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New calcareous soil–alginate composites for efficient uptake of Fe(III), Mn(II) and As(V) from water

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ABSTRACT

In the present study, various grades of sodium alginates were extracted from different brown macroalgae and their characteristics were investigated using FTIR, UV–vis and EA. The alginates were used in combination with different proportions of calcareous soil to develop new composite microparticles as potential sorbents for efficient uptake of Fe(III), Mn(II) and As(V) from water. Under the investigated conditions (1 g of composite equilibrated in 100 ml of standard metal ion solution), the composites have removed almost 100% of Fe(III) in the concentration range of 0.5–16.0 mg l^{-1}. Soil, alginate and composites exhibited the highest removal (about 89%) of Mn(II) at 0.5 mg l^{-1}. Reasonable removal efficiency (50–60%) was recorded at 0.5 mg l^{-1} of As(V) whereas, increasing the initial As(V) concentration resulted in marked decrease in removal efficiency. The collected equilibrium data were also fitted to both Langmuir and Freundlich isotherms for all the developed composites.

1. Introduction

Heavy metals have a wide range of potential applications in various fields, however many of them are highly toxic even at low concentrations and being non-biodegradable tend to accumulate in living organisms and cause different diseases and health disorders (Reddy, Seshaiah, Reddy, Rao, & Wang, 2010). Hence, such heavy metals must be removed from the polluted water streams in response to environmental legislation and enforcement. Besides, polluted water streams and groundwater often contains some heavy metals such as iron and manganese, which can not only affect the color and flavor of water but also accumulate to cause hindrance in the water equipment and pipelines (Gotoh, Matsushima, & Kikuchi, 2004).

Iron, manganese and arsenic are three of the major toxic metal ions that are hazardous to life. Iron levels below 0.3 mg l^{-1} were characterized as unnoticeable, whereas iron concentrations in the range of 0.3–3 mg l^{-1} were considered acceptable (WHO, 1996).

Manganese is naturally occurring in various groundwaters and surface water sources and also in soils that may erode into these waters. On the other hand, human activities are also responsible for a significant part of the manganese contamination in water in some regions.

In higher concentrations, iron and manganese were also found to cause various problems such as staining laundry and water use fixtures, developing a metallic or vinyl type taste in the water, often appearing as a crusty sheen on the water's surface and supporting the growth of iron and manganese bacteria, which can clog strainers, valves and pumps.

Arsenic, a toxic trace element, occurs in both natural and industrial waters. Recently, arsenic contamination of surface and groundwater at toxic levels has become a growing concern on a global perspective. Besides, there have been several reports of arsenic poisoning in various countries such as India (Das et al., 1996), Bangladesh (Hoque et al., 2000), Vietnam (Berg et al., 2001) China, and Taiwan (Tseng et al., 1968). It has been found that long-term drinking of water contaminated with arsenic can cause kidney, bladder, lung, liver, skin, and nerve tissues injuries (Roberts et al., 2004; Thirunavukkarasu, Viraraghavan, & Subramanian, 2003).

Over the last few decades, a significant body of research has focused mainly on developing more effective approaches for

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removal of heavy metals from polluted water streams or improving conventional techniques such as chemical precipitation (Harper & Kingham, 1992), ion exchange, filtration, and electrodialysis (Balaji, Yokoyama, & Matsunaga, 2005). Current applied methods including ion exchange and electrodialysis have relatively high operation and maintenance costs. Chemical precipitation is, however inexpensive but still unable of removing trace concentrations of heavy metal ions. Adsorption strategy is expected to overcome such shortcomings, and used in a wide range of potential applications.

Of various widely used sorbents, naturally occurring materials, including natural polymers, soil, and their composites have been accepted as feasible sorbent materials for reducing the cost of waste water treatment (Bailey, Olin, Bricka, & Adrian, 1999). An important class of polymers that was found beneficial in metal ions removal is the class of biopolymers isolated from algae such as sodium alginates due to their ability to form complexes with metal ions (Banerjee, Nayak, & Lahiri, 2007).

Sodium alginate, a natural polysaccharide obtained from brown macro-algae, is a copolymer of varying compositions of β-1,4 linked L-guluronic and D-manuronic acids (Banerjee et al., 2007; El-Sherbiny, 2010; El-Sherbiny, Abdel-Bary, & Harding, 2010). Several alginate-based sorbents have been investigated for metal uptake from aqueous solutions for possible application in water treatment processes. For instance, alginate beads were found effective in the removal of a wide range of heavy toxic metal cations, such as Ni, Cu, Zn, Cd, Hg, Pb, Nd, Eu, Yb, and Ra (Min & Hering, 1998; Nayak & Lahiri, 2005).

In the current study, various grades of sodium alginates were extracted via a modified procedure from three different types of brown macro-algae; *Turbinaria murryana*, *Cystoseira spinosa* and *Sargassum* sp. The brown macro-algae were collected in mid-fall from a local protected area in Egypt. Selection of the algal species and the collection season was based on the relatively high content of alginate as found in our earlier study (Shukr, Azab, Abdel-Hamid, & El-Sherbiny, 2010). The various extracted alginates were characterized and then used in combination with different proportions of a locally collected calcareous soil to develop novel series of hydrogel composite microparticles. The developed composites were investigated as sorbents for efficient uptake of iron, manganese and arsenic from aqueous solutions for possible application in water treatment processes.

2. Experimental

2.1. Materials

Calcareous soil samples were collected from the North-western coast of Egypt at El-Alamien area between latitudes 30°44′30″–30°49′40″ North and longitudes 29°00′–29°28′ East and it is situated about 80 km to the west of Alexandria City. Analytically grade (AR) salts of iron ($FeCl_3$), manganese ($MnCl_2{\cdot}4H_2O$), arsenic ($Na_2HAsO_4{\cdot}7H_2O$), $CaCl_2$, NaCl, Na_2CO_3, ethanol, HCl, H_2SO_4, KCr_2O_7, $FeSO_4{\cdot}7H_2O$, sodium acetate, ammonium acetate, and double distilled deionized water were used as provided.

2.2. Methods

2.2.1. Collection of brown algae biomass

Biomass samples of the brown macro-algae; *T. murryana*, *C. spinosa* and *Sargassum* sp. (belonging to the order: *Fucales*, class: *Phaeophyceae*) were collected during the mid-fall 2010 from the littoral algal community of seashore of the Nabq protected area located 30 km north east of Sharm El-Sheikh city, Aqaba gulf, Red sea, Egypt. Selection of the brown algae species and the collection season was based on the relatively high content of alginate (Shukr et al., 2010).

