise real wastewater and thus variation in influent wastewater concentration of nutrients was observed in these studies.

3.2.1. VF-CW followed by Ca-Alg-Al dross beads fixed bed system for real municipal wastewater treatment

Fig. 4(a) and (b) represent the percentage of phosphate and ammonium removal from the real municipal wastewater treatment in VF-CW followed by Ca-Alg-Al dross beads fixed bed system. The 1st cycle of the test was carried out for 30 days. From Fig. 4(a), high phosphate removal of 85 ± 0.41 % can be observed till 8 days of operation in Ca-Alg-Al dross beads column, while, thereafter it decreases to 42.56 ± 0.32 % by 14 days and more to 23.79 ± 1.55 % by 23 days. Eventually, at the end of 30 days phosphate removal decreased to 9.49 ± 1.42 % in Ca-Alg-Al dross beads column. High phosphate removal till 8 days of operation can be due to high surface area and free active sites provided by a fixed bed of Ca-Alg-Al dross beads, thus allowing a high number of binding sites available for phosphate adsorption/uptake. However, a decrease in removal with time can be attributed to the saturation of active sites for phosphate adsorption (Swain et al., 2013). Further, Fig. 4(a) also indicates low phosphate removal in VF-CW throughout the study *i.e.,* average of 12.79 ± 8.10 % which may be ascribed to (i) less adsorption capacity of filter material (siliceous gravels) used in VF-CW and (ii) low phosphate uptake by *Canna indica* vegetation as a nutrient. Limited phosphate uptake is also supported by our previous study, in which a CW was operated with the same feed of municipal wastewater as in current study and planted with *Canna indica* vegetation. The fully grown plants revealed maximum phosphate assimilation of 0.52 mg/g in the stem, 0.39 mg/g in the root, and 0.5 mg/g in the leaves of *Canna indica* (Mittal et al., 2023a).

Ammonium removal was also examined through VF-CW followed by Ca-Alg-Al dross beads fixed bed system which is represented in Fig. 4(b). In CWs, ammonium removal is mainly dependent on the availability of oxygen, whereas other phenomena such as uptake by plants and adsorption over CW substrate can also play a minor role in ammonium removal. In our study, oxygen can be supplemented by (i) atmospheric oxygen diffusion and (ii) secretion through root exudates of planted *Canna indica* vegetation. However, low average ammonium removal of 9.10 ± 8.9 % was observed in the CW column in our experiments. This can be explained by (i) less adsorption capacity of filter material (siliceous gravels) used in CWs, (ii) least uptake by *Canna indica* vegetation since it was not fully flourished, and (iii) low dissolved oxygen availability in the CW column from both atmospheric diffusion and root exudates, thus restricting ammonium oxidation. Further, in Fig. 4(b), average ammonium removal in Ca-Alg-Al dross beads fixed bed column was noted as 29.32 ± 1.69 % in 30 days of operation. Elemental

