Encapsulated Green Magnetic Nanoparticles for the Removal of Toxic Pb²⁺ and Cd²⁺ from Water: Development, Characterization and Application

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Abstract

Current research is based on an innovative approach of the fabrication of encapsulated sustainable, green, phyto-genic magnetic nanoparticles (PMNPs), to inhibit the generation of secondary pollutants (Iron/ Fe^0) during water treatment applications. These novel bio-magnetic membrane capsules (BMMCs) were prepared using two-step titration gel crosslink method, with polyvinyl alcohol and sodium alginate matrix as the model encapsulating materials to eliminate potentially toxic metals (Pb^{2+} and Cd^{2+}) from water. The development of BMMCs was characterized by FTIR, XRD, XPS, SEM, VSM, TGA and EDX techniques. The effects of various operating parameters, adsorbent dose, contact time, solution pH, temperature, initial concentration of metals cations and co-existing ions were studied. The hysteresis loops have illustrated an excellent super-paramagnetic nature, demonstrating the smooth encapsulation of PMNPs without losing their magnetic properties. The maximum monolayer adsorptive capacities estimated at pH 6.5 by the Langmuir isotherm model were 548 and 610.67 mg/g for Pb^{2+} and Cd^{2+} , respectively. The novel BMMCs did not only control oxidation of PMNPs but also sustained the adsorptive removal over a wide range of pH (3-8), and the electrostatic interaction and ion-exchange were the core adsorption mechanisms. The BMMCs could easily be regenerated using 25% HNO_3 as an eluent for successful usage in seven repeated cycles. Therefore, the BMMCs as a material can be used as an excellent sorbent or composite material to remove toxic metals Pb^{2+} and Cd^{2+} , showing strong potential for improving water and wastewater treatment technologies.

Keywords: Magnetic nanoparticles; Adsorptive performance; Titration gel; Membrane capsules; Pb^{2+} ; Cd^{2+}

1. Introduction

Potentially toxic metals (PTMs) in water and wastewater are conceived as the most significant pollutants, which are responsible for deteriorating aquatic and biotic environment, due to their carcinogenic, non-biodegradability, bioaccumulation and toxicity (Pourret 2018; Ali et al., 2019; Bhunia et al., 2018). PTMs cations (e.g. Cr^{6+} , Pb^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , etc.) are released from several industries, including battery manufacturing, metal finishing, mining, textile, dyeing, ceramics, lead smelters, paper coloring, electroplating, leather tanning, pigment, and painting (Nussinovitch and Dagan, 2015). Among them, lead (Pb^{2+}) and cadmium (Cd^{2+}) cations are extensively utilized in large industries, for instance, jewellerys, shield production,

process vessels and bullet production (Li et al., 2016; Shih et al., 2018). Water contamination by these metals cations is greatly dangerous to the human life and can initiate various types of health problems i.e. abdominal pain, choking, dysfunction, cancer, lung infection, damage to the brain, kidney disorders, nephropathy and genetic disorders in the fetus (Kyzas et al., 2014). Importantly, the inhalation of Cd-containing dust is cause of lung infection in human beings and animals. In addition, the intake of Pb and Cd containing food is mainly deriving kidney disorders. Owing to their destructive effects, the acceptable concentration of Pb^{2+} and Cd^{2+} in drinking water should not exceed 10 and 5 $\mu\text{g/L}$, respectively, as implied by the United States of Environmental Protection Agency (USEPA) (Karthik and Meenakshi, 2015). Thus, it is need of the day to eradicate these metals from drinking water and wastewaters to keep safe and healthy water environment for public and aquatic life.

Presently, various processes and technologies (photocatalytic degradation, ion-exchange, membrane filtration, chemical precipitation, adsorption, reverse osmosis, solvent extraction, electrodialysis, and phytoextraction) have been utilized for the elimination of these PTMs from water and wastewaters (Do and Lee 2013). However, certain shortcomings i.e. high operating and installation costs, generation of toxic sludge and liquid waste, low performance, etc., are hindering its applications on a commercial scale (Kuang et al., 2013). Among them, adsorption is assumed to be a cost-effective, reliable and technically viable process to remove and recover these PTMs, by their easy and simple operation, high sorption capacity, regeneration, and reusability for consecutive treatment cycles. Regarding this, various types of sorbents including industrial by-products, minerals, biomass, agricultural wastes, and zeolites have been employed. However, the implementation of these sorbents was low due to having low uptake capacity and lower frequency of regeneration and reusability (Lin et al., 2015; Park et al., 2007). Hence, there is a great research interest for the development of novel sorbent, having maximum uptake and higher reusability. To handle these situations, nowadays, nanotechnology is playing an important role in developing sorbent of desire quality. Currently, various types of nanoparticles, nanostructures, and their composites have been prepared via different techniques i.e. sol-gel, electrochemical, ball milling, chemical co-precipitation, hydrothermal, micro-emulsion, green, bio-reduction, etc. However, most of the methods are costly and non-environmental friendly due to the involvement of toxic and harmful chemicals during the fabrication of nano-sorbent. Among them, green, bio-reduction approach is comparatively much better to prepare green nanoparticles (NPs) or sorbents without employing toxic surfactants.

Various types of green magnetic NPs have been utilized for the elimination and recovery of metals from wastewaters, as documented previously (Ali et al., 2017a, 2017b; Ali et al., 2018a, 2018b, 2018c, 2018d, 2018e). However, some real issues (low adsorptive capacity and poor stability for long-term applications due to the oxidation or etching or dissolution of iron/ Fe^0 into aqueous media, to generate secondary pollutants) are impending to transfer this technology from laboratory scale to commercial level. Despite this fact, various types of techniques have been developed to improve stability and binding and active sites on the surface of green sorbent. However, these methods did not improve their stability and uptake capacity up to the marks, due to the lack of enough active sites on the surface of green sorbent. Various researchers have utilized different techniques including encapsulation, loading, embedding, and assembling of magnetic NPs into various kinds of materials such as graphene oxide (GO), chitosan, β -cyclodextrin/poly(acrylic acid), polyacrylonitrile (PAN), sodium alginate (SA), cellulose, poly(vinyl alcohol) (PVA), etc., for improving its stability and uptake capability owing to the manifestation of various functional groups such as hydroxyl, sulfonic, amine, phosphate and carboxylic (Amiri et al., 2017; Arellano et al., 2013). However, so far there is no reported study available to highlight the loading or encapsulation of green sorbent into these materials.

Therefore, the aim of the present research was to fabricate novel bio-magnetic membrane capsules (BMMCs) by two-step titration gel crosslink method for the removal of Pb^{2+} and Cd^{2+} from the aqueous environment. To achieve this aim following core objectives were set **(a)** Development of novel BMMCs in order to control dissolution or etching or disintegration of PMNPs and as well as to enhance adsorptive performance of PMNPs for eliminating Pb^{2+} and Cd^{2+} from water; **(b)** to characterize and ensure smooth loading and encapsulation of PMNPs into PVA-SA matrix via using various methods such as Fourier transforms infrared spectroscopy (FTIR), Vibrating sample magnetometer (VSM), Scanning Electron Microscope with integrated energy dispersive X-ray system (SEM-EDX), X-ray photoelectron spectroscopy (XPS), powder X-ray diffractometer (XRD) and Thermo gravimetric analyzer (TGA); **(c)** Investigation of the effects of several operating parameters i.e. adsorbent dosage, contact time, reaction temperature, solution pH, initial concentration of metals cations and co-existing ions on the adsorptive performance of BMMCs; **(d)** to engage several isotherms, kinetics and thermodynamic equations for fitting the experimental data to scrutinize probable adsorption mechanisms; **(e)** Development of a suitable regeneration scheme to make cost-effective sorbent, and determination of the potential of reusability of BMMCs for consecutive treatment cycles; and **(f)** Finally, conduction of FTIR and XPS studies after the sorption of

metals cations by the BMMCs for examining the changes in functional groups to propose the adsorption mechanism.

2. Materials and Methods

2.1. Chemicals and Instruments

The details of the chemicals and instrumentations used in the present study have been provided in the supplementary information (Text-SI-III).

2.2. Development of Bio-Magnetic Membrane Capsules (BMMCs)

BMMCs were developed via simple two-step titration gel crosslink method by the cross-linking of PVA and SA solutions using primary cross-linking agents (H_3BO_3 and CaCl_2) and secondary cross-linking agent (GA) in the presence of PMNPs. PVA (10.0 wt %) solution was made by dispersing 10.0 g PVA powder in 100 mL distilled water and kept at 95°C under vigorous stirring at a speed of 150 rpm/min for 24 h, to ensure homogenous mixing and swelling. SA-PMNPs solution (3.0 wt %) was made by mixing 3.0 g SA powder in 97 mL PMNPs solution and kept at 95°C in oven for 24 h, to obtain a homogenous suspension. Primary cross-linking solution such as oversaturated solutions of calcium chloride (5 wt %) and boric acid were prepared separately by dissolving 25.0 g CaCl_2 and 20.0 g H_3BO_3 into 500 mL distilled water and pH of the mixture was sustained at 4 using 0.1 mol/L NaOH and HCl. Similarly, a secondary cross-linking solution such as GA (1 wt %) was prepared separately by adding 2 mL GA (50% dissolved in H_2O) into 98 mL of distilled water. Thereafter, 4:1 (v/v) = [PVA (10.0 wt %) : SA-PMNPs (3.0 wt %)] = 20.0 g PVA : 5.0 g SA-PMNPs solution was prepared or mixed and stirred together for at least 3 h, until a homogenous suspension was obtained, and then ultrasonic oscillated for at least 2 h to ensure a homogenous quality. After this, the casting solution i.e. PVA-SA-PMNPs was transferred into a syringe that had needle diameter around about 3.2 mm, and it was placed horizontally in a syringe pump by adjusting feed flow rate of 13 mL/h. Thereafter, the mixture droplet was injected into primary cross-linking solution via syringe pump by keeping a distance of 8 cm between needle tip to primary cross-linking agents solution surface. Then, the prepared capsules were kept into primary cross-linking agent's solution for 24 h to form BMMCs with a good toughness, ductility, and solid external surface. Then prepared BMMCs were gently separated from primary cross-linking agents solution, and immersed into secondary cross-linking agent solution i.e. GA (1 wt %) for 8 h to improve shape robustness and characteristic mechanical properties. Thereafter, the prepared MMCs) were separated and washed thoroughly five to six times with distilled water. Finally, these capsules

were stored in a freeze dryer for further adsorption experimental studies. The schematic of BMMCs fabrication is shown in Fig. 1.

2.3. Characterization of Bio-Magnetic Membrane Capsules (BMMCs)

The details regarding characterization of bio-magnetic membrane capsules (BMMCs) have been explained in the supplementary information (Text-SIV).