2.2.2. Extraction of sodium alginate from algae biomass

The alginates extracted in this study were obtained in the form of water soluble sodium salts according to the procedure reported by Truus, Vaher, and Taure (2001). Briefly, a mass of 20 g of air-dried brown algae was boiled in 300 ml of distilled water for 30 min, filtered and the wet algal biomass was boiled for further 30 min in 0.5% (w/v) aqueous $CaCl_2$ solution. The mixture was then allowed to cool down to room temperature, filtered and the algal biomass was boiled for 1 h in 300 ml of 0.5% (w/v) NaCl solution. The filtration process was repeated and the algal biomass was boiled for 30 min in 3% Na_2CO_3 solution with vigorous stirring. This step involves conversion of alginic acid into soluble sodium salt, which remains in the extract. A highly viscous solution was then obtained in addition to the insoluble algal residue. The mixture was filtered through a cloth filter with squeezing and the filtrate was treated with ethanol to precipitate the sodium alginate. The obtained alginate was air-dried, collected, ground into powder and stored until further investigation. No bleaching treatment was applied to the extracted sodium alginate and therefore, the color was relatively brown.

2.2.3. Characterization of the extracted alginates

The average molecular weights (M_w) of the extracted alginates were determined using the Mancini et al. protocol (Mancini, Moresi, & Sappino, 1996) with the aid of Cannon-Fenske Routine Viscometer (Cannon Instrument Co., State College, PA 16801, USA). Different dilutions of sodium alginate samples were prepared in 0.1 M NaCl solvent. During viscosity measurements, alginate solutions and the solvent, as a control, were maintained at 20°C (±0.1 °C) via immersing in a temperature-controlled circulating water bath. The elution times of both solvent and the different alginate solutions were measured in triplicates. Then, the reduced viscosities (η_{red}) were calculated from the average values of elution times according to the following relationship:

$$\eta_{\text{red}} = \frac{t - t_o}{C} \times t_o$$

where t and t_o are the average elution times of alginate solutions and the solvent (NaCl 0.1 M), and C is the concentration of alginate solutions. The curves of reduced viscosity versus concentration were then built, and the intrinsic viscosity, $[\eta]$ ($L.g^{-1}$) was obtained by extrapolating η_{red} when concentration tends toward zero by means of linear regression. The average molecular weight, M_w (Da) was then obtained using the following equation (Mancini et al., 1996):

$$[\eta] = 1.228 \times 10^{-4} \times M_w^{0.963}$$

The UV–vis spectra of 0.1% aqueous solutions of the alginate samples extracted from different brown algae were recorded in the range of 200–800 nm using Unicam UV–vis spectrometer (UVII) with the aid of ATI Unicom UV–vis. vision software V 3.20. The analysis was performed at room temperature using quartz cuvets (1 cm optical path). FTIR characterization of solid samples of alginates was carried out with a Mattson 5000 FTIR spectrometer. The dried samples were pressed with KBr and their FTIR spectra were recorded at 25 °C in the range of 400–4000 cm^{-1}. Also, the viscosities of the alginates extracted from different algal species were measured with Brookfield DV-III Ultra Programmable Rheometer. Three different concentrations of the aqueous alginate solutions (0.5%, 1% and 1.5%, w/v) were prepared and measured at different velocities from 20 to 500 rpm.

2.2.4. Characterization of calcareous soil

A series of routine analyses has been performed for determining the physicochemical properties of the used calcareous soil. These analyses are summarized as follow:

(*a*) A pH meter was used to determine the pH of the saturated calcareous soil paste with the aid of glass and calomel electrodes using buffer solutions of pHs 7.0 and 9.2 as standards. (*b*) Electrical conductivities (EC) of the saturated extracts were measured by an EC meter. (*c*) Total calcium carbonate content ($CaCO_3$%) was determined by a calcimeteric method using 6 N HCl solutions. A pre-weighed soil sample (5 g) was treated with 1:1 HCl and the volume of CO_2 gas liberated from the $CaCO_3$ present in the soil was determined using the following relationship:

$$\mathrm{CaCO_3}(\%) = \frac{\mathrm{CO_2\,released\,(ml)} \times (0.00399)}{\mathrm{weight\ of\ soil\ sample\,(g)}}$$

(*d*) The cations and anions contents in the saturated soil paste (mequiv./l) were also measured. (*e*) Organic matter content (O.M.%) was measured by a method described by Walkley and Black (1934). One gram of soil sample was mixed well with 10 ml of 1 N potassium dichromate solution in a 50 ml conical flask. Then, a 20 ml of commercial concentrated H_2SO_4 was added and the mixture was kept for 30 min. Afterwards, the contents were diluted by adding 200 ml of distilled water followed by addition of 1 ml of diphenylamine indicator and titrated against 1 N $FeSO_4{\cdot}7H_2O$ until the solution turned purple or blue. (*f*) Cation exchange capacity of the soil (CEC, mequiv./100 g soil) was estimated by taking 4 g of soil and saturating it with 33 ml of 1 N sodium acetate (pH = 8.2) followed by repeated washing for four times with decanting the liquid. Soil sample was then washed with 33 ml of ethanol (95%) for three times. Finally the adsorbed sodium ions were removed through three times washing by 33 ml of 1N ammonium acetate (pH 7.0) with decanting each washing into 100 ml volumetric flask. The concentration of sodium ions in the collected washings was determined by flame photometer (model PFP.7, Jenway). This concentration of sodium ions represented the CEC of the soil under investigation. (*g*) Soil particle size analysis was carried out by the addition of 40 ml of 1% sodium hexa-metaphosphate solution to 40 g of the soil sample and kept overnight. Soil was then transferred to a dispersion cup and dispersed with the help of a mechanical stirrer. Reading was recorded with the aid of Bouyoucos hydrometer and the soil texture was determined using a triangle of International Society of Soil Science.

2.2.5. Preparation of alginate hydrogel particles

The alginate hydrogel particles were prepared via ionotropic gelation according to (Abdel-Hamid, 1996). Briefly, the aqueous alginate solutions (3%) were dropped into 80 ml of gently stirred (250 rpm) $CaCl_2$ solution (2%) using prostatic pump at a dropping rate of 1.0 ml/min. The formed particles were left overnight in the $CaCl_2$ solution to harden. The hardened particles were then separated from $CaCl_2$ solution and washed several times by distilled water, dried at 50 °C to a constant weight, and stored in sealed vessels to prevent moisture absorption.

2.2.6. Preparation of calcareous soil–alginate composite particles

The composites were developed according to procedures adapted from (Rashad, Mohy Eldin, & Abd El Latif, 2005). Briefly, the predetermined amounts of finely powdered calcareous soil were add to the alginate solutions (3%) of different grades to obtain 1:1, 1:2, and 1:3 (w/w) ratios of alginate:soil. The homogenous mixtures of alginate and soil were then dropped, at a dropping rate of 1.0 ml/min, into 2% $CaCl_2$ solution using prostatic pump with gentle stirring at room temperature producing hydrogel composite particles. The formed composites were left overnight in $CaCl_2$ solution to harden. The hardened particles were then separated from $CaCl_2$ solution, washed several times by distilled water, dried at 50 °C to constant weight and stored in sealed vessels to evade moisture absorption.

2.2.7. Size measurements of the developed particles

An average size of 25 particles from each dried alginate hydrogel particles and also from the different calcareous soil–alginate composite particles were measured using electronic digital caliper, 0–150 mm.