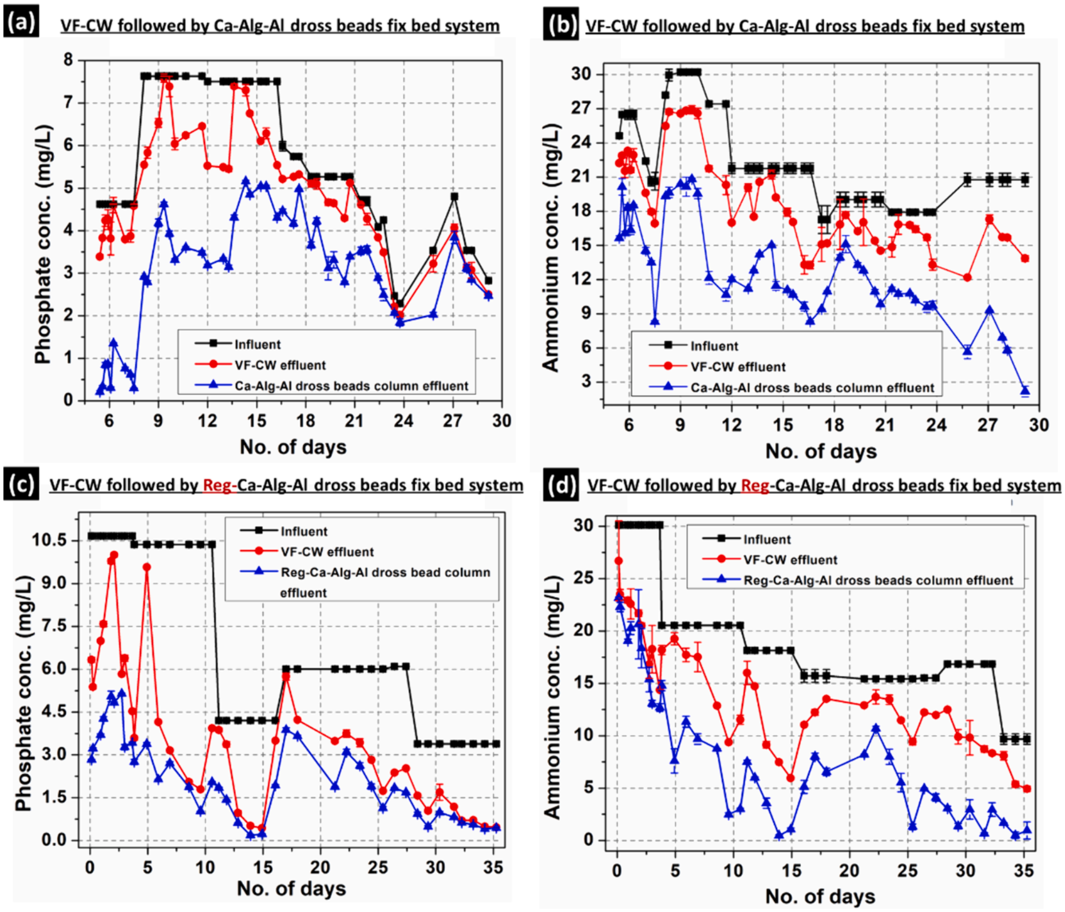

Fig. 4. (a) Phosphate and (b) ammonium removal with VF-CW followed by Ca-Alg-Al dross column respectively, (c) phosphate, and (d) ammonium removal with VF-CW followed by regenerated Ca-Alg-Al dross column, respectively.

mapping results can explain this adequate ammonium removal through Ca-Alg-Al dross column. Where, a high concentration of exchangeable Mg^{+2}, Na^{+} metal ions present in Ca-Alg-Al dross bead can substitute ammonium present in the wastewater through an ion exchange mechanism, as elaborated in the SEM-EDX discussion. Furthermore, other pollutant removal results such as chemical oxygen demand (COD) were not shown since COD concentration in the influent was found to be low *i. e.,* 40 ± 20 mg/L from which most was removed in the CW column.