2.4. Adsorption Experiments

2.4.1. Adsorption Experiments Using Single System

Adsorptive performance of the prepared novel BMMCs was examined in batch mode by employing Pb^{2+} and Cd^{2+} as two model potentially toxic metals cations. All the trials were conducted in 50 mL Erlenmeyer flasks, shaken at 100 rpm. First, different influencing operating parameters were evaluated such as BMMCs dosages (0.0062-0.062 g/L), solution pH (2-8), initial metals cations concentration (10-1000 mg/L), temperature (298.15-333.15K) and contact time (0-48 h). The metal salts (i.e. 1.59 g $\text{Pb}(\text{NO}_3)_2$ for Pb^{2+} and 2.49 g $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$ for Cd^{2+}) were mixed into 1000 mL distilled water using a magnetic stirrer to get 1000 mg/L of metals cations stock solution. In the course of optimization studies, initial metals cations concentration was stable at 200 mg/L, while, the pH of the solution was fixed at 6.5 excluding the solution pH experiments. For the sorption isotherm and kinetics studies, the initial concentrations of Pb^{2+} and Cd^{2+} varied from 50 to 1000 mg/L at pH 6.5 and an amount of 0.03 g/L of freeze-dried BMMCs were inserted into 40 mL of each metals cations solution and agitated at 100 rpm. The amalgam was allowed to interact with the BMMCs for 48 h at 298.15K to achieve equilibrium. For the sorption kinetics studies, the final concentration of pollutants was calculated at the end of 1, 3, 5, 8, 12, 15, 18, 20, 24, 30, 35, 42 and 48 h by Atomic Absorption Spectrometry (AAS) at $\lambda_{\text{max}} = 283.3$ nm for Pb^{2+} and $\lambda_{\text{max}} = 254$ nm for Cd^{2+} . The data obtained by isotherm and kinetics experiments were fitted into different models to observe possible interaction and removal mechanisms of metals cations by BMMCs (equations are given in supplementary information, Text-SV). The final debate was organized based on the values of the regression coefficient (R^2). In addition, the thermodynamic parameters were also estimated at 298.15, 303.15, 313, 323.15 and 333.15 K (equations are given in supplementary information, **Text-SV**). All the adsorption experiments had been replicated four times, and then their average values were employed to make the final debate and graphs. In the end, the novel super-paramagnetic BMMCs were collected from the solution by a simple hand-held magnet. Finally, the following equations were utilized to calculate adsorption capacity and removal efficiency:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100\% \text{ --- (1)}$$

$$\text{Adsorption amount, } q_e \text{ (mg/g)} = \frac{(C_o - C_e) * V}{M} \text{ --- (2)}$$

Where, C_o (mg/L) and C_t (mg/L) are the initial and final metals cations concentration at zero/ (0 h) and time (t h), respectively. Further, C_e (mg/L) is the concentration of metals cations at time equilibrium. M (g) is the quantity of BMMCs and V (L) is the capacity of metals cations solution.

2.4.2. Adsorption Experiments using Binary System and Potential of BMMCs Reusability

In order to investigate adsorption selectivity or competition, binary system (Pb^{2+} and Cd^{2+}) trials were performed. A combined Pb^{2+} and Cd^{2+} solution was organized by keeping Pb^{2+} concentration stable (200 mg/L), while, Cd^{2+} concentration increased from 10 to 100 mg/L. Then, 0.03 g/L freeze dried BMMCs was mixed in a 40 mL of mixed solution including metals cations (Pb^{2+}/Cd^{2+}) ratio of 200:10, 200:50 and 200:100, respectively at pH 6.5 at room temperature ($25 \pm 2^\circ C$) and atmospheric pressure, and stirred at 100 rpm. The amalgam was allowed to interact with the BMMCs for 24 h and the final concentrations were calculated by AAS, and their removal efficiencies were assessed by equation (5). Furthermore, the stability and reusability of BMMCs were also explored. For this purpose, initially, different chemicals (HNO_3 , HCl , KCl , $CaCl_2$, and $EDTA$) were employed as an eluent to desorb metals cations from BMMCs. After optimization, HNO_3 was selected to regenerate BMMCs and, then consecutive sorption-desorption cyclic studies were performed up to ten times. Then, 0.03 g/L of BMMCs was inserting in 40 mL metals cations solution (200 mg/L), and the final concentration was estimated at equilibrium (24 h) by AAS. Thereafter, the BMMCs were separated from solution using simple magnet and added in a 20 mL of (25 % HNO_3) solution, and shaken for 6 h. After this, BMMCs were again separated using simple hand held magnet and washed three times with pure distilled water, and it was re-used in the removal of metals cations. The following equations were employed to estimate adsorption and desorption efficiency:

$$\text{Adsorption efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100\% \text{ --- (3)}$$

$$\text{Desorption efficiency, } \eta(\%) = \frac{M_{\text{desorbed}}}{M_{\text{sorbed}}} \times 100\% = \frac{(C_r \times V_r)}{(C_o - C_e) \times V} \times 100\% \quad (4)$$

where, M_{desorbed} and M_{sorbed} are the amount of metals cations sorbed and desorbed from or on or in the BMMCs. V (L) and V_r (L) is the volume of feed and regeneration solution, respectively.

Fig. 1 Schematic of the encapsulation of phytogetic magnetic nanoparticles (PMNPs) into bio-magnetic membrane capsules (BMMCs), (a) fabricated BMMCs; and conceptual possible cross-linking networks of (b) polyvinyl alcohol, sodium alginate and glutaraldehyde (PVA-SA-GA); (c) SA- CaCl_2 ; and (d) polyvinyl and boric acid (PVA- H_3BO_3) during the fabrication of BMMCs.

3. Results and Discussion

3.1. Characterization of Bio-magnetic Membrane Capsules (BMMCs)

3.1.1. Micromeritic Studies

Table 1 is illustrating the micro-meritic results of the prepared novel BMMCs. According to the aspect ratio values, the prepared BMMCs were close to a perfect sphere. Other parameters such as diameter, weight, and density were also estimated both on wet and freeze dry basis. The findings demonstrating that the BMMCs could hold approximately 90% water content because of the manifestation of enrich hydrophilic functional groups. On average, the diameter of the prepared BMMCs was 4 ± 0.02 mm (Fig. SI).

Table 1 Physical properties (micro-meritic results) of the prepared bio-magnetic membrane capsules (BMMCs).

Parameters	Unit	Values
Average wet weight/ capsule	g	0.064 ± 0.001
Average freeze dried weight/ capsule	g	0.0062 ± 0.0001
Average maximum diameter	mm	4 ± 0.02
Average minimum diameter	mm	3.93 ± 0.01
Average density (on wet basis)	g/m^3	261.56 ± 0.05
Average density (on dry basis)	g/m^3	2700 ± 0.5
Aspect ratio (on average)	(-)	1.01 ± 0.03
Average water content	(%)	90.37 ± 0.05

3.1.2. FTIR, Powder XRD, TGA and EDX Analyses

The FTIR study was conducted to recognize the formation mechanism of the novel BMMCs, i.e. to observe the smooth encapsulation of PMNPs, FTIR spectrum of PVA and SA mixture was given in Fig. 2(I)a. The results suggested that the hydrophilic functional groups i.e. -OH/ hydroxyl groups (at $3600\text{-}3300\text{ cm}^{-1}$) and carboxyl groups (at $3191\text{-}2898\text{ cm}^{-1}$) have interacted with each other and established a uniform mixture (Kahya et al., 2010). The bands at $3600\text{-}3300\text{ cm}^{-1}$ were ascribed to O-H stretching vibrational peaks of polyphenolic groups and the stripes at $3191\text{-}2898\text{ cm}^{-1}$ were attributed to -C-H/ -CH₂/ CH₃ stretching vibrational peaks of alkanes (Bekin et al., 20014). In addition, the characteristic peaks appeared (at around 1637 and 893 cm^{-1}) were indicating C=O stretching and the presence of O-Na bonds in -COONa radical of sodium alginate (SA), respectively (Thankam et al., 2013). Moreover, the pikes at $1562\text{-}1363\text{ cm}^{-1}$ were assigned to C-OH stretching/ -COO⁻ groups of SA. Similarly, the band peak at 1039 cm^{-1} was allocated to C-OH stretching of PVA (Samanta et al., 2014). Thus, the results of FTIR spectrum of PVA-SA mixture demonstrated that the amalgam was homogenous and hydrophilic functional groups were well interacted with each other via electrostatic forces due to hydrogen bonding (Dragan, 2014). Similarly, initially, the FTIR spectrum of PVA-SA-PMNPs mixture was also studied to observe the influence of PMNPs accumulation into PVA and SA solution (Fig. 2(I)b). The results indicated that the intensity of the peaks (at $3600\text{-}3300\text{ cm}^{-1}$) and (at $3191\text{-}2898\text{ cm}^{-1}$) was slightly reduced. It was might be due to the space occupied by PMNPs (Huang et al., 2017). An absorption peak was grown (at 489 cm^{-1}), and it can be appointed to Fe-O, confirming the existence of PMNPs in the PVA-SA mixture (Ali et al.,

2018a, 2018b). However, the chemical structure did not change significantly except color of the amalgam altered from light yellow to black after inserting PMNPs solution.

To better understand the formation mechanism of BMMCs, the FTIR spectra of BMMCs were studied after the incorporation of primary and secondary cross-linking agents (Fig. 2(I)c,d). It was observed that the cross-linking reaction occurred quickly by casting a drop of PVA-SA-PMNPs mixture into oversaturated CaCl_2 and H_3BO_3 solution and then an interpenetrating polymer network (IPN) structure was developed (Hoon et al., 2003; Yue et al., 2016; Messaoud et al., 2016). First, semi-interpenetrating polymer network (SIPN) configuration was formed due to the crosslinking of G units (in SA chains) with Ca^{2+} via chelation, covalent and hydrogen bonding in the manifestation of PVA-PMNPs (Jao et al., 2009). This described that an ionic bonding was developed between Ca^{2+} and $-\text{COOH}$ of SA and fractional covalent bonding was occurred between Ca^{2+} and oxygen atom (O) of ether groups, respectively. Meantime, another SIPN structure was formed through crosslinking of B^{3+} with PVA via hydrogen bonding in the presence of SA-PMNPs (Akbari et al., 2017). It can be noticed that CaCl_2 and H_3BO_3 was continuously utilizing $-\text{OH}$ and $-\text{COONa}$ radical in PVA and SA, and meantime the B-O, B-CR and B-O-B stretching characteristics peaks were appeared at around 1406, 1061 and 696 cm^{-1} (Fig. 2(I)c), as reported by Bekin et al. 2014. However, the band of O-Na bond (at 893 cm^{-1}) was disappeared or significantly reduced, intimating inter or intra hydrogen bonding among PVA, SA and primary cross-linking agents (Samanta et al., 2014). The characteristic peaks around 1560 and 1480 cm^{-1} can be endorsed to the anti-symmetric and symmetric stretching vibrational peaks of $-\text{COH}/-\text{COO}^-$ groups in the polymer network (Fig. 2(I)c), suggesting the formation of an IPN structure (Thankam et al., 2013). Meantime, the intensity of characteristic peaks of $-\text{OH}$ and $-\text{COH}$ was also reduced, indicating the formation of uniform, dense and compact egg-shaped BMMC.