2.2.8. Surface morphology of the developed particles

The surface morphology of alginate and soil–alginate composite particles (1:3), based on the sodium alginate extracted from *Turbinaria murryana*, as example, was examined with the aid of a scanning electron microscope (JEOLJSM-5500LV SEM, JEOL Ltd., Japan) with using high vacuum mode. Samples were placed on aluminum stub, sputtered with gold using Bal-tec. scd. 050 sputter coater and the samples were then scanned at an accelerating voltage of 20 kV.

2.2.9. Swelling profiles

The swelling behavior of various alginate and soil–alginate composite particles with different compositions was determined in distilled water at room temperature. The swelled samples were weighed at intervals (0.5, 1, 2, 3, 4, 5 and 6 h) after blotting the surface liquid, until equilibrium swelling was attained. This swelling process was repeated three times for each sample and the percent of swelling was calculated by the following equation:

$$\mathrm{Swelling}\,(\%) = \frac{100\,(W_t - W_o)}{W_o}$$

where W_o is the initial weight and W_t is the weight of the swelled particles at time *t*. Each data point is an average of three independent determinations.

2.2.10. Metal uptake study

Analytical grade (AR) $FeCl_3$, $MnCl_2{\cdot}4H_2O$ and $Na_2HAsO_4{\cdot}7H_2O$ salts were dissolved in double distilled deionized water to prepare different standard solutions of concentrations 0.5, 1, 2, 4, 8 and 16 mg l^{-1} of each metal ion. The initial concentrations of the salt solutions were checked with the aid of atomic absorption spectrophotometer (G.B.C Avanta Σ Australia). Volumes of 100 ml of different standard test metal ion solutions were transferred to dry clean 250 ml Pyrex conical flasks. Three replicate flasks were used for each metal ion concentration. Then, a constant weight of 1 g of the investigated sorbents (dry powder calcareous soil, alginate hydrogel particles, or soil–alginate composite particles of different compositions) was added to each metal ion test solution. The contact time between investigated sorbents and the metal ion test solutions was kept constant at 1 h with a manual shaking of each flask every 15 min. The test solutions were then filtered through Whatman No. 1 filter papers and the filtrates were collected into clean Pyrex glass test tubes for metal analysis. Metal analysis was performed according to procedures adapted from American Public Health Association. The method involved direct aspiration into air–acetylene flame of atomic absorption spectrophotometer (G.B.C Avanta Σ Australia). The technique employing hollow cathode lamps was adopted for the analysis of the test metals; Fe, Mn, and As. In the case of As, nitrogen was used as a purge gas and sodium borohydride ($NaBH_4$) was the reductant. The collected equilibrium data for the studied metal ions over the concentration range from 0.5 to 16.0 mg l^{-1} at 25 °C were fit to both Langmuir and Freundlich isotherms for all the developed composites sorbents.

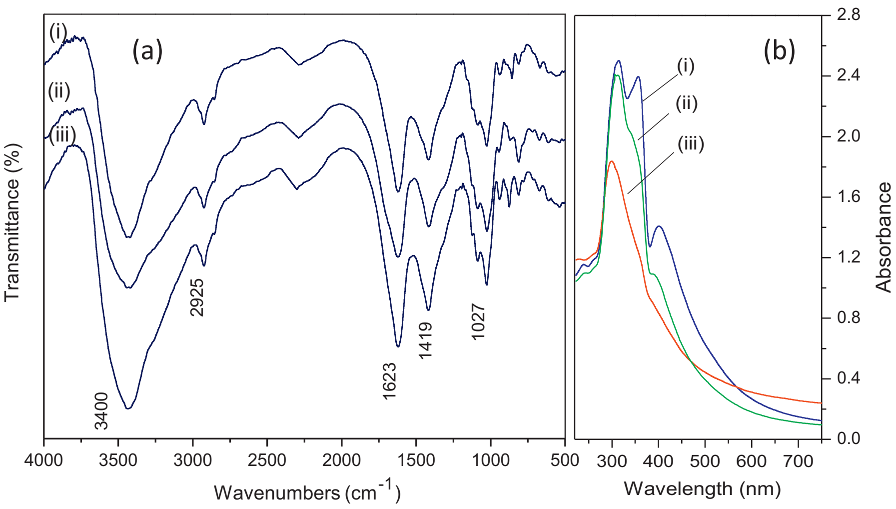


Fig. 1. FTIR spectra (a) and UV–vis spectrophotometry (b) of the alginates extracted from (i) *C. spinosa*, (ii) *Sargassum* sp. and (iii) *Turbinaria murryana*.

2.2.11. Statistical analysis

The collected data was analyzed and expressed as mean ± SD. The effect of various parameters on the metal uptake capacity of the prepared alginate-based hydrogels and composite particles were statistically analyzed by one-way ANOVA using Excel (Microsoft Office 2007). Differences were considered significant at the level of $p < 0.05$.

3. Results and discussion

3.1. Extraction and characterization of alginates

The alginate has been extracted from three different brown algal species collected in the fall season; *T. murryana, Sargassum* sp. and *Cystoseira spinosa*. It has been found that the alginate content (expressed as % of algal dry weight biomass) vary considerably among the different algal species. For instance, *Sargassum* sp. showed the highest production (50.3%) of sodium alginates followed by *T. murrayana* (47.4%) and then *C. spinosa* (39.6%).

The viscosity average molecular weights (M_w) of the extracted alginates were determined using Mancini et al. protocol (Mancini et al., 1996) and found to vary according to the algal source of extraction. For instance, the M_w of alginates obtained from *T. murrayana, Sargassum* sp. and *C. spinosa* were found to be 87.1, 129.3 and 69.7 kDa, respectively.

Fig. 1a shows the FTIR spectra of the extracted alginates. It is apparent from the figure that the alginates obtained from the three investigated brown algal species; *T. murryana*, *Sargassum* sp. and *C. spinosa* maintained closely similar spectral peaks. The peaks appeared around 3400 cm^{-1} are corresponding to the OH stretching vibration and intermolecular H-bonds. The peak at 2925 cm^{-1} is corresponding to the stretching vibration of the aliphatic C—H, whereas the spectral absorption noted at 1623 and 1419 cm^{-1} can be assigned for the symmetric and asymmetric stretching vibrations of the carboxylate groups, respectively (El-Sherbiny et al., 2010). These IR spectra also confirmed the purity of the extracted alginate samples.

The structure of the extracted alginates has been also confirmed with the aid of UV–vis spectrometry as illustrated in Fig. 1b. As apparent from the figure, all the produced alginates, irrespective their extraction origin showed almost similar UV–vis absorption spectra with a UV maximum appeared at λ_{max} 316 nm in the case of *C. spinosa* and *Sargassum* sp. This absorption band has shifted to a relatively lower value at λ_{max} 298 nm in case of the alginate extracted from *T. murrayana*. The UV–vis spectra of the extracted alginates also revealed other absorption bands at 356 and 398 nm. These UV–vis absorption bands can be attributed to chromophoric groups of the alginates such as the OH groups (Shukr et al., 2010).