Further, to estimate the reuse potential of Ca-Alg-Al dross beads fixed bed column, it was regenerated with 1 M NaOH. Whereas, VF-CW column remained the same for the regeneration study. Fig. 4(c) and (d) demonstrate the phosphate and ammonium removal in VF-CW followed by a regenerated Ca-Alg-Al dross beads fixed bed system. In the VF-CW column, an increase in the phosphate and ammonium removal can be observed in comparison to previous phase results achieving an average of 51.42 ± 25.64 % of phosphate removal and 30.92 ± 15.76 % of ammonium removal. Enhanced nutrient removal can be the contribution of fully grown *Canna indica* species with time in VF-CW by means of (i) uptake of nutrients by the fully-grown *Canna indica* (Cui et al., 2010), and (iii) ammonium oxidation owing to enhanced dissolved oxygen supplied by the root of matured *Canna indica* vegetation (Gupta et al., 2021). Although accumulated phosphorus in plants can be reintroduced into the water in the CW column, this is more likely because phosphorus is primarily stored in the roots of the plants, and the removal efficiency in the CW is relatively low (Ayaz et al., 2012; Kadlec, 2005; Martín et al., 2013). To avoid these situations, further treatment of VF-CW effluent with regenerated Ca-Alg-Al dross beads fixed bed column is imperative. The regenerated Ca-Alg-Al dross beads fixed bed system has shown phosphate removal of 55 % initially which further declined to 4 % at the end of 35 days of operation as shown in Fig. 4(c). This decline in removal seems to be dependent on influent phosphate concentration as observed in Fig. 4(c), since in the initial days of column operation, it has received a high influent phosphate concentration *i.e.*, 6.33 mg/L but at the end of operation time, influent phosphate concentration has declined to as low as 0.46 mg/L. Besides, this experiment observed a decrease in phosphate removal after column regeneration. However, our previous batch study results demonstrated high regeneration capacity, suggesting in-situ regeneration process of material in a column is less effective than the batch regeneration process, understandably due to increased system complexity (Mittal et al., 2023b). Conversely, with time, ammonium removal increased in regenerated Ca-Alg-Al dross bead column from 4.23 % to 93.44 % (Fig. 4(d)) which can be the result of ammonium adsorption onto Ca-Alg-Al dross beads through the ion exchange process with Na^{+} and Mg^{+2}, as discussed earlier. Nevertheless, in our previous phase results, average ammonium removal was only noted as 29.32 ± 1.69 %, indicating the involvement of additional mechanisms for elevated ammonium removal. This can be explained by the formation of struvite formation since the ion exchange mechanism increases the concentration of Mg^{+2} cation in the solution which can further involve in the struvite formation process with ammonium and phosphate ions present in the regenerated Ca-Alg-Al dross column (as shown in Fig. 7). Together with this, as discussed earlier, high residual phosphate concentration in the regenerated Ca-Alg-Al dross column due to its low removal efficiency can further expedite the ion exchange process for rapid formation of struvite as product. In the present work, struvite precipitation appears to be thermodynamically viable, with two primary factors playing a significant role: pH and the dissolved concentrations of N, P, and Mg. The recommended pH range for struvite formation, as specified by Siciliano et al. (2020) is 7–11, whereas, Hao et al. (2013), mentions it near neutral for pure struvite formation. In this current research, our systems successfully uphold this range, as the pH of eutrophic water and municipal wastewater after nutrient adsorption was found near circumneutral. Additionally, the concentration of dissolved P: N: Mg molar ratio falls within the range of 0.1–0.3: 2.7–4.9: 0.2–0.6, as determined through multiple EDX analyses of N and P-loaded Ca-Alg-Al dross beads. These ratios also align with the conditions for struvite formation by other studies (Aguado et al., 2019; Xavier et al., 2014). Aguilar-Pozo et al. (2023) reported a P:Mg molar ratio of 1:1 and 1:2, the percentage of phosphate precipitated was 53–72 % and 89–97 %, respectively (Aguilar-Pozo et al., 2023). However, regarding the most favourable molar ratios, a great divergence among the literature are reported, deviating from the theoretical P: N:Mg ratio of 1:1:1 for struvite formation, primarily due to its strong dependence on the chemical and physical characteristics of wastewater (Siciliano et al., 2020).