Further, during secondary cross-linking with GA, both SINP structure of SA and PVA bonded with GA individually and an IPN configuration was developed by cross-linking of $-\text{COH}$ groups in GA with $-\text{OH}$ groups in SA and PVA to develop acetyls and ether linkages by mounting characteristic pikes of $\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{B}-\text{OH}$ and BOB stretching vibrations at around 1666, 1074, 941 and 640 cm^{-1} (Dragan 2014). It showed that during secondary cross-linking, PVA and SA cross-linked via van der waals forces and hydrogen bonding, promoting a physical entanglement and chemically cross linked polymer network in membrane capsules (Huang et al., 2017). Hence, GA performed as a ‘knot’ or ‘joint’ to combine SA and PVA together via co-cross-linking reaction that endorsed overall mechanical properties of capsule membrane and make them more beneficial for adsorption process (Fig. 2(I)d) (Akbari et al., 2017). On the

other hand, the chemical structure changing in the capsule membrane was actually unnoticeable by FTIR due to the encapsulation of PMNPs, but the characteristic peak can be noticed at around 480 cm^{-1} in both spectra (Fig. 2(I)c,d), suggesting the existence of smooth encapsulation of PMNPs into membrane capsules (Ali et al., 2018a). The encapsulated PMNPs had their own functional groups ($-\text{OH}$ and $-\text{COO}^-$), that will also help to increase anions active spots for the adsorption of cationic pollutants (Ali et al., 2018a). In addition, the prepared BMMCs adsorbent can easily be separated from effluent just by applying simple hand-held magnet and can be re-employed for multiple treatment cycles after regeneration. This encapsulation technique will also help to resolve PMNPs disintegration problems and the stability of PMNPs. In addition, the functional groups can be maintained for long-term applications (Ali et al., 2018a). Altogether, the FTIR results confirmed the smooth formation of BMMCs via chelation, hydrogen-bonding and van der Waals forces by employing primary and secondary cross-linking agents, in addition to uniform/ proper encapsulation of PMNPs into PVA-SA matrix. The conceptual possible cross-linking networks of SA- CaCl_2 , PVA- H_3BO_3 and PVA-SA-GA during the fabrication of bio-magnetic membrane capsules (BMMCs) are shown in Fig. 1.

The powder XRD patterns of the prepared BMMCs were also studied (Fig. 2(II)). First, the XRD pattern of PVA-SA-PMNPs mixture was carried out to investigate the presence and smooth mixing of PMNPs into PVA-SA matrix (Fig. 2(II)a). The outcomes of XRD study describing a series of precise diffraction peaks emerging at around $2\theta = 30^\circ, 35^\circ, 43.2^\circ, 57.1^\circ$ and 62.9° respectively. These peaks can be indexed as/ were associated to (220), (311), (400), (511) and (440) planes of pure iron oxide/ Fe_3O_4 . The obtained peaks were very close to the published reports, as described in JCPDS card No. 19-0629 (Wang et al., 2017; Guo et al., 2017; Zhang et al., 2011; Akbari, A., 2017). The peaks at $2\theta = 30^\circ, 35^\circ$ and 62.9° were mainly hinting the existence of iron oxide/ PMNPs, as reported by Ali et al. 2018a, 2018b. The average diameter/ crystallite size measurements of the PMNPs were also carried out by using Debye-Scherrer's equation and it was estimated about 35-40 nm, as previously reported in authors published report (Ali et al., 2018a). Moreover, a typical broad reflection peak at around $2\theta = 20^\circ$ appeared which can be assigned to C (001) reflection of amorphous carbons that might be composed in irregular shapes (Akbari, A., 2017). The existence of C (001) reflection mainly depicted the presence of C-OH containing functional groups ($-\text{OH}$, $-\text{COOH}$, $-\text{C-H}$, etc.), which were mainly associated to the mixture of PVA-SA-PMNPs in the sample, and confirming the homogenous mixing of PVA-SA mixture with PMNPs solution (Guo et al., 2017; Zhang et al., 2011). In contrast, Fig. 2(II)b showed that the intensity of the peaks was significantly decreased during the fabrication process/ or after reaction of PVA-SA-PMNPs mixture with primary and

secondary cross-linking agents, mentioning the successful cross-linking. The intensity of the characteristic peak at around $2\theta = 20^\circ$ was significantly decreased, indicating the consumption of C-OH containing functional groups during the fabrication process (Akbari, A., 2017). In addition, the strong characteristic peaks of iron oxide at around $2\theta = 35^\circ$, 43.2° , and 62.9° also appeared, indicating the presence of PMNPs in the fabricated BMMCs, despite this facts that the intensity of these peaks was lowered than as compared to Fig. 2(II)a (Ali et al., 2018a). This might be due to the amalgamation of primary and secondary cross-linking agents with PVA-SA-PMNPs mixture. Thus, the XRD findings verified the presence of PMNPs and depletion of C-OH containing functional groups in the fabrication process of BMMCs.

The EDX study was also conducted to identify the chemical or elemental composition, and the presence of PMNPs in the prepared BMMCs (Fig. 2(III)). According to the EDX examination, BMMCs were composed of the elements of carbon (C), oxygen (O), sodium (Na), sulfur (S), chloride (Cl), potassium (K), calcium (Ca) and iron (Fe). The EDX profile contained intense peaks of C and O in addition to Na, S, Cl, K, Ca and Fe (Fig. 2(III)). The C and O peaks in EDX profile were associated with the hydrophilic functional groups (-OH and -COOH), mainly associated with the PVA, SA, GA and PMNPs solution. On the other hand, the presence of Fe peaks in the EDX spectrum confirmed the encapsulation of PMNPs in the BMMCs (Fig. 2(III)). The peaks of Ca and Cl can be associated with the primary cross-linking agent i.e. CaCl_2 . While the intense peak of Na was mainly linked to SA. In addition, the presence of K and S peaks can be assigned to the plant bio-molecules, present in the leaves extract. The results indicated that the atomic percentages as acquired by the EDX quantification were C (61.21%), O (35.08%), Na (0.72%), S (0.43%), Cl (1.17%), K (0.20%), Ca (0.78%) and Fe (0.40%) (Fig. 2(III)). The presence of Fe homogenously distributed throughout the sample, hinted the smooth loading of PMNPs in the PVA-SA mixture, though in a small amount (1.56 %). For the fabrication of BMMCs, 4:1 (v/v) = [PVA (10.0 wt %): SA-PMNPs (3.0 wt %)] = 20.0 g PVA: 5.0 g SA-PMNPs solution was used. Thus, based on the EDX quantification, the total amount of C, O and Na was 91.88 %, excluding the amount of S, Cl, K and Ca. Whereas, the amount of Fe element was 1.56% and this reading was very close to our theoretical calculation i.e. 0.430 g (2 wt % PMNPs in 4: 1 (v/v) = PVA-[SA-PMNPs]). Overall, the EDX results ensured the manifestation of C, O, Na, Cl, Ca and Fe in the fabricated BMMCs (Fig. 2(III)).

The thermal stability and capping structure of functional groups of the prepared BMMCs was noticed by using thermal gravimetric analyzer (TGA). The TGA curve of the prepared BMMCs described three major mass loss steps in the tested temperature range of 0-800°C (Fig. 2(IV)). The first mass or weight loss (18 %) appeared in the temperature range of 34-250°C,

indicating the removal of water (Ali et al., 2018a). The second major weight loss (40%) occurred at 250-370°C, suggesting the elimination or pyrolysis or decomposition or, loss of hydrophilic functional groups of the PVA-SA (Hong et al., 2018). Finally, third weight loss (26%) occurred in the temperature range of 370-560°C, suggesting the decomposition of polymer structure of PMNPs (Liang et al., 2014). Moreover, no weight loss was detected above 560°C and BMMCs exhibits 16% weight residue.

Fig. 2 (I) The Fourier transform infrared (FTIR) spectra of (a) polyvinyl alcohol and sodium alginate (PVA-SA), (b) polyvinyl alcohol, sodium alginate and phytogetic magnetic nanoparticles (PVA-SA-PMNPs), (c) PVA-SA-PMNPs after primary cross-linking and (d) fabricated bio-magnetic membrane capsules (BMMCs); (II) Powder X-ray diffraction patterns of (a) PVA-SA-PMNPs and (b) the prepared bio-magnetic membrane capsules (BMMCs) after the reaction with primary and secondary cross-linking agents (displaying the amorphous carbon and magnetite structures); (III) Energy dispersive X-ray (EDX) image of the prepared bio-magnetic membrane capsule (BMMCs) [inset table is the weight and atomic percentages the present elements]; and (IV) thermal gravimetric analyzer (TGA) plot/ curve of the fabricated BMMCs

The TGA findings proposed that the weight percentages of moisture, PVA-SA and PMNPs were 18, 40 and 26%, respectively. These results clearly indicated that the fabricated BMMCs were fully capped with hydrophilic functional groups (–OH, –COOH, –C-H, etc.), mainly associated to PVA-SA-PMNPs, and were responsible to decrease capsules overall thermal

stability and in the meantime increasing adsorptive capability (Huang et al., 2017). On the other hand, the water content of the prepared BMMCs was also calculated to be 90.23% (Table 1). Thus it is clear that on average, the actual weight of the prepared capsules was 10 ± 3 %, as calculated by theoretically and practically (by TGA) means.

3.1.3. Morphological studies of BMMCs

SEM analysis was carried out to understand the morphology of the prepared BMMCs and to verify the presence of encapsulated PMNPs. Fig. 3 illustrated the morphological changes of the freeze-dried BMMCs from the outer layer to the core. The prepared BMMCs possessed top dense, macro-voids and micro-porous type like architecture. Some cracks or small fractures were also noted on the surface of the membrane capsules, along with the presence of different ranges of pores diameter from the outer surface to core. Overall, the prepared BMMCs showed a micro-porous capsule ‘shell’ and macro-porous core structure. The holes with a diameter ranging from 8 to 45 μm were developed in the core owing to the presence of high water content (~90%), suggesting that PVA-SA kept relatively large surface area and spongy configuration (Fig. 3a,b,c,d). The thickness of the capsule shell was 52 ± 8.5 μm and apertures in the cross-section of the capsule shell were about 3 ± 0.5 μm (Fig. 3d). The SEM results strongly suggested that the morphology of the prepared BMMCs were influenced due to the development of chemical bonds. This morphology can be explained in this way that a ‘fish egg’ shape type spherical shell-nuclei was formed as a casting solution drop injected into primary cross-linking agent solution ($\text{CaCl}_2 + \text{H}_3\text{BO}_3$). Initially, a compact, dense and micro-porous egg box membrane shape was formed due to the consumption of $-\text{COO}^-/\text{OH}^-$ functional groups by the interaction with Ca^{2+} and B^{3+} . As the outer surface formed, a gradient was developed between primary cross-linking agent solution and PVA-SA mixture to develop inner core (Fig. 3d).