3.2. Viscosity measurements of the extracted alginates

Fig. 2a shows the viscosity profiles of the alginates extracted from *T. murryana*, *Sargassum* sp. and *C. spinosa*. As apparent from the figure, increasing the concentration of alginate solutions from 0.5% up to 1.5% has led to a significant ($p < 0.05$) increase in the viscosity especially in the case of alginates extracted from *T. murryana* and *Sargassum* sp. Fig. 2b–d shows the change in viscosity of the alginate solutions of different concentrations (0.5, 1.0 and 1.5%, w/v) at different speeds of the rheometer's rotor (20–250 rpm). As can be noted from the figure, the viscosities of the lower alginate concentrations (0.5 and 1.0%, w/v) remain almost constant with increasing the rotor speed. However in the case of high concentrations (1.5%, w/v), increasing the speed of rheometer's rotor has led to a relatively significant reduction in the viscosity values. This reduction of viscosity upon increasing rotor speed can be attributed to an increase in the shear forces which can break down the agglomerates of alginate chains and consequently decreases the solution viscosity.

3.3. Analysis of the calcareous soil

The main physicochemical characteristics of the used calcareous soil were determined using series of routine analyses. For instance, the pH of the saturated soil paste was found to be 8.46 and its electrical conductivity (EC) was found to be 2.2 ds/m. The other properties such as soil texture and clay % were also measured and it has been found that the soil texture is sandy clay loam and its percentages of sand, silt and clay are 48.75, 22.5 and 28.75%, respectively. The cations and anions content in the saturated soil paste (mequiv./l) were also determined. For instance, the contents of the soluble cations; Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were found to be 13.15, 8.92, 4.80 and 3.97 mequiv./l, respectively whereas, the contents of the soluble anions; HCO_3^{-}, Cl^{-} and SO_4^{2-} are 4.3, 6.07 and 20.1, respectively.

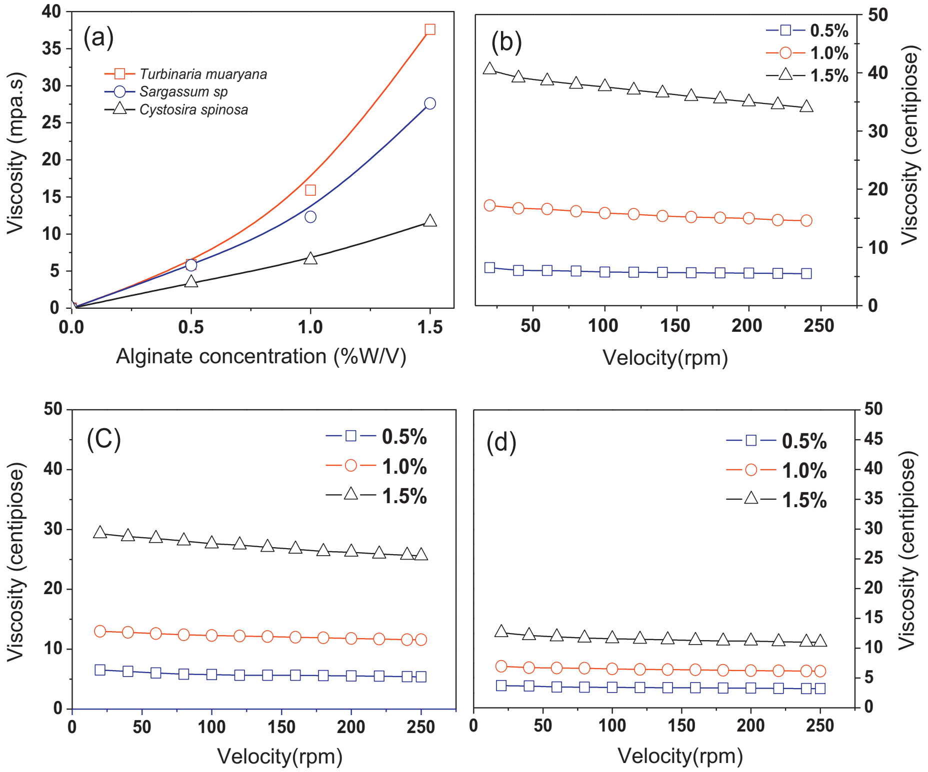


Fig. 2. Viscosity profiles (a) and viscosity–velocity relationship of different concentrations of the alginate solutions (0.5, 1.0, and 1.5%) extracted from various brown algae; (b) *Turbinaria murryana*, (c) *Sargassum* sp., and (d) *Cystoseira spinosa*.

3.4. Preparation and characterization of alginates hydrogels and calcareous soil–alginate composite particles

The three extracted grades of sodium alginates were used either alone or in combination with different proportions of a locally available calcareous soil to develop new series of hydrogel composites. The developed alginate-based composites particles were obtained via ionotropic crosslinking of alginate chains using Ca^{2+} ions. Then, the resulting particles were investigated as potential sorbents for efficient uptake of Fe(III), Mn(II) and As(V) from aqueous solutions toward possible application in water treatment processes.

3.4.1. Particle size measurements

The average particle size of the developed hydrogel and composites particles was measured for both wet and air dried beads as shown in Table 1. From the table, it can be noted, in general, that the size (mm) of the wet particles is significantly ($p < 0.001$) larger than the corresponding sizes of same particles after air drying at room temperature. For instance, the average size of the wet particles developed in this study fall in the range of 2.85 ± 0.12 to 3.86 ± 0.15 mm whereas the corresponding sizes of the air dried particles were in the range of 1.26 ± 0.18 to 2.42 ± 0.09 mm. Also, from the size measurements, it has been found that increasing the soil content in the developed hydrogel composites has led to a significant increase in particle size. For instance, the size of the wet particles based on alginate alone that was extracted from *Turbinaria murryana* (T0) was 2.92 ± 0.76 mm. This size has increased to 3.56 ± 0.15, 3.78 ± 0.10 and 3.84 ± 0.08, upon increasing the soil weight ratio in the alginate:soil composite from 1:1 (T1) to 1:2 (T2), and 1:3 (T3), respectively. The same behavior was also noted in the case of dried particles. For instance, the sizes of the dry T0, T1, T2, and T3 particles were found to be 1.26 ± 0.18, 1.67 ± 0.16, 1.86 ± 0.136 and 2.42 ± 0.099, respectively. This increase in particle size upon increasing the soil content can be attributed to the reduction in the crosslinking extent of the alginate matrices.

Table 1
The composition of the developed alginate and calcareous soil–alginate hydrogel composites and their dry and wet average particle size.