Current study holds several advantages in terms of applying the VF-CW column prior to the Ca-Alg-Al dross beads fix bed column since it prevented the bead destruction through suspended particles present in real municipal wastewater. Nevertheless, several other reported studies on simultaneous ammonium and phosphate removal including FeOOH (iron oxide) (Ma et al., 2020), shale as a substrate in horizontal subsurface flow CWs (Drizo et al., 1997), ceramsite and magnetite as substrates for phosphorous treatment of swine wastewater (Dong et al., 2021) and various other substrates (Si et al., 2021; Yang et al., 2018; Zhu et al., 2011) have substituted the CWs substrate with the adsorbent rather than using adsorbent as separate step tertiary treatment removal process. This direct application of adsorbent in CWs column as substrate can elevate system complexity, considering that CW plants also follow complex mechanisms and processes. Furthermore, once the adsorbent reaches its saturation point, the removal of all the adsorbent from the CW system along with the plants can pose a significant challenge. The use of adsorbent as a tertiary or separate treatment process provides a clear visualization of the independent effect of adsorbent on removal efficiency. This, in turn, facilitates a more comprehensive understanding of pollutant removal mechanisms and enhances control over the process. A further advantage of the present research lies in the incorporation of AD encapsulated within beads rather than employing raw AD powder. This choice serves to avoid complexity in the process and mitigate the risk of potential clogging.

In summary, VF-CW followed by Ca-Alg-Al dross beads fixed bed system and VF-CW followed by regenerated Ca-Alg-Al dross beads fixed bed system have demonstrated successful functioning and application for simultaneous phosphate and ammonium from real municipal wastewater treatment in our study. Consequently, Ca-Alg-Al dross beads fixed bed column can be employed as tertiary wastewater treatment or as an additional step for the treatment of residual nutrients from wastewater after treatment through CWs.

3.2.2. Ca-Alg-Al dross beads mounted floating constructed wetlands (FCW)

Ca-Alg-Al dross beads mounted FCW was studied to determine the potential of Ca-Alg-Al dross beads for remediation and up-gradation of eutrophic lentic water bodies like lakes, ponds, *etc.* The hydraulic retention time (HRT) of the Ca-Alg-Al dross beads mounted FCW was maintained at 6 days. Fig. 1(b) shows the arrangement of Ca-Alg-Al dross beads mounted FCW system for phosphate and ammonium removal. In continuous 15 cycles of experiments, Ca-Alg-Al dross based mounted FCW system demonstrated an average of 33.75 ± 11.43 %, 61.082 ± 13.71 %, and 79.18 ± 8.56 % phosphate removal on the 2nd, 4th, and 6th day, respectively. Whereas average ammonium removal on the 2nd, 4th, and 6th day was found to be 26 ± 9.92 %, 45.45 ± 20.19 %, and 65.45 ± 21.04 %, respectively. The most significant rise in ammonium and phosphate removal is evident on the 2nd day, which points to the active engagement of Ca-Alg-Al dross beads with the fresh real wastewater. This is attributed to the initial abundance of adsorption sites and the high pollutant concentration gradient in the wastewater. However, with time, even with the decrease in available adsorption sites, an increase in ammonium and phosphate removal can be observed with an increase in HRT from Fig. 5(a) and (b). This can be related to the presence of vegetation through (i) adsorption by the densely grown roots of *Canna indica* (Cui et al., 2010) and (ii) nutrient uptake through roots (Beebe et al., 2014). However, limited nutrient uptake is revealed by our previous study as discussed in previous section (Mittal et al., 2023a). In addition, a very limited amount of nutrient uptake by *Canna indica* has been reported by several researchers (Li et al., 2013; Vymazal, 2007; Yang et al., 2022; Zhang et al., 2009). Moreover, Fig. 5(a) and (b) show that there is very low ammonium and phosphate concentration in influent, however, even though, high ammonium and phosphate removal efficiencies can be observed, suggesting that Ca-Alg-Al dross bead can be considered a suitable adsorbent in eutrophic waters with relatively low concentration of pollutants. Further, COD was not discussed due to the very low COD concentration in the influent itself.