Fig. 3 Scanning electron microscopic (SEM) micrographs of (a) the fabricated bio-magnetic membrane capsules (BMMCs), (b) cross-sectional area of the BMMCs, (c) surface layer of the BMMCs, (d, e & h) core of the BMMCs, (f) real pictorial view of the surface layer of the BMMCs; and (g) real pictorial view of the cross-sectional area of the BMMCs

The thickness of the capsules “shell” prolonged inward with the passage of time but vetoed the leakage of solution from capsule inner core, which may be responsible to decrease the chance and speed of smooth interaction between polymer and reagents, that led to the improvement of the pore size. In addition, GA (secondary cross-linking agent) played an important role in modifying the capsules morphology by creating looser and macro-porous assembly in the core, which further enhanced the density of pores (Fig. 3e). The pores size remarkably decreased after incorporating GA because it has an excellent ‘healing’ potency due to the manifestation of –OH, which performed a crucial role in maintaining smooth interaction between polymer and reagents (Fig. 3e). Moreover, the PMNPs were agglomerated into micro-sized packs by

the strong hydrogen bonding, and these were well dispersed in the PVA-SA mixture, resulting in notably enhanced mechanical properties (Fig. 3e,n). Furthermore, the spongy macro-structure remarkably improved the surface area in the core, and it may facilitate the moment of pollutants (toxic dyes and HM ions) within the core network by creating pore's channel. This will also enhance the adsorptive capability of the capsule adsorbent by generating more vacant or active sites for adsorbate.

3.1.4. Vibrating sample magnetometer (VSM) analyses

The hysteresis loop of the freeze-dried BMMCs was also obtained using VSM at temperature 300 K by perturbing magnetic field from -15 to + 15 KOe (**Fig. 4**). The saturation magnetization (M_s) value at temperature 300 K was discovered to be 11.02 emu/g, which is useful for the repeated magnetic separation. Despite this fact, the obtained value was approximately 2.5 times lower than the M_s of PMNPs (50.95 emu/g), as reported previously by Ali et al. (2018a). The values of remanence magnetization (M_s) and coercivity (H_c) was zero, mentioning that the prepared material has super-paramagnetic behaviour. Importantly, the super-paramagnetic nature of PMNPs did not damage due to the encapsulation of PMNPs into PVA and SA mixture. However, the value of M_s was affected. Moreover, despite having very low Fe content (1.56%) of the PMNPs, the prepared BMMCs had a very high saturation magnetization (11.02emu/g). It means that a slight loading of PMNPs into capsules is enough to enhance significant high M_s value, which will not only make capsules suitable for easy magnetic separation from the aqueous environment, but also demonstrate superior chemical stability against acid attack in contrast to naked PMNPs, that faced oxidation of the particles, resultant decreases the stability of PMNPs for long-term applications. Overall, the prepared novel BMMCs showed comparatively highest saturation magnetization value and magnetic separation time (10 sec) than most of the other documented composite materials (**Fig. 4**), which is highly prerequisite for improving water and wastewater treatment processes and maintaining treatment systems economically feasible (Table 2). Importantly, the recovery of HM ions can also be achieved.

Fig. 4 M-H hysteresis loop/vibrating sample magnetometer (VSM) measurement of the prepared PMNPs and bio-magnetic membrane capsules (BMMCs) at temperature 300 Km, and the inseted figure is indicating the magnetic separation of the prepared BMMCs in aqueous environment using simple hand-held magnet.

Table 2 Comparison of Bio-magnetic membrane capsules (BMMCs) with other reported some magnetic composite sorbents in term of magnetic separation time and saturation magnetization (M_s).

Magnetic sorbents	Magnetic separation time (s)	M_s (emu/g)	References
PVA-SA-embedded Fe_3O_4 magnetic nanoparticles (MNPs)	-	5	Huang et al., 2017
Fe_3O_4 @mesoC	-	5.5	Zhang et al., 2011
Fe_3O_4 @ SiO_2 @CS-TETA-GO	-	8.22	Wang et al., 2017
Bio-magnetic membrane capsules (BMMCs)	10	11.02	Present study
FeCo/GC NCs@MSNs	-	17.1	Hong et al., 2018
Fe_3O_4 @(PAH/GO-COOH) ₂ nanocomposites	-	21.5	Guo et al., 2017
CMC-g-CMPVA film loaded with $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles	-	36.87	Dahlan et al., 2017

3.2. Removal of Potentially Toxic Metals Cations (Pb^{2+} and Cd^{2+}) by Bio-Magnetic Membrane Capsules (BMMCs)

3.2.1. Influence of Various Operating Parameters

3.2.1.1. Influence of adsorbent dosage

The effect of adsorbent dosage on the removal of metals cations by BMMCs was investigated at an initial metals cations concentration of 200 mg/L. The findings shown that the elimination efficiencies of Pb^{2+} and Cd^{2+} by BMMCs were increased (from 70.96 to 96.89% for Pb^{2+} and 87.01 to 91.47% for Cd^{2+}) by increasing BMMCs dosages (from 0.0064 to 0.062 g/L). The elimination of both metals cations rapidly increased in the start, as the quantity of BMMCs improved from 0.0062 to 0.03 g/L, and then it was more or less uniform by further improving the BMMCs dosage from 0.03 to 0.062 g/L (Fig. 5a). This rise in elimination performance might be due to the accessibility of higher active and vacant sites on the BMMCs or existence of greater surface area for cations sorption (Huang et al., 2013). On average, 94.56 and 91.47% of removal was achieved for Pb^{2+} and Cd^{2+} , respectively by using BMMCs dosage of 0.03 g/L. While, it was noticed that beyond this dosage of 0.03 g/L, the ejection of both metals cations was slowly increased, suggesting the equilibrium between adsorbate and adsorbent. Therefore, 0.03 g/L of BMMCs, as an optimum dose was selected for subsequent experiments.

3.2.1.2. Influence of solution pH

The pH value of the metals emulsion can change the binding sites, surface charges, mixture chemistry and chemical interaction of BMMCs by varying the degree of ionization of the adsorbate molecules and scope of detachment of functional groups present on the BMMCs. Therefore, in the present work, the influence of pH was observed in the range of pH 2-8 at an initial metals cations concentration of 200 mg/L for 24 h (Fig. 5b). As depicted in Fig. 5b, the ejection of both metals cations (Pb^{2+} and Cd^{2+}) were increased by increasing pH from 2 to 6.5/7, and then it was faintly reduced after pH 7 to 8. It is already known that at different pH values, both Pb^{2+} and Cd^{2+} subsists in different segments such as $\text{Pb}^{2+}/\text{Cd}^{2+}$, $\text{Pb}(\text{OH})_3/\text{Cd}(\text{OH})_3/\text{Pb}(\text{OH})^+/\text{Cd}(\text{OH})^+$ and $\text{Pb}(\text{OH})_2/\text{Cd}(\text{OH})_2$ which could effects on the removal performance. In this work, the removal efficiency of Pb^{2+} was enhanced from 16.2 to 94.56 % as pH boosted from 2 to 6.5/7, and then declined slightly to 92.99% in the range of pH 7-8. However, the elimination performance of Cd^{2+} was improved from 10.23 to 91.47% as pH risen from 2-6.5/7, and then further lessened after pH 7 (Fig. 5b). Below and above pH 6-7, a decreasing trend in removal for both metals cations was noticed. This trend can be explained in two ways. First, at

low pH (2-6), the number of protons (H^+) potency was high in emulsion because of the protonation of hydrophilic functional groups present on or in the BMMCs, which competed with Pb^{2+} and Cd^{2+} to capture active sites, and meantime generated Coulombic repulsion or electrostatic repulsion between metals cations and positively charged BMMCs, which significantly lower the removal efficiency of both metals cations. In contrast, at higher pH (6-7), the amount of H^+ in solution was low, which minimized the repulsive foresees, and meantime increased interactions between adsorbate and adsorbent by the hydrogen bonding mechanisms along-with ion-exchange, and consequently, a greater ejection of both metals cations was achieved. Secondly, the pH_{PZC} of the BMMCs was 2.19 (Fig. 5c), as calculated by pH drift method reported by Ali et al. 2018a, 2018b (**Test-SVI**).

Fig. 5 Influence of various operating parameter on the adsorptive performance of bio-magnetic membrane capsules (BMMCs) in the removal of metals cations in single system, (a) doses of BMMCs [dosage = 0.0062-0.062 g/L; C_0 = 200 mg/L; pH = 6.5, temperature = 298.15K; contact time = 48 h; agitation = 100rpm]; (b) solution pH [dosage = 0.03 g/L; C_0 = 200 mg/L; pH = 2-8, temperature = 298.15K; contact time = 48 h; agitation = 100rpm]; (c) pH_{PZC} of BMMCs; [dosage = 0.03 g/L; Volume of 0.005 mol/L NaCl = 20 mL; pH = 2-14, temperature = 298.15K; contact time = 48 h; agitation = 100rpm] (d) initial metal cations concentration (mg/L) [dosage = 0.03 g/L; C_0 = 10-1000 mg/L; pH = 6.5, temperature =

298.15K; contact time = 48 h; agitation = 100rpm]; (e) initial reaction temperature (K) [dosage = 0.03 g/L; C_o = 200 mg/L; pH = 6.5, temperature = 298.15-333.15K; contact time = 48 h; agitation = 100rpm]; and (f) contact time (h); [dosage = 0.03 g/L; C_o = 200 mg/L; pH = 6.5, temperature = 298.15K; contact time = 0-48 h; agitation = 100rpm]

Hence, at $\text{pH} < \text{pH}_{\text{PZC}}$, the shell of the BMMCs was positively charged thereby improving electrostatic repulsion with the metals cations, and meanwhile the availability of higher amount of H^+ strength in solution battled the metals cations for vacant sites, which eventually prevented the removal of metals cations by BMMCs. Furthermore, at $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of the BMMCs was negatively charged, so improving electrostatic interaction with the metals cations and adsorbent, which eventually improved the removal of metals cations by BMMCs. However, at $\text{pH} > 7$, the removal of both metals cations decreased again. It might be due to possible precipitation of metals cations and hydroxyl salts or cluster impact between metals cations with OH^- , as formerly reported by many researchers (Bushra et al., 2015). Overall, on average, a maximum of 94.56% of Pb^{2+} and 91.47% of Cd^{2+} elimination performance was accomplished at pH 6.5/7. The possible interaction of Pb^{2+} and Cd^{2+} with BMMCs and removal of both metals cations by the hydrogen bonding along-with ion-exchange mechanism in the pH range of 2-8 is shown in the following equations:

For ion exchange:

At $\text{pH} > 7$

For hydrogen bonding:

At pH 5-7

Where, R is the carrier of the PVA, SA and PMNPs in the BMMCs. Therefore, the initial pH of 6.5 was kept an optimum for subsequent experiments, directing to the maximum ejection of both metals cations.