Sample code	Weight ratio		Average particle size (mm) ± SD	
	Alginate	Soil	Wet beads	Dry beads
T0	1	0	2.92 ± 0.76	1.26 ± 0.18
S0	1	0	2.87 ± 0.05	1.49 ± 0.22
C0	1	0	2.85 ± 0.12	1.50 ± 0.09
T1	1	1	3.56 ± 0.15	1.67 ± 0.16
S1	1	1	3.51 ± 0.07	1.73 ± 0.20
C1	1	1	3.51 ± 0.15	1.61 ± 0.16
T2	1	2	3.78 ± 0.10	1.86 ± 0.14
S2	1	2	3.69 ± 0.13	1.71 ± 0.23
C2	1	2	3.76 ± 0.17	1.98 ± 0.23
T3	1	3	3.84 ± 0.08	2.42 ± 0.09
S3	1	3	3.82 ± 0.12	2.12 ± 0.23
C3	1	3	3.86 ± 0.15	2.02 ± 0.19

T: *Turbinaria murayana*, S: *Sargassum* sp. and C: *Cystoseira spinosa*.

3.4.2. Surface morphology of the particles

The surface morphology of the developed alginate and calcareous soil–alginate composites particles is shown in Fig. 3a and b. As can be noted from the figure, the alginate hydrogel particles (Fig. 3a) have, in general, a very rough and wavy surface. This surface morphology of the alginate particles has turned to show more dense, integrated and relatively smooth surface (Fig. 3b) in the case of calcareous soil–alginate composites. This smoothness tends to reflect a satisfactory degree of homogeneity in the developed alginate–soil composites.

3.4.3. Swelling measurements

Swelling measurements of the developed alginate and alginate–soil hydrogel particles were carried out for 6 h in distilled

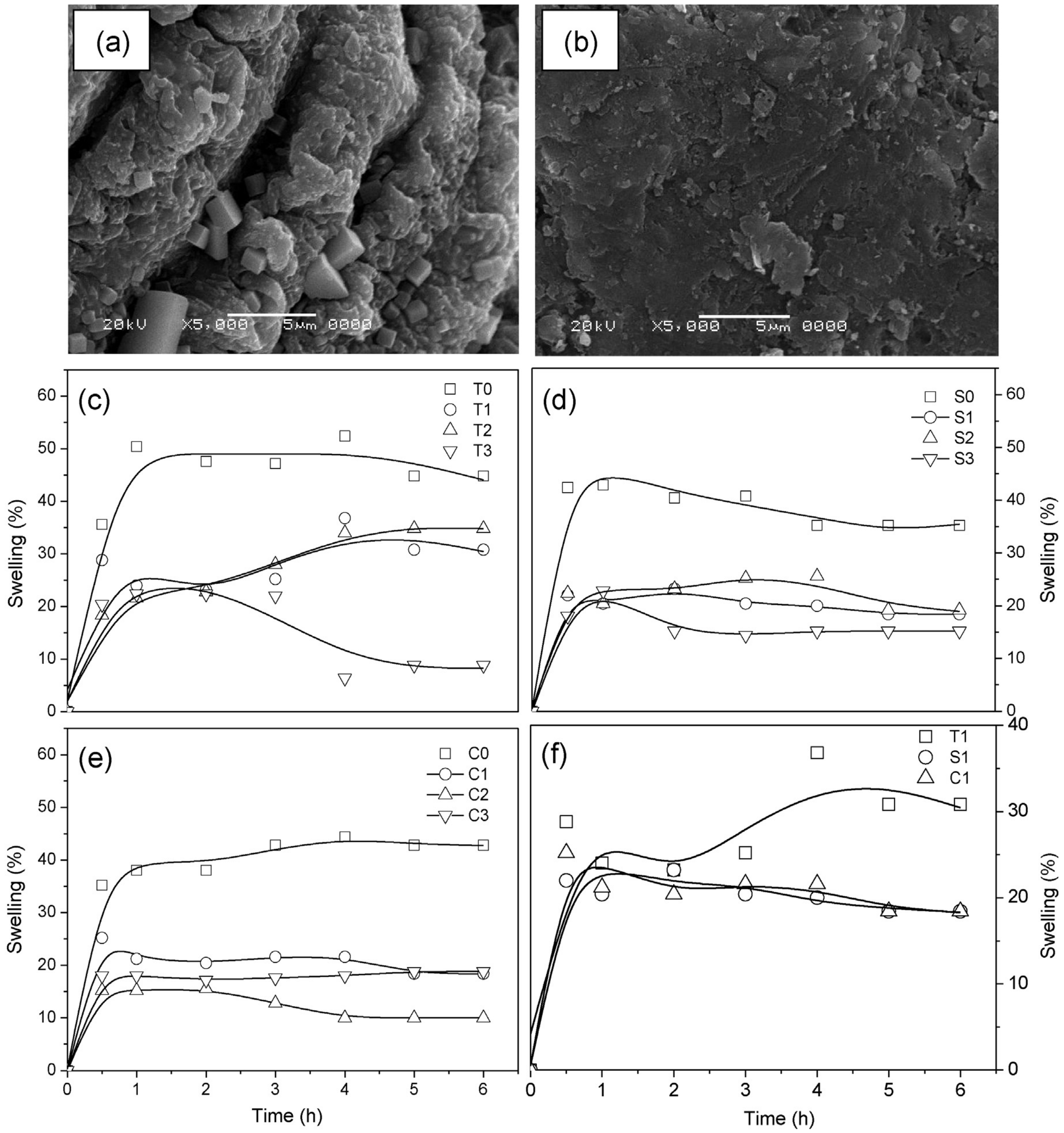


Fig. 3. Surface morphology of the developed (a) alginate hydrogel particles and (b) calcareous soil–alginate composite particles, in addition to the swelling behavior of the composite particles of different compositions (c)–(e), and (f) comparative swelling patterns of composites based on alginates of different origins.

water as shown in Fig. 3c–f. From Fig. 3c, the swelling extent of the dry particles based on alginate extracted from *Turbinaria murryana* (T0) increased with time until attaining equilibrium at about 51%. Mixing the alginate with calcareous soil at different weight ratios of 1:1 (T1) and 1:2 (T2) led to a relative reduction in the swelling % of the hydrogel particles. Further increase in the soil content as in T3 showed a further significant reduction in the swelling values attained at equilibrium. The same swelling patterns have been also observed in the case of hydrogel particles based on the alginates extracted from *Sargassum* sp. (S0, S1, S2 and S3) as in Fig. 3d and also the hydrogel particles based on the alginates extracted from *C. spinosa* (C0, C1, C2 and C3) as in Fig. 3e. This reduction in equilibrium swelling may be attributed to the decrease in the alginate content which was able to form hydrogels. Fig. 3f illustrates a swelling comparison between alginate–soil particles based on alginates extracted from the three different algal sources (T1, S1, and C1). As can be noted from the figure, the particles prepared from the alginates extracted from *T. murryana* (T1) showed a relatively higher swelling values at equilibrium than that based on alginates obtained from *Sargassum* sp. (S1) and *C. spinosa* (C1). This tends to indicate the ability of the alginates extracted from both *Sargassum* sp. and *C. spinosa* to form stronger crosslinks with Ca^{2+} ions than the alginates extracted from *T. murryana*.