3.2.3. Algal growth assessment

Further, an algal experiment was carried out to examine the capability of Ca-Alg-Al dross beads mounted FCW treated water towards algal growth stimulation or resurgence of eutrophication. Results shown in Fig. 6 reveal that, irrespective of any sample, algal cells can support temporary growth of algae in DDW for the initial few days (till 8th days) which may be because of nutrient release from dead biomass. Further, after 8 days, algal growth in each sample starts declining, wherein, algal growth in S-4 and S-6 samples is even less than DDW (control). This indicates that S-4 and S-6 treated samples of FCW can inhibit algal growth which may result from the removal of nutrients to the level *i.e.,* N/P < 4 and N/P < 2.5 respectively. Whereas, high growth in I-0 and S-2 also corroborates with its high N/P ratios of ≈10 and <8.5, respectively (Figler et al., 2021; Lee et al., 2013). The findings are further corroborated by the Redfield N:P mass ratio of 7:1. An increase in this ratio signifies a higher presence of organic matter in the water, leading to nutrient enrichment and the potential onset of eutrophication (Chorus and Spijkerman, 2021; Sidabutar et al., 2020). Conclusively, it can be deduced that treated water from Ca-Alg-Al dross beads mounted FCW system can arrest the algal growth in treated water for a long time. Thus, Ca-Alg-Al dross beads mounted FCW has shown promising results for remediation and up-gradation of eutrophic lentic water bodies like lakes, ponds, etc.

3.3. Proposed N and P removal mechanism on the developed Ca-Alg-Al dross beads

To develop a clear understanding of the mechanism involved in ammonium and phosphate adsorption over developed versatile adsorbent Ca-Alg-Al dross beads, the adsorbent before and after adsorption was characterized and examined with the help of FTIR and SEM-EDX analysis, and the residual solution was examined through ion chromatography. SEM-EDX and ion chromatography results (Supplementary Table S1 and Fig. S1) indicated that ammonium adsorption over Ca-Alg-Al dross occurred through ion exchange with Mg^{+2} and Na^{+}. This ion exchange releases Mg^{+2} into the solution, which can then react with ammonium and phosphate to form struvite ($MgNH_4PO_4 \cdot 6H_2O$) as shown in Fig. 7. Maintaining the ideal pH and P: N: Mg molar ratio, our study suggests potential struvite formation, facilitating ammonium and phosphate removal. These findings align with experimental study results conducted to understand the simultaneous removal of ammonium with phosphate which shows significantly low ammonium removal using Ca-Alg-Al dross beads. However, a mixture of ammonium and phosphate containing Ca-Alg-Al dross beads solution demonstrated the removal of both ammonium and phosphate with final concentrations reaching 4.54 mg/L and 0.139 mg/L respectively, from the initial of 13 mg/L ammonium and 10 mg/L phosphate in 60 min of contact time. Thus, struvite formation could be contributing to the enhancement of ammonium removal together with ion exchange. Similar results were also reported

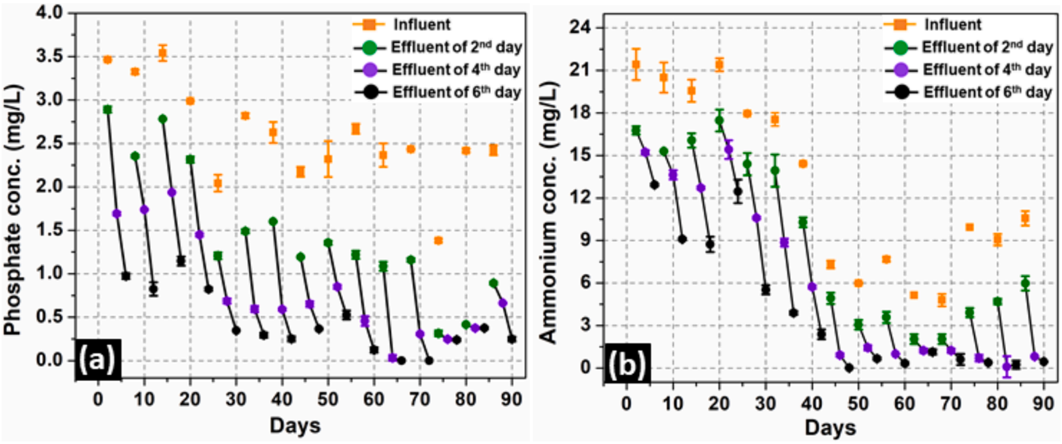

Fig. 5. (a) Phosphate removal (b) ammonium removal in Ca-Alg-Al dross beads mounted FCW system.