3.2.1.3. Influence of initial metals ions concentration, temperature and contact time

The effect of initial metals cations concentration on the elimination performance of BMMCs was monitored by altering concentration from 10 to 1000 mg/L at pH 6.5 using BMMCs dosage of 0.03 g/L (Fig. 5d). As displayed in Fig. 5d, the elimination performance of both metals cations was declined with the increase of metals cations from 10 to 1000 mg/L. This behaviour may indicate depletion of vacant sites on or in the BMMCs against excessive metals cations. The influence of reaction temperature on the ejection of metals cations by BMMCs was also noticed by varying temperature from 298.15 to 333.15K (Fig. 5e). Fig. 5e is representing that the elimination capacity of both metals cations was increased with the increase of reaction temperature, suggested that removal was spontaneous and exothermic in nature (Araújo et al., 2018). Similarly, the effect of contact time was also noticed by taking initial metals cations concentration of 200 mg/L at pH 6.5 using BMMCs dose of 0.03 g/L. As shown in Fig. 5h, the removal of metals cations occurred in two steps in the time range of 0-48 h. The first stage was rapid and more than 80% of the metal cations removed within the first 20 h. The second stage was slower and approached to equilibrium until maximum removal was noticed. It is a common trend that firstly metals cations sorbed on or in the BMMCs due to the accessibility of higher non-cross-linked hydrophilic functional groups (-OH and -COOH) or amount of vacant or active sites for adsorption. Later, a slower cross-linking phase happened due to the diffusion through the already developed inner channel, which made difficult for pollutants to capture rest of the active sites due to the establishment of electrostatic opposing forces between metals cations attached on the surface of BMMCs and those in suspension, and therefore triggered to reduce the sorption process (Gedam and Dongre, 2015). Overall, the optimal equilibrium time was 24 h.

3.2.2. Adsorption Kinetics

Adsorption kinetics of metals cations onto BMMCs were investigated with kinetics models such as Pseudo first order, Pseudo-second order, Elovich, Intraparticle diffusion and Liquid film diffusion. It was considered that various independent mechanisms might be convoluted in governing adsorption kinetics throughout sorptive removal of metals cations that can govern in parallel or series (Ghaedi et al., 2011). For example, (i) bulk transport, (ii) film diffusion/ external mass transfer, (iii) intraparticle diffusion, and (iv) chemisorption or chemical reaction (Chen and Wang, 2007).

Fig. 6 Adsorption kinetics of (a) lead ions (Pb^{2+}), (b) cadmium ions (Cd^{2+}); the linear plot of pseudo-second-order model for (c) lead (Pb^{2+}) and (d) cadmium (Cd^{2+}); the linear plot of Intraparticle diffusion model for (e) lead (Pb^{2+}) and (f) cadmium (Cd^{2+}) by the BMMCs [dosage = 0.03 g/L; C_0 = 50-1000 mg/L; pH = 6.5, temperature = 298.15K; contact time = 0-48 h; agitation = 100rpm]

First, the effect of contact time on the sorption of metals cations was noticed by altering the cations concentration from 50 to 1000 mg/L. The findings indicated that elimination efficiency was raised, as the concentration of metals cations increased, and approached to equilibrium. However, the equilibrium time was varied for different concentrations of metals cations. At low metals cations concentrations, the equilibrium adsorption time was achieved in the contact time of less than 15 h. On average, the rapid sorption rate was attained within 20 h, while at 24 h sorption equilibrium was achieved. At equilibrium, a maximum of 548 and 610.66 mg/g of sorption capacity was achieved for Pb^{2+} and Cd^{2+} respectively (Fig. 6a,b). This high sorption capacity of metals cations might also be attributed to the synergistic complexation between metals cations and hydrophilic functional groups (-OH and -COOH) attached on or in the BMMCs, previously confirmed by FTIR, EDX and XPS analyses. In order to observe the adsorption process and to estimate the kinetic factors of metals cations sorption on or in the BMMCs, the experimental data were further fitted into various sorption kinetics equations and debate was made based on the regression coefficient (R^2) values and sorption rates obtained from the experiments and calculated by the model equations. The results are given in Table 3&4. As shown in Fig.6 (c and d), and the regression coefficient values ($R^2 > 0.96$) in Table 3&4, it can be proposed that metals cations adsorption data on/ in the BMMCs were effectively explained by pseudo-second-order kinetics model and suggesting the manifestation of chemisorption and/ or ion-exchange mechanism. Also, the calculated values of q_e did not deviate much from the experimental values (Table 3&4). On the other hand, the values of k_2 were lesser than as compared to h (Table 3&4), hinted primarily a rapid sorption of metal cations and then subsequently obeyed by slow adsorption.

Moreover, the adsorption and desorption potential was also observed by Elovich's kinetic model. A linear graph was plotted between $\ln t$ vs q_t , and the value of β was estimated from the slope of the graph, while the value of α was found out by the ratio of q_e/t . The findings illustrated that the value of α was greater than as compared to β , implicit BMMCs had superior adsorption rate than desorption (Table 3&4). However, the values of R^2 were lower than pseudo-second-order kinetic model, indicating the lesser applicability of this model. Moreover, Intraparticle diffusion kinetic model was employed to confirm the diffusion mechanism between metals cations and BMMCs. The applicability of this model was ensured by drawing graph between $t^{0.5}$ vs q_t . Generally, following adsorption process can be observed by employing this model: (a) chemisorption and or/ ion-exchange, (b) film diffusion, (c) intraparticle diffusion, and (d) bulk diffusion (Ali et al., 2018a). The results indicated that R^2 values were

weakly linked with the experimental data (Table 3&4). Similarly, the graph lines did not pass through the origin, suggesting the non-applicability of the intraparticle diffusion model. However, the data points can be explained in double line with the difference in slope and intercept, implied that more than one process (boundary layer adsorption) might be implicated. For instance, the first straight line had a significant slope, suggesting that initially, metals cations covered/ interacted with the external surface/ vacant sites of the BMMCs via film diffusion, and then these cations entered into the solid phase or pores of the membrane capsules via intra-particle diffusion, which is shown in second straight line. Furthermore, the values of k_{ipd} and intercept (I) were also improved as the concentration of metal cations increased in the solution, suggesting the boundary layer diffusion effect occurred owing to the entering of metals cations into the pores of membrane capsules (Fig. 6e,f). Consequently, it can be declared that metal cations sorbed on/ in the membrane capsules owing to the presence of both surface adsorption (ion-exchange/ or chemisorption) and boundary layer adsorption or intra-particle diffusion.

Finally, Liquid film kinetic model was also utilized to confirm the film diffusion mechanism. A linear graph was plotted between t vs $\ln(1-F)$ to ensure the applicability of this model and the value of k_{fd} was estimate by the slope of this graph. The estimated values are presented in Table 3 & 4. The finding revealed that R^2 values were poorly corrected to the experimental data and graph line did not pass through the origin, suggesting the non-applicability of this model. It might be due to fast shaking during the adsorption experiments, which could generate discrepancy between rates of mass transfer in the initial and final stages of the process (Kumar et al., 2015). Hence, based on the sorption kinetic enquiries, at this stage, it can be suggested that chemisorption and/ or ion exchange might be core adsorption mechanism.

Table 3 Kinetic parameters for the adsorption of Pb⁺² by Bio-magnetic Membrane Capsules (BMMCs) at different initial concentration

Kinetic models and equations	Parameters	Pb ⁺²						
		50	100	200	300	500	800	1000
<i>Pseudo-first-order</i> $\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.3.3}$	q _e (exp.) (mg/g)	65.133	125.87	255.33	369.75	481.33	526.67	548
	K ₁ (min ⁻¹)	-0.0543	-0.0407	-0.0491	-0.0523	-0.0655	-0.067	-0.0585
	q _e (cal.) (mg/g)	65.333	129.47	258.93	373.33	500	538.67	540.33
	R ²	0.68	0.8715	0.9505	0.9697	0.8897	0.8161	0.7359
<i>Pseudo-second-order</i> $\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$	K ₂ (min ⁻¹)	0.0135	0.0074	0.0035	0.0025	0.0018	0.0017	0.0017
	q _e (cal.) (mg/g)	65.333	129.47	258.93	373.33	500	538.67	540.33
	h (mg g ⁻¹ .min ⁻¹)	13.067	25.893	51.787	74.667	100	107.73	109.6
	R ²	0.9628	0.9951	0.9854	0.9926	0.9679	0.9807	0.9866
<i>Elovich</i> $q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$	α (mg g ⁻¹ .min ⁻¹)	13.066	25.89	51.78	74.66	100	107.73	109.6
	β (g/mg)	18.534	32.699	68.748	96.898	139.12	148.29	144.45
	R ²	0.935	0.9068	0.9832	0.9681	0.923	0.9568	0.8753
	K _{ipd} (mg g ⁻¹ .min ^{-0.5})	29.217	57.89	115.79	166.95	223.60	240.89	245.07
<i>Intraparticle diffusion</i> $q_t = k_{ipd}t^{0.5}$	I	8.3515	32.323	35.709	69.643	77.898	78.509	129.74
	R ²	0.8516	0.7853	0.921	0.8801	0.8277	0.8806	0.7508
<i>Liquid film diffusion</i> $\ln(1 - F) = -k_{fd}t$	K _{fd} (g/mg)	-0.075	-0.152	-0.126	-0.141	-0.077	-0.113	-0.110
	I	-1.3125	-2.19	-1.138	-1.32	-1.618	-1.160	-1.3644
	R ²	0.2849	0.0073	0.075	0.0709	0.1099	0.1037	0.1732

Key: Given in supplementary information (Text-SVII)

Table 4 Kinetic parameters for the adsorption of cadmium ions (Cd⁺²) by Bio-magnetic Membrane Capsules (BMMCs) at different initial concentration