3.5. Metal uptake study

The composites developed in the current study were investigated as potential sorbents for efficient uptake of Fe(III), Mn(II) and As(V) from aqueous solutions for possible application in water treatment. The obvious variation in residual levels of different metal ions (Figs. 4–6) indicated substantial differences in removal efficiency that were largely dependent on the adsorbent type (calcareous soil, alginate, or their composites), type of metal ion and its concentration. Compared to other metal ions, in general,

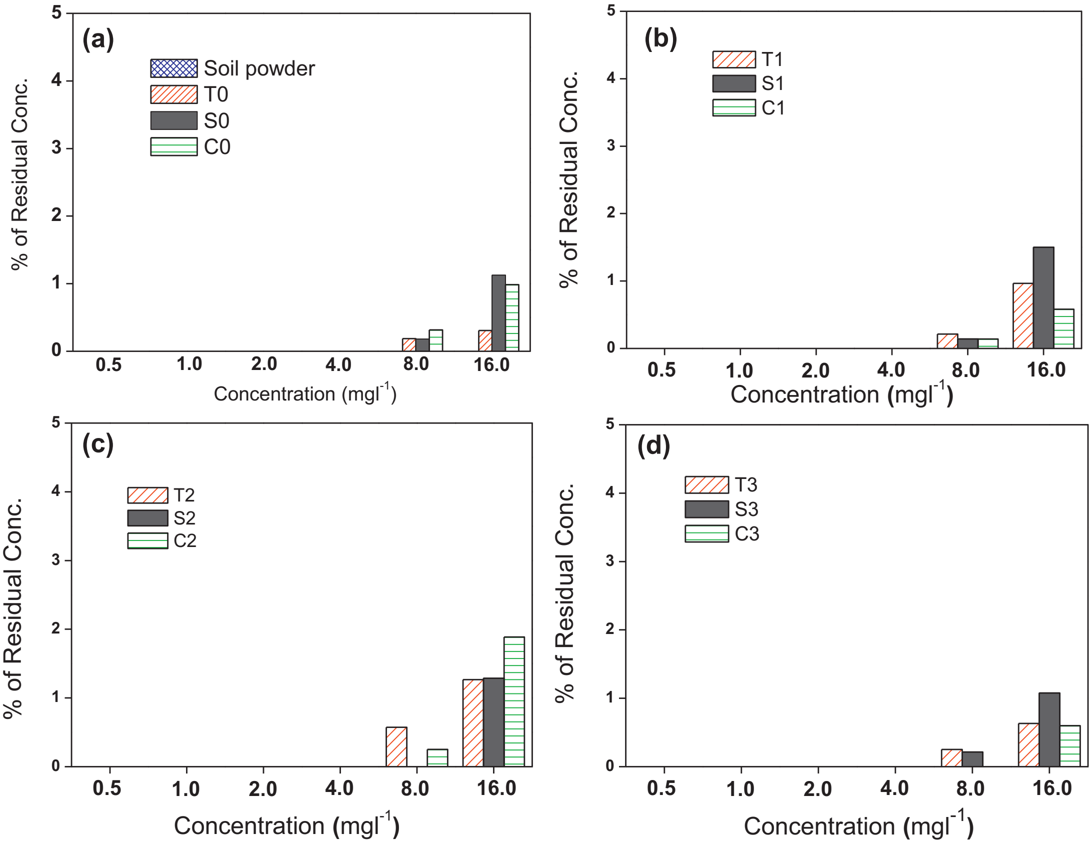


Fig. 4. Percentage of residual Fe(III) ions in 100 ml of their standard solutions (0.5–16 mg $^{-1}$) after 1 h contact time with 1 g of (a) calcareous soil and alginates particles of different origins, (b) alginate:soil (1:1), (c) alginate:soil (1:2), and (d) alginate:soil (1:3) composite particles.

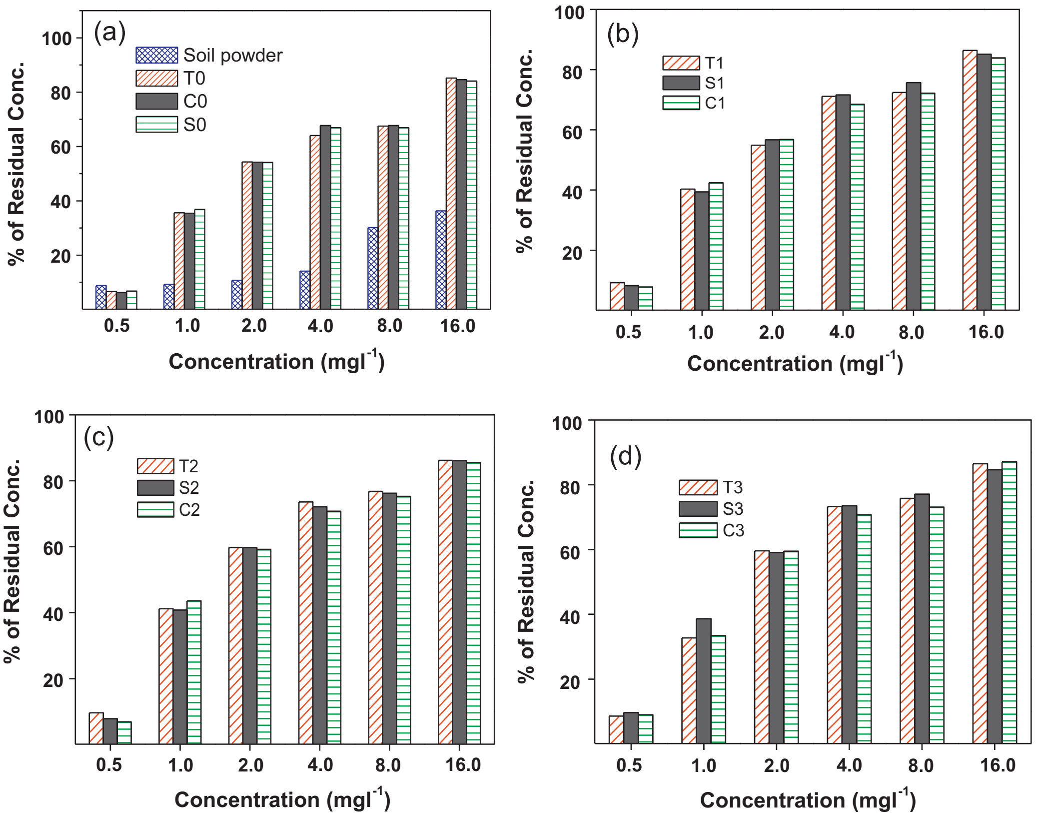


Fig. 5. Percentage of residual Mn(II) ions in 100 ml of their standard solutions (0.5–16 mg $^{-1}$) after 1 h contact time with 1 g of (a) calcareous soil and alginates particles of different origins, (b) alginate:soil (1:1), (c) alginate:soil (1:2), and (d) alginate:soil (1:3) composite particles.