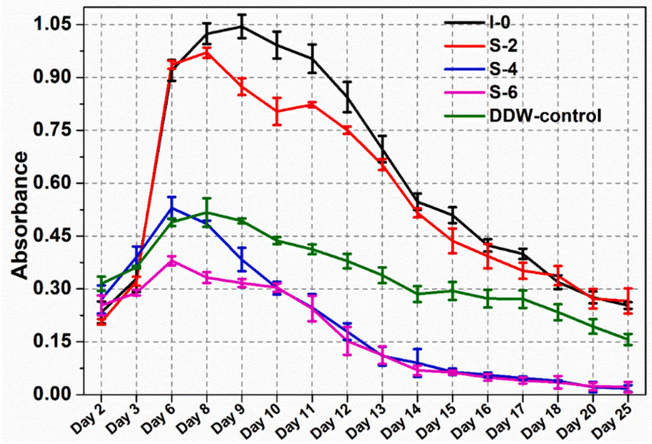

Fig. 6. Algal growth study, where I-0 shows initial, S-2, S-4, and S-6 denote for 2nd, 4th, and 6th day treated samples, respectively and DDW represents control sample.

by Yin and Kong (2014a) while investigating the simultaneous removal of phosphate and ammonium from eutrophic waters with natural calcium rich attapulgite. On the other hand, anion (phosphate) adsorption is favourable only when pHpzc is above the solution pH. pHpzc of Ca-Alg-Al dross beads was estimated ca. 8.5, which was adopted from our previous study on the investigation of Ca-Alg-Al dross adsorbent to remove phosphate in batch studies (Mittal et al., 2023b). When Ca-Alg-Al dross beads were used as adsorbent in municipal wastewater or eutrophic water treatments, the typical pH range of 6–7 renders the surface of Ca-Alg-Al dross beads positively charged. This charge facilitates the electrostatic attraction for phosphate adsorption through the interaction of Metal-OH$_2^+$ with $H_2PO_4^{2-}$ (Fig. 7). Also, Ca is known to act as bridge in anion adsorption and might have contributed towards phosphate adsorption here. Moreover, phosphate oxyanion ($H_2PO_4^-$) can also associate with –OH surface group (*i.e.,* metal hydroxide or Al-OH) by formation of complexes. The formed complex could be mononuclear monodentate inner sphere complexation since only the P–O functional group was revealed in the FTIR study, as shown in Fig. 1. Furthermore, EDX also revealed a plausible removal of phosphate from solution through ion exchange with Cl^- present in Ca-Alg-Al dross bead interlayers. In summary, the phosphate removal mechanism can be deduced as electrostatic attraction, ion exchange, cation bridging and mononuclear monodentate inner sphere complexation with Ca-Alg-Al dross beads, whereas, ammonium removal resulting from ion exchange between interlayer cations (Mg^{+2}, Na^+) present in Ca-Alg-Al dross beads with ammonium.