Kinetic models and equations	Parameters	Cd ⁺²						
		50	100	200	300	500	800	1000
<i>Pseudo-first-order</i> $\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.3.3}$	q _e (exp.) (mg/g)	64	121.6	264	388	520	593.33	610.67
	K ₁ (min ⁻¹)	-0.0418	-0.0488	-0.0556	-0.0575	-0.063	-0.0645	-0.0651
	q _e (cal.) (mg/g)	64.667	127.33	262.4	394.4	520	593	610
	R ²	0.8564	0.9549	0.9216	0.966	0.838	0.7492	0.7484
<i>Pseudo-second-order</i> $\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$	K ₂ (min ⁻¹)	0.0142	0.0071	0.0036	0.0024	0.0018	0.0015	0.0015
	q _e (cal.) (mg/g)	64.667	127.33	262.4	394.4	520	593	610
	h (mg g ⁻¹ .min ⁻¹)	12.933	25.46	52.48	78.88	104	118.67	122.13
	R ²	0.9892	0.9836	0.9909	0.9921	0.9964	0.9843	0.9842
<i>Elovich</i> $q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$	α (mg g ⁻¹ .min ⁻¹)	12.933	25.46	52.48	78.88	104	118.66	122.133
	β (g/mg)	16.998	34.588	65.775	102.61	130.44	162	167.1
	R ²	0.9747	0.9777	0.9641	0.9749	0.9269	0.9413	0.9444
	K _{ipd} (mg g ⁻¹ .min ^{-0.5})	28.919	56.94	117.34	176.38	232.55	265.34	273.09
<i>Intraparticle diffusion</i> $q_t = k_{ipd}t^{0.5}$	I	11.046	16.92	52.669	70.38	130.49	100.68	101.65
	R ²	0.8983	0.9112	0.8849	0.8914	0.8141	0.8477	0.8514
	K _{fd} (g/mg)	-0.144	-0.115	-0.175	-0.138	-0.193	-0.117	-0.113
<i>Liquid film diffusion</i> $\ln(1 - F) = -k_{fd}t$	I	-1.55	-1.4318	-1.4433	-1.4586	-1.38	-0.8221	-0.7949
	R ²	0.0175	0.0331	0.0665	0.0705	0.2181	0.1765	0.1881

Key: Given in supplementary information (Text-SVII)

3.2.3. Sorption isotherm study

For estimating adsorption capacity, four types of equilibrium model i.e. Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms were utilized to address the metals cations interaction with BMMCs (Table 5). The results indicated that adsorptive performance improved as the initial concentration of metals cations mounted and then approached to saturation at $C_0 = 700$ mg/L for Pb^{2+} and $C_0 = 800$ mg/L for Cd^{2+} (Fig. 7a). Ahead of this, there was no considerable adsorptive performance boosted. Table 5 represented, that the results obtained by fitting experimental data into various isotherm model equations. According to the findings, Langmuir model presented the finest fit to the experimental data of metals cations sorption on or in the BMMCs, since it revealed greater $R^2 = 0.97$ (for Pb^{2+}) and $R^2 = 0.99$ for (Cd^{2+}) value than other isotherm models (Fig. 7b), suggesting the monolayer adsorption of metals cations on or in the BMMCs (Fig. 7b). It means that the membrane capsules surface was homogeneous and all the vacant sites had the same empathy to adsorbate or metals cations. In addition, the favourability of the sorption was checked by estimated K_L values. If $K_L > 1$ sorption isotherm is unfavourable, if $K_L = 1$ sorption isotherm is linear, if $K_L = 0$ sorption is irreversible isotherm and if $0 < K_L < 1$ then sorption is favourable. The results indicated that the range of K_L values for Pb^{2+} and Cd^{2+} were 0.99-0.77 and 0.99-0.34, respectively and intimating promising adsorption. The results indicated the monolayer metals cations adsorption on or in the homogenous sites of BMMCs. The calculated maximum adsorption capacities for both metals cations are given in Table 5. Overall, the clues found from the isotherm and kinetic surveys along with the fact that metals cations and hydrophilic functional groups attached on/ in the BMMCs are oppositely charged, suggesting the ion-exchange might be the leading adsorptive removal mechanism of metals cations on or in the BMMCs (Kemer et al., 2009).

3.2.4. Thermodynamic studies

To investigate the nature of adsorption and the influence of reaction temperature in the removal of metals cations by BMMCs, thermodynamic parameters were also estimated. The values of ΔG° were negative at all the reaction temperatures, suggested the thermodynamically viable spontaneous nature of the metal cations adsorption on/ in the BMMCs (Gandhi and Meenakashi 2012). In contrast, the values of ΔG° were boosted as the reaction temperature increased. This indicated a better possibility of adsorption at the higher reaction temperature (Table 6). The negative value of enthalpy (ΔH°) of adsorption for both metals cations indicated the exothermic

nature of sorption in the reaction temperature range of 298.15-333.15K. Importantly, these values were greater than 20.9 KJ/mol, inferred that adsorption of both cations on or in the BMMCs mainly occurred due to the ion-exchange or chemisorption mechanism, as formerly ensured in kinetic and isotherm enquiries. In contrast, the values of entropy (ΔS°) for Pb^{2+} and Cd^{2+} were found to be -4.36 and -5.97 KJ/mol, respectively. This negative value indicates a decrease in uncertainty/ adsorbed species level of freedom at the solid-solution interface during the whole sorption process. In addition, it was also perceived that the ejection of both metals cations was increased as the reaction temperature increased (from 298.15 to 333.15K), while the adsorptive performance was slightly decreased/ almost stable (Fig. 7c,d).

Table 5 Isotherm constants for adsorption of lead ions (Pb^{+2}) and cadmium (Cd^{+2}) on/ in the bio-magnetic membrane capsules (BMMCs).

Isotherm models	Equations	Parameters	Values	
			Pb^{+2}	Cd^{+2}
Langmuir isotherm model	$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}}$	q_{max} (mg/L)	548	610.66
		b (L/mg)	0.0005	0.0043
		K_L	0.99-0.77	0.99-0.34
		R^2	0.9717	0.9728
Freundlich Isotherm model	$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log k_F$	$K_L = \frac{1}{1 + bC_e}$		
		$1/n$	0.539	0.6392
		K_f (mg/L)	1.4217	1.3961
		R^2	0.626	0.6936
Temkin isotherm model	$q_e = \left(\frac{RT}{B_T}\right) \log C_e + \left(\frac{RT}{B_T}\right) \log K_T$	K_T (L/g)	76.803	144.05
		B_T (KJ/mol)	186.65	171.94
		R^2	0.9622	0.8481
Dubinin-Radushkevich isotherm model	$\ln q_e = \ln q_m - \beta \varepsilon^2$	q_{max} (mg/L)	548	610.66
		E (KJ/mol)	0.4550	0.3136
		β (mol^2/J^2)	2.4147	5.085
		R^2	0.6341	0.3329

Key: Given in supplementary information (Text-SVIII)

Fig. 7 (a) Sorption isotherm curve for the sorption of metals cations by BMMCs [dosage = 0.03 g/L; C_0 = 50-1000 mg/L; pH = 6.5, temperature = 298.15K; contact time = 48 h; agitation = 100rpm]; (b) the linear plot of Langmuir isotherm model for lead ions (Pb²⁺) and cadmium ions (Cd²⁺) sorption on/ in the BMMCs; (c) Thermodynamic plots for the sorption of Pb²⁺ and Cd²⁺ by BMMCs in the range of temperature from 298.15 to 333.15K; (d) effect of reaction temperature on the removal efficiency and adsorptive capacity of Pb²⁺ and Cd²⁺ by BMMCs in the range of temperature from 298.15 to 333.15K [dosage = 0.03 g/L; C_0 = 200 mg/L; pH = 6.5, contact time = 0-48 h; agitation = 100rpm]; (e) removal of lead and cadmium ions (Pb²⁺ and Cd²⁺) in binary system by the BMMCs [Pb²⁺ = 200 mg/L; Cd²⁺ = 10, 50 and 100 mg/L; dosage = 0.03 g/L; pH = 6.5, temperature = 298.15K; contact time = 48 h; agitation = 100rpm]; and (f) study of the stability and reusability of BMMCs for consecutive

sorption-desorption cycles of Pb^{2+} and Cd^{2+} [20 mL of 25% HNO_3 acidic regeneration solution; dosage = 0.03 g/L; C_o = 200 mg/L; pH = 6.5, temperature = 298.15K; contact time = 48 h; agitation = 100rpm]

Table 6 Thermodynamic parameters values for the adsorption of lead ions (Pb^{2+}) and cadmium (Cd^{2+}) by Bio-magnetic Membrane Capsules (BMMCs) at different reaction temperature (K).

Equations	Temperature (K)	ΔG° (KJ/mol)		ΔH° (KJ/mol)		ΔS° (KJ/mol K)	
		Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
ΔG°	298.15	-9416.32	-10923.45				
$= -RT \ln K_D$	303.15	-10408.42	-11950.48				
$\ln K_D$	313	-11551.46	-13292.36	-23.43	-	-4.36	-5.97
ΔS°	323.15	-12512.16	-14736.84		32.66		
$= \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$	333.15	-14950.48	-17385.10				

Key: Given in supplementary information (Text-SIX)

3.3. Adsorptive Removal of Potentially Toxic Metals Cations using BMMCs by Binary System

Generally, wastewater is a combination of different cations, anions and other types of pollutants. Therefore, to investigate the adsorption selectivity and cations interferences to remove targeted pollutant by BMMCs, a binary (Pb^{2+} and Cd^{2+}) system was also attempted by fixing concentration of metals cations stable at 200 mg/L and pH 6.5. As shown in Fig. 7e, BMMCs represented higher selectivity of Pb^{2+} ions than Cd^{2+} ions, and the prepared BMMCs endured elimination of Pb^{2+} even by enhancing the initial potency of Cd^{2+} from 10 to 100 mg/L. In contrast, the elimination efficacy of Cd^{2+} was declined from 77% to 41.7% in the co-presence of Pb^{2+} . The greater selectivity of Pb^{2+} ions in the co-presence of Cd^{2+} was discovered to be associated with the empathy/ attraction of the metals cations to the alginate carboxyl ($-\text{COOH}$) groups attached on/ in the BMMCs, as the affinity raised, so the removal efficiency was also increased (Bhunja et al., 2018). In the present work, Pb^{2+} had higher affinity than Cd^{2+} to cross-link with alginate carboxyl groups. Surprisingly, this affinity was increased as the intensity of Cd^{2+} was boosted (from 10 to 100mg/L) in a binary system. This might be due to the development of electrostatic repulsion among excess positively charged Cd^{2+} present in the solution and/ or the repulsion between un-sorbed cations and the sorbed metals cations on/ in the BMMCs, which provided a better opportunity for Pb^{2+} to cross-link with alginate carboxyl groups due to having higher affinity than Cd^{2+} . Overall, the removal efficiency of both metals cations was affected in the binary system than that of the single system, this perhaps due to the snooping by the co-presence metals cations with low affinity to alginate. Our results were well connected with findings reported by other researchers (Nussinovitch and Dagan, 2015; Kyzas et al., 2014; Kesenci et al., 2002; Do and Lee, 2013; Park et al., 2007).