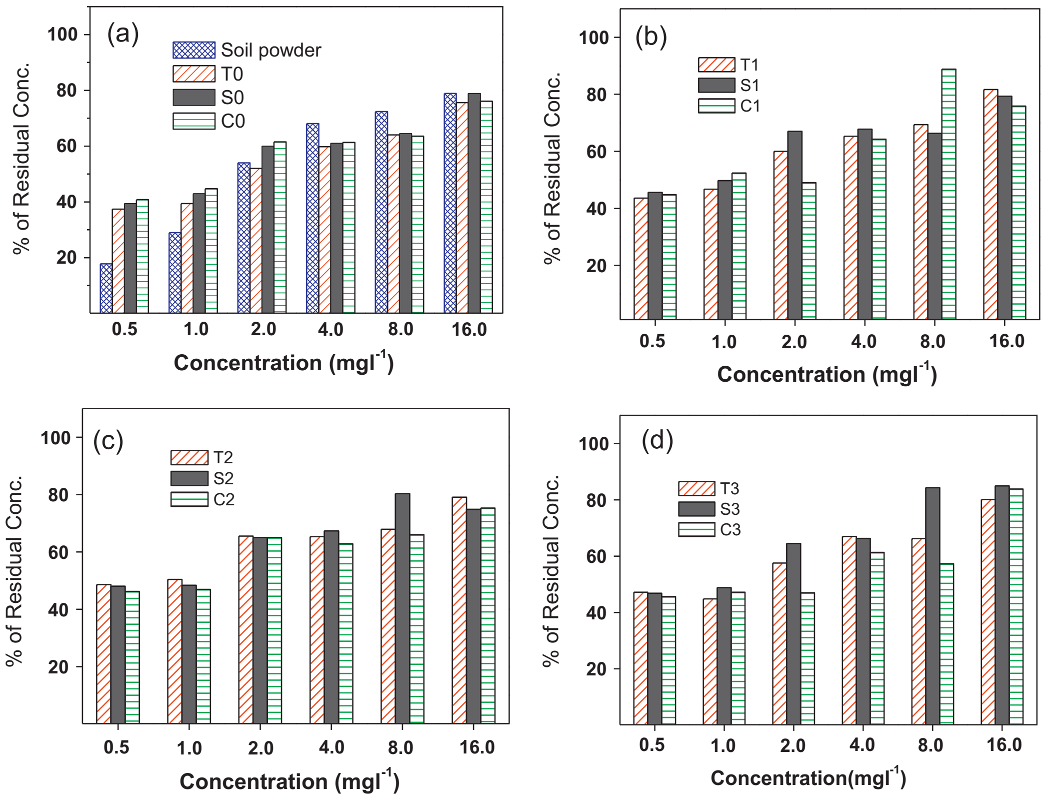


Fig. 6. Percentage of residual As(V) ions in 100 ml of their standard solutions (0.5–16 mg $^{-1}$) after 1 h contact time with 1 g of (a) calcareous soil and alginates particles of different origins, (b) alginate:soil (1:1), (c) alginate:soil (1:2), and (d) alginate:soil (1:3) composite particles.

the highest removal efficiencies were recorded in the case of Fe(III) ions (Fig. 4). For instance, both the soil and alginate particles (1 g) have removed 100% of the Fe(III) ions in the concentrations range 0.5–4.0 mg l^{-1}. At higher Fe(III) concentrations (8.0–16.0 mg l^{-1}), 100% removal efficiency was achieved by calcareous soil and more than 97.4%, 92.7% and 93.5% removal was attained by various alginate particles (T0, S0, and C0), respectively (Fig. 4a). In the case of various developed soil–alginate composites, the removal efficiencies of Fe(III) were also more than 87% in most cases with complete removal of the lower Fe(III) concentrations up to 4.0 mg l^{-1}. Besides, *Sargassum* alginate–soil (1:2) and *Cystoseira* alginate–soil (1:3) showed 100% removal of Fe(III) ions (Fig. 4c and d).

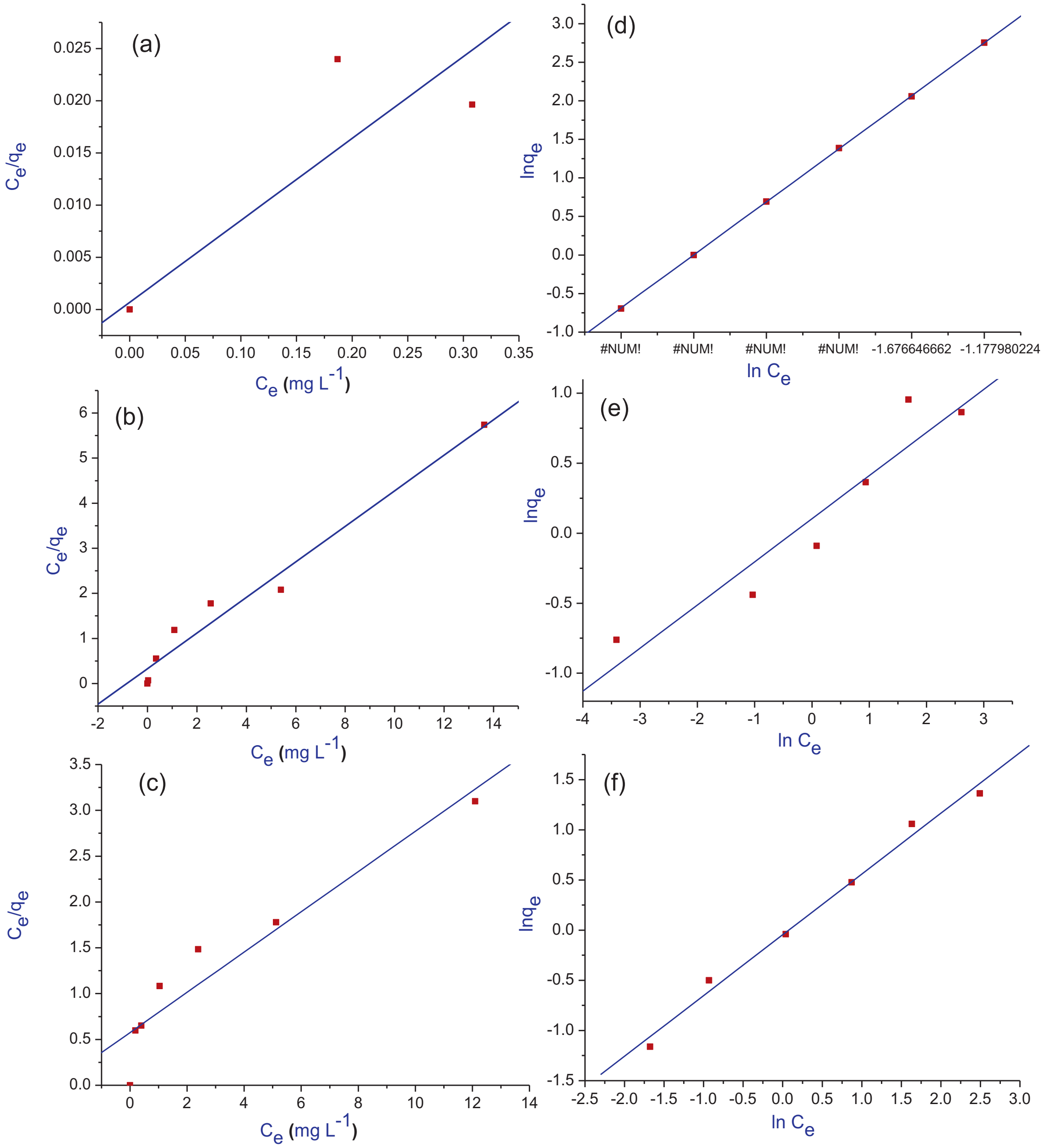
In the case of Mn(II), the calcareous soil and alginates whether used singly or in combinations, in form of composites, have removed more than 89% of Mn(II) ions at 0.5 mg l^{-1} concentration level. The percentages of the residual Mn(II) ions of various standard solutions treated with soil or alginate particles (Fig. 5a), 1:1 alginate:soil (Fig. 5b), 1:2 alginate:soil (Fig. 5c), and 1:3 alginate:soil (Fig. 5d), clearly indicate considerable differences in removal efficiencies that were almost independent on the origin of alginate but mainly dependent on the initial Mn(II) concentration. As can be noted also from Fig. 5, increasing the concentration of Mn(II) ions led to a highly significant ($p \le 0.01$) decrease in the removal efficiencies irrespective the composition of the alginate–soil composite.