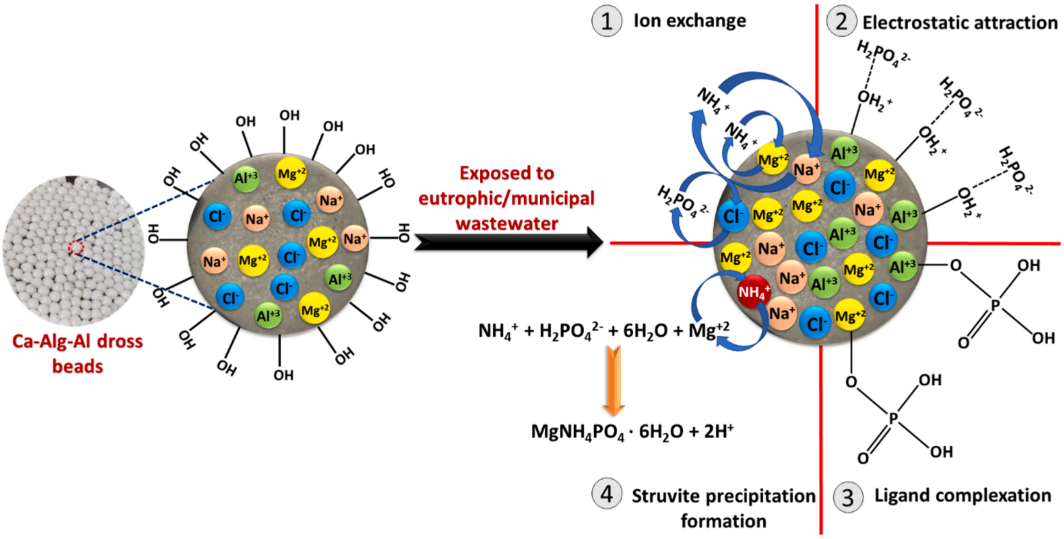

Fig. 7. Mechanism of simultaneous ammonium and phosphate adsorption on Ca-Alg-Al dross beads.

4. Conclusion and environmental implications

In summary, this research offers a versatile, efficient, and low-cost Ca-Alg-Al dross material for the dual management of phosphate and ammonium from real wastewater. The Ca-Alg-Al dross beads have shown promising nutrient removal efficiency along with feasible and simplified operation in two different aqueous environmental systems demonstrated in this study *i.e.*, VF-CWs followed by Ca-Alg-Al dross beads fixed bed system and Ca-Alg-Al dross beads mounted FCW imitating lentic ecosystems. Furthermore, the algal growth inhibition potential of Ca-Alg-Al dross beads mounted FCW system treated water assures that it is safe for discharge or remediate non-flowing polluted water bodies like ponds, lakes and will not stimulate eutrophication immediately. Accordingly, the system can be easily adapted and scaled for practical use in lake restoration, remediation, and up-gradation of eutrophic lentic water bodies. SEM-EDX, FTIR, and IC results uncovered the removal of phosphate through electrostatic attraction, monodentate inner sphere complexation and ion exchange with Cl^- present in interlayers of Ca-Alg-Al dross beads. Whereas, ammonium removal was mainly ascribed to exchanging of Mg^{+2} and Na^+ in the Ca-Alg-Al dross beads. Moving forward, the forthcoming analysis shall include the influence of co-existing ions and physicochemical parameters in the natural wastewaters on nutrient removal together with deep insight into life span, the regeneration capacity of material, and the approach of regeneration in real fields.

CRediT authorship contribution statement

Yamini Mittal: Writing – original draft, Methodology, Formal analysis, Data curation. **Pratiksha Srivastava:** Writing – review & editing, Validation, Supervision, Conceptualization. **Naresh Kumar:** Writing – review & editing, Supervision. **Bankim Chandra Tripathy:** Writing – review & editing, Supervision. **Fernando Martinez:** Writing – review & editing, Supervision. **Asheesh Kumar Yadav:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This work reports financial support was provided by Council of Scientific and Industrial Research Institute of Minerals and Materials Technology. AKY reports a relationship with Council of Scientific and Industrial Research Institute of Minerals and Materials Technology Department of Hydro & ElectroMetallurgy that includes: funding grants. AKY has patent pending to none. Asheesh Kumar Yadav reports financial support, administrative support, equipment, drugs, or supplies, statistical analysis, travel, and writing assistance were provided by Council of Scientific and Industrial Research Institute of Minerals and Materials Technology. Asheesh K Yadav reports financial support was provided by Council for Scientific and Industrial Research. Asheesh K Yadav reports financial support was provided by DST India. Yamini Mittal reports financial support was provided by Council for Scientific and Industrial Research. Asheesh K Yadav and Others has patent pending to CSIR. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2024.131205.

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