3.4. Stability and Reusability of Bio-magnetic Membrane Capsules (BMMCs)

The stability, regeneration, and reusability of adsorbents/ membrane capsules is an important index for its real and practical implementations in industry. For this purpose, initially, different chemicals (HNO_3 , HCl , KCl , CaCl_2 , and EDTA) were employed as an eluent to desorb metal cations from BMMCs. From them, EDTA , HCl and HNO_3 performed well, however, KCl and CaCl_2 did not desorb metal cations effectively from BMMCs. In addition, HNO_3 was optimized and tested as a regeneration solution for BMMCs to desorb metal cations. For this purpose, the concentration of HNO_3 was varied from 10 to 100% in order to desorb metal cations from BMMCs. It was noticed that the desorption efficiency of the adsorbed metal cations improved with an increase in the HNO_3 concentration. While the stability of the BMMCs significantly damaged beyond 30% of HNO_3 concentration. This increase in desorption efficiency can be due to the ion-exchange mechanism between metal cations and H^+ from HNO_3 , which replaced the adsorbed metal cations from hydrophilic functional groups of BMMCs, hence re-establishing the membrane capsule's function owing to the superior affinity for metal cations than protons. This affinity was improved as the concentration of HNO_3 increased, while, at the meantime the stability of membrane capsules was significantly affected owing to the leakage/ seepage/ dissolution of iron/ PMNPs from BMMCs, which weakened the hydrogen bonding among PVA, SA, GA and PMNPs, and resulted in the morphology of BMMCs being significantly damaged due to the oxidizing properties of HNO_3 . Therefore, 25% of HNO_3 was chosen as an eluent to test the BMMCs reusability for better performance. As shown in Fig. 7f, the sorption-desorption efficiency of Pb^{2+} and Cd^{2+} by BMMCs was tested for ten (10) consecutive treatment cycles. The findings depicted that the BMMCs preserved its working up-to seven (07) consecutive treatment cycles, and then steadily declined. Since the desorption efficiency was not 100%, so it can be considered that a segment of sorbed metal cations was remained on/ inside the BMMCs owing to the presence of micro-porous shell to macro-porous core structure/ channel. In addition, the leakage of iron/ PMNPs was not observed throughout the first seven (07) consecutive treatment cycles. While, beyond this, the reusability of BMMCs significantly declined. This might be due to the destruction of BMMCs morphology/ structure caused by the leakage/ seepage/ dissolution of iron/ PMNPs or lack of vacant/ active sites on/ in the BMMCs. Overall, more than 80 % of sorption-desorption efficiency was obtained for Pb^{2+} and Cd^{2+} respectively, up to seven cycles without losing stability. Whereas, it declined to 36 and 30% for Pb^{2+} and Cd^{2+} respectively, up to ten cycles. This decrease in sorption-desorption efficiency might be owing to the seepage of iron/ PMNPs, damage in morphology or lack in the accessibility of free sites on/ in the BMMCs (because a portion of the sorbed metal cations

remained inside). Overall, the prepared BMMCs can be reused up to seven consecutive treatment cycles and they could effectively adsorb more than 80% metal cations from water/ wastewater in a continuous process.

3.5. Proposed Removal Mechanism of Metals Cations by Bio-magnetic Membrane Capsules (BMMCs)

In order to explore the adsorption mechanism/ removal mechanism of metals cations by BMMCs, FTIR and XPS analyses were also employed in addition to kinetics, isotherms, thermodynamic and reusability studies. First, the FTIR spectrum was obtained after the sorption of Pb^{2+} and Cd^{2+} by BMMCs (Fig. 8). The results illustrated two major changes at around $3600\text{--}3300\text{ cm}^{-1}$ and $1500\text{--}1300\text{ cm}^{-1}$, which can be appointed to the broadening vibrations of hydroxyl/ $-\text{O}^-$ and carboxyl/ $-\text{COO}^-$ functional groups. These changes show the adsorption of metals ions on/ in the BMMCs via electrostatic interaction and/ or ion-exchange mechanism e.g. $(\text{R}-\text{O})^- \cdots \text{Pb}^{2+}$; $(\text{R}-\text{COO})^- \cdots \text{Pb}^{2+}$; $(\text{R}-\text{O})^- \cdots \text{Cd}^{2+}$; and $(\text{R}-\text{COO})^- \cdots \text{Cd}^{2+}$. Moreover, an absorption peak at 489 cm^{-1} (for Fe-O) did not influence, suggested the good stability/ smooth encapsulation of PMNPs on/ in the BMMCs (Fig. 8a,b,c). Hence, the FTIR outcomes indicated the adsorption of Pb^{2+} and Cd^{2+} via the attachment with hydrophilic functional groups ($-\text{O}^-$ and $-\text{COO}^-$), present on/ in the bio-magnetic membrane capsules BMMCs.

Fig. 8 Fourier transform infrared (FTIR) spectra of (a) bio-magnetic membrane capsules (BMMCs), (b) after the adsorption of lead ions (Pb^{2+}), and (c) after the adsorption of cadmium ions (Cd^{2+}).

Furthermore, the X-ray photoelectron spectroscopic (XPS) technique was also employed to explore the probable removal mechanism and fluctuation of chemical elements on the surface of BMMCs before and after the adsorption of metals cations. As expected, the XPS results illustrated two major peaks at around 284.6 and 532.25 eV, which were associated to C 1s and O 1s, respectively (Fig. 9a). In addition, a small peak at around 709.9 eV for Fe 2p, suggested the existence/ encapsulation of PMNPs on/ in the bio-magnetic membrane capsules (Fig. 9a). After the sorption of Pb^{2+} and Cd^{2+} , two new peaks of Pb 4f and Cd 3d appeared, showing that Pb^{2+} and Cd^{2+} were adsorbed/ attached on/ in the BMMCs (Fig. 9a). In order to well understand the adsorptive mechanism of Pb^{2+} and Cd^{2+} by BMMCs, the high-resolution spectra of Pb 4f and Cd 3d were also carried out (Fig. 9b,c). The satellite peaks at around 138.32 and 143.39 eV (in the XPS profile of Pb 4f) can be endorsed to the attendance of the oxidation state of Pb^{2+} , which were correlated to the binding energies for the $4f_{7/2}$ and $4f_{5/2}$ orbitals. However, there was no peak appeared at 136.6 eV, that is specified for the binding energy of neutral lead (Pb) (Fig. 9b). In contrast, two independent peaks at around 405.4 and 412.37 eV appeared in the XPS profile of Cd 3d, which can be assigned to the Cd^{2+} binding energies for the $3d_{5/2}$ and $3d_{3/2}$ detours (Fig. 9c). The existence of these XPS pikes for Pb^{2+} and Cd^{2+} suggested the sorption of these metals cations on/ in the BMMCs. Furthermore, the high-resolution spectra of C 1s and O 1s were also studies before and after the sorption of metals cations. High-resolution XPS spectra of O 1s showed only one main peak at 532.25 eV, which can be assigned to the hydrophilic functional groups (-OH and O-C-O) (Fig. 9k,l,m). Similarly, the high-resolution spectra of C 1s depicted two main peaks at 284.6 and 287.8 eV in the binding energy range of 275-305 eV (Fig. 9n,x,y). As expected, these attributes suggested the availability of two C with different chemical nature. The major pike at around 284.6 eV in C 1s can be allocated to -OH or alcoholic/ C-O groups, which might be linked to the hydrophilic functional groups that present in/ on the surface of PVA, SA, GA, and PMNPs. After the sorption of Pb^{2+} and Cd^{2+} , considerable changes can be discovered in C 1s and O 1s high-resolution spectra. At length, the atomic contents of O-H/ C-O-C decreased from 41.86 to 25.27% after the sorption of Pb^{2+} , and from 41.86 to 26.22% after the sorption of Cd^{2+} . This also illustrated that the hydrophilic functional groups (-O⁻ and -COO⁻) were implicated/ consumed while the sorption of Pb^{2+} and Cd^{2+} by BMMCs, because oxygen (O) atoms possessed two pairs of lone electrons. The summery of peak assignments and group contents before and after the sorption of Pb^{2+} and Cd^{2+} are documented in Table 7.

Fig. 9 X-ray photoelectron spectra (XPS) of BMMCs (a) before, and after the adsorption of (b) Pb^{2+} , (c) Cd^{2+} ; high resolution XPS spectra of (d) Pb 4f, (e) Cd 3d; high resolution XPS spectra of Fe 2p (f) before and after the adsorption of (g) Pb^{2+} , (h) Cd^{2+} ; high resolution XPS spectra of O 1s (k) before, and after the adsorption of (l) Pb^{2+} , (m) Cd^{2+} ions; high resolution XPS spectra of C 1s (n) before, and after the adsorption of (x) Pb^{2+} and (y) Cd^{2+}

Table 7 High resolution X-ray photoelectron spectroscopy (XPS) analysis of bio-magnetic membrane capsules (BMMCs) after the sorption of lead and cadmium ions (Pb^{2+} and Cd^{2+}).

Region	Assignment	Before adsorption		After adsorption of Pb^{2+}		After adsorption of Cd^{2+}	
		Peak Be (eV)	Atomic %	Peak Be (eV)	Atomic %	Peak Be (eV)	Atomic %
O 1s	O-H, C-O-C	532.25	41.86	532.46	25.27	532.48	26.22
C 1s	C-O	284.6	56.15	284.7	73.28	284.8	72.51
Fe 2p	Fe 2p _{3/2}	709.9	0.48	711.44	0.47	711.46	0.47
Pb 4f	Pb 4f _{7/2}	138.32	0	138.32	0.98	-	-
Cd 3d	Cd 3d _{5/2}	405.4	0	-	-	405.4	0.80

Moreover, the high-resolution XPS spectra of Fe 2p were also carried out (before and after the adsorption of Pb^{2+} and Cd^{2+}) to investigate the structure of iron oxide and its function in the sorption of metals cations (Fig. 9f,g,h). As expected, two small peaks at 709.9 and 724.7 eV emerged in the binding range of 700-740 eV, which were related to Fe 2p_{3/2} and Fe 2p_{1/2} respectively, confirming the presence of PMNPs/ Fe₃O₄ on/ in the BMMCs. The peak at Fe 2p_{3/2} is typically associated for Fe in iron oxide/ PMNPs. The peaks intensities were low because a small amount of PMNPs was incorporated during the fabrication of BMMCs. Whereas, there were no significant changes found in the XPS profile of Fe 2p after the sorption of Pb^{2+} and Cd^{2+} , suggested the good stability of PMNPs into PVA-SA matrix and sorption of metals cations on/ in the BMMCs instead of reduction by iron/ Fe. Importantly, the XPS results well matched with FTIR outcomes and approved the sorption of Pb^{2+} and Cd^{2+} on/ in the BMMCs. Based on the findings obtained by the FTIR and XPS analysis along-with the clues found from isotherms, kinetics thermodynamic and reusability studies, it can be documented that metals cations mainly removed/ adsorbed via chemisorption and/ or ion-exchange mechanism along with hydrogen bonding owing the manifestation of huge amount of hydrophilic functional groups (-OH and -COOH) on/ in the BMMCs. The chemical sorption of Pb^{2+} and Cd^{2+} by BMMCs can be expressed as:

Where, R is the matrix of the PVA, SA, and PMNPs in the BMMCs. In addition, the proposed adsorptive mechanism/ removal mechanism of metals cations (Pb^{2+} and Cd^{2+}) by the

prepared BMMCs and possible interaction of BMMCs with metals cations via ion-exchange and hydrogen bonding to adsorb Pb^{2+} and Cd^{2+} in the pH range of 2-8 is shown in Fig. 10.