Fig. 5 also demonstrates that the calcareous soil alone exhibited superior removal efficiency when compared to pure alginate particles and soil–alginate composites. For instance, the removal efficiency of the calcareous soil for the Mn(II) ions ranged between 63.7% and 90.8% at 16.0 mg l^{-1} and 1.0 mg l^{-1}, respectively. The lowest removal efficiency of alginate and alginate–soil particles ranged between 12.9% and 15.9% recorded at 16.0 mg $^{-1}$, whereas the highest removal efficiency was between 89.6% and 92.4% reported at 0.5 mg $^{-1}$.

Fig. 6 shows the percentages of the residual As(V) ions of various standard solutions treated with soil and alginate particles (Fig. 6a), 1:1 alginate:soil (Fig. 6b), 1:2 alginate:soil (Fig. 6c), and 1:3 alginate:soil composites (Fig. 6d). The figure reveals relative differences in removal efficiencies of the As(V) ions that were almost independent on the origin of alginate but dependent particularly on the initial As(V) concentration. Fig. 6 also shows that increasing the concentration of As(V) ions has led to a relatively significant ($p \le 0.01$) decrease in the removal of As(V) ions by the soil–alginate composites.

The removal of the investigated metal ions by calcareous soil may be attributed to the chemisorption process which occurs on the soil surface depending on the oxide and clay mineral types. Besides, the presence of $CaCO_3$ and buffering capacity of calcareous soil is facilitating the precipitation of metal ions in a carbonate form depending on the solubility product constant (K_{sp}) of each elemental form. The K_{sp} of $CaCO_3$ at 25 °C is 4.7×10^{-9}, and the precipitation process will occur if the K_{sp} of the carbonate form of the studied element is less than the K_{sp} of $CaCO_3$ (Dickerson, Gray, & Haight, 1979, chaps. 5 and 9). Depending on this fact, it is expected that considerable amounts of the investigated heavy metals, particularly Fe(III) and Mn(II) were precipitated in the carbonate form where the K_{sp} values of $FeCO_3$ and $MnCO_3$ are 2.1×10^{-11} and 8.8×10^{-11}, respectively (Dickerson et al., 1979, chaps. 5 and 9).

In the case of calcareous soil–alginate composites, it can be suggested that the removal of the investigated heavy metal ions has been achieved through a combination of various mechanisms. These include the role of calcareous soil in facilitating the removal of heavy metals through precipitation process (Dickerson et al., 1979, chaps. 5 and 9) in addition to adsorption on soil and alginate surfaces. Besides, a chemical interaction through complexation



Metal ions	Langmuir isotherm constant				
	K_L (L/mg)	q_{max}	R_L	R	SD
Fe	42.5127	14.8876	0.04493	0.92149	0.00456
Mn	1.19618	2.53485	0.62575	0.98476	0.37752
As	0.38021	4.56621	0.84026	0.95142	0.34088

	Freundlich isotherm constant			
	K_F (mg g^{-1})	1/n	R_F^2	SD
Fe	0.25242	0.68834	0.99999	0.00748
Mn	1.109223	0.30799	0.94833	0.24781
As	0.954851	0.60518	0.99496	0.10712

Fig. 7. Langmuir plot for (a) Fe(III), (b) Mn(II) and (c) As(III), and the Freundlich plot for (d) Fe(III), (e) Mn(II), and (f) As(III), in addition to both Langmuir and Freundlich isotherm parameters obtained using *Turbinaria muaryana*–alginate particles (T0) as example.

may also occur between the heavy metal ions and the hydroxyl groups on the alginate strands (Abd El Latif, Mohy Eldin, & Rashad, 2006; Rashad, Mohy Eldin, & Abd El Latif, 2005).

3.5.1. *Adsorption isotherms*

The collected equilibrium data for the studied metal ions over the concentration range from 0.5 to 16.0 mg $^{-1}$ at 25 °C were fitted to both Langmuir and Freundlich isotherms for all the developed composite adsorbents. The Langmuir isotherm has generated a satisfactory fit to the experimental data as indicated by coefficients determination (Fig. 7). This may be due to a homogenous distribution of active sites on the alginate surface as the Langmuir equation assumes that the polymer surface is homogenous and a monolayer of adsorbed metal ions is formed. The monolayer formation in the present metal uptake system has been confirmed by the linear plot obtained in Fig. 7a–c for the Fe(III), Mn(II), and As(III), respectively.

Freundlich isotherm was also studied and indicated that these developed composite adsorbents generated a fit to the experimental data even more satisfactory than Langmuir equation which has been confirmed by the linear plots represented in Fig. 7d–f for Fe(III), Mn(II), and As(III), respectively. These obtained results tend to suggest occurrence of both chemical (monolayer formation) and physical (multilayer adsorption) interaction between the developed composites adsorbents and the investigated metal ions.

4. Conclusions

In the present study, the alginates extracted from different brown macro algae were used in combination with different ratios of calcareous soil to develop new series of composites to be used as potential metal ions sorbents. The developed alginate-based composites have removed almost 100% of Fe(III) and achieved about 90% removal efficiency of Mn(II) in some cases. However, the developed formulations showed a limited efficiency in removal of As(V) ions. The effect of certain parameters such as pH and temperature on the efficiency of metal ions removal in addition to the desorption ability and reusability of the developed composites are currently under investigation and will be published elsewhere.

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