3.6. Comparison of Bio-magnetic Membrane Capsules (BMMCs) with other Employed Sorbents to Remove Metals Cations

Table 8 is illustrating that our prepared BMMCs had comparatively much better adsorptive capacity to remove potentially toxic metals cations than most of the other employed sorbents. In addition, BMMCs can also be reused for at-least seven (07) consecutive treatment cycles and they can also be separated from aqueous media within ten (10) second just by employing simple magnet. Importantly, PVA-SA matrix did not only emerge as an excellent encapsulating material to control dissolution of green/ phytogenic magnetic nanoparticles but also improve its adsorptive performance up-to-the marks to transfer green nanotechnology from lab scale to commercial and real applications for the treatment of domestic and industrial effluents.

Fig. 10 Proposed adsorptive mechanism/ removal mechanism of metals cations (Pb^{2+} and Cd^{2+}) by bio-magnetic membrane capsules (BMMCs) and possible interaction of BMMCs with metals cations via ion-exchange and hydrogen bonding to adsorb Pb^{2+} and Cd^{2+} in the pH range of 2-8. [inset figures are the real pictorial view of the (a) outer boundary/ layer of the freeze-dried BMMC, and (b) cross-sectional area/ view of the freeze-dried BMMC showing 'micro-porous shell to macro-porous core structure/ channel for the possible transportation of pollutants from surface to inner core']

Table 8 Comparison of bio-magnetic membrane capsules (BMMCs) with other employed sorbents for the adsorptive removal of potentially toxic metals cations (lead (Pb^{2+}) and (Cd^{2+}) cadmium ions) from wastewater

Sorbent	q_e (mg/g)	Reference
Cadmium ions (Cd^{2+})		
Polyaniline grafted chitosan (PGC)	14.33	Karthik and Meenakshi 2015
Fe_3O_4 -P(Cys/HEA) hydrogel	19.50	Hua et al., 2014
Fe_3O_4 -cyclodextrin	22.70	Badrudodoza et al., 2013
Peanut husk	26.88	Cheng et al., 2016
Fe_3O_4 -GS	27.80	Guo et al., 2014
Biochar	32.737	Li et al., 2017
Chitosan modified with sulfoxine chelate agent	32.9	Vitali et al., 2008
DEAMTPP@ Fe_3O_4 MNPs	49.1	Venkateswarlu and Yoon, 2015
Thiocyanato-functionalized silica gel	49.3	Li et al., 2011
Magnetic treatment of biochar (BC- FeO_x)	67.363	Li et al., 2017
Orange peel- Fe_2O_3 (MNP-OPP)	71.43	Gupta and Nayak, 2012
Alkaline treatment of biochar (BC-NaOH)	72.369	Li et al., 2017
3-MPA@PMNPs	79.8	Ali et al., 2018a
Poly(ethyleneglycol dimethacrylate-co-acrylamide) beads	95.3	Kesenci et al., 2002
Chitosan/PVA	142.9	Kumar et al., 2009
Poly(methacrylicacid)-grafted chitosan microspheres	146.1	Huang et al., 2013
Chelating polyacrylonitrile beads	156	Bhunja et al., 2018
poly(styrenesulfonicacid)-impregnatedalginatecapsule(PSSA-AC)	184.12	Wei et al., 2016
Liquid-core gellan-alginate capsules with lecithin	197	Nussinovitch and Dagan, 2015
Thiourea-modified magnetic ion-imprinted chitosan/ TiO_2 composite	256.41	Chen et al., 2012
Thiosemicarbazide modified chitosan (TCS)	257.2	Li et al., 2016
Poly(itaconic acid) grafted chitosan with glutaraldehyde cross-linking	405	Kyzas et al., 2014
Bio-magnetic membrane capsules (BMMCs)	610.67	Present study
Lead ions (Pb^{2+})		
Polyaniline grafted chitosan (PGC)	16.07	Karthik and Meenakshi, 2015
Fe_3O_4 @silica-XG composites	21.3	Peng et al., 2014
Iodate doped chitosan	22.2	Gedam and Dongre, 2015
Activated carbon	26.5	Sekar et al., 2004
Iron oxide nanoparticle	29	Nassar 2010
Lobeira fruit (<i>Solanumlycocarpum</i>)	51.02	Araújo et al., 2018
Polyaniline Sn(IV) tungstomolybdate nanocomposite (PSTM)	44.64	Bushra et al., 2015
Fe_3O_4 -cyclodextrin	64.5	Badrudodoza et al., 2013
Lignanxanthate resin	64.9	Li et al., 2015
3-MPA@PMNPs	68.41	Ali et a., 2018a
Palm shell activated Carbon	95.2	Issabayeva et al., 2006

Silver nanoparticles deposited multi-walled carbon nanotubes	104.28	Chen and Wang, 2007
Chelating polyacrylonitrile beads	145	Bhunja et al., 2018
Aliquat-336 impregnated chitosan	187.61	Kumar et al., 2015
Biocharealginate capsule (8:1)	263.2	Do and Lee, 2013
Liquid-core gellan–alginate capsules without lecithin	267	Nussinovitch and Dagan, 2015
Liquid-core gellan–alginate capsules with lecithin	316	Nussinovitch and Dagan, 2015
Ion-imprinted chitosan fiber	324.6	Lin et al., 2015
Thiosemicarbazide modified chitosan (TCS)	325.2	Li et al., 2016
Poly(itaconic acid) grafted chitosan with glutaraldehyde cross-linking	334	Kyzas et al., 2014
Triethylenetetramine grafted magnetic chitosan	370.63	Kuang et al., 2013
Silica gel/chitosan composite	416.67	Gandhi and Meenakashi, 2012
Alginate gel	526.0	Park et al., 2007
Bio-magnetic membrane capsules (BMMCs)	548	Present study
Poly(ethyleneglycoldimethacrylate-co-acrylamide) beads	671	Kesenci et al., 2002

4. Conclusions

Overall, the oxidation or disintegration of PMNPs due to the dissolution of iron (Fe^0) in aqueous solution was successfully controlled by encapsulating PMNPs into PVA-SA matrix. Subsequently, novel BMMCs were developed using the two-step titration crosslink method for the efficient ejection of potentially toxic metals cations (Pb^{2+} and Cd^{2+}) from the water. The fabrication, morphology, surface properties, and magnetic measurements were examined by the FTIR, powder XRD, SEM, EDX, XPS and VSM analyses techniques. The results showed that intra/inter-molecular hydrogen bonding played an imperative role to maintain the stability of PMNPs into PVA-SA matrix because PMNPs had hydroxyl/ -OH functional groups on their surface which made strong hydrogen bonding with the hydroxyl/ -OH functional groups present in the PVA-SA matrix. SEM analyses showed that BMMCs had micro-porous shell to the macroporous core like morphology/ structure. VSM results indicated that hysteresis loops depicted an excellent super-paramagnetic nature, suggested the smooth encapsulation of PMNPs without losing their magnetic properties. The saturation magnetization (Ms) value was discovered to be 11.02 emu/g. TGA results indicated that BMMCs were fully capped with hydrophilic functional groups (i.e. -OH and -COOH).

On average, a maximum of 94.56% of Pb^{2+} and 91.47% of Cd^{2+} removal efficiency was achieved within the contact time of 24h at pH 6.5 and 200 mg/L of initial metal ions concentration by using BMMCs dosage of 0.03 g/L or 30 mg. The prepared BMMCs did not

only control oxidation of PMNPs but also maintain adsorptive removal over a wide pH ranges (3-8). The maximum monolayer uptake/ adsorptive capacity of Pb^{2+} and Cd^{2+} was 548 and 610.67 mg/g, respectively, as estimated by Langmuir isotherm model. Importantly, these values were higher than most of the previously published results. This excellent adsorptive performance can be ascribed due to the attendance of a large amount of hydrophilic functional groups i.e. -OH and -COOH (subsisted on the surface of PMNPs and in the PVA-SA matrix), as confirmed via FTIR and XPS techniques. The kinetics and thermodynamic results indicated that sorption was exothermic and chemisorption nature and experimental statistics matched well with pseudo-second-order mode, implied that metals cations mainly removed via the ion-exchange mechanism. Desorption results indicated that BMMCs can easily be renewed just by using 25% HNO_3 as a desorbing agent and the regenerated BMMCs can be successfully used for seven (07) cycles. Importantly, the BMMCs showed rapid separation time of 10 seconds just by employing a simple hand-held magnet. The changes in functional groups after the sorption of metals cations obtained by the FTIR and XPS analyses and their results depicted that electrostatic interaction and ion-exchange was the core adsorption mechanism due to the manifestation of hydrophilic functional groups (-OH and -COOH) on/ in the BMMCs.

Therefore, the fabricated novel BMMCs represented the comparable highest adsorptive capacity to remove metals cations from water. Therefore, the membrane capsule sorbent as a material is showing a new direction for application in the removal and recovery of metals cations, and it can be utilized to treat water and wastewater in a cost-effective way, particularly relevant to developing countries.

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Author Contributions

All authors contributed to the analysis of data and preparation of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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Supplementary Information

Text-SI

The chemicals such as sodium alginate (SA) powders (Sinopharm Chemical Reagent Co., Ltd. China), polyvinyl alcohol (PVA) having MW 146,000-186,000, (Sigma-Aldrich, 99% hydrolyzed), glutaraldehyde (GA) (Aladdin Reagents Co., Ltd. (China), 50.0% vol. in H₂O), and boracic acid (H₃BO₃) (Sinopharm Chemical Reagent Co., Ltd. China), anhydrous calcium chloride (CaCl₂) (Sinopharm Chemical Reagent Co., Ltd. China), hydrochloric acid (HCl) (Sinopharm Chemical Reagent Co., Ltd. China), sodium hydroxide (NaOH) (Sinopharm Chemical Reagent Co., Ltd. China), Pb(NO₃)₂, CdSO₄ · 4H₂O, (Merck, 99%), ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous sulfate (FeSO₄·7H₂O), ethanol (C₂H₅OH) (Merck, 99.9%), HNO₃ (Merck, 99.9%), KCl (Merck, 99.9%), and EDTA (Merck, 99.9%) were utilized. All the chemicals and reagents were analytically pure and used without further purifications. The ultra-pure water or distilled water were gained from Qingdao water purification agency having a resistivity of 18 MΩ cm to make all aqueous solutions. The pH adjustment was made using 0.1 mol/L NaOH and HCl aqueous solutions throughout all the experiments depending on the requirements. The process for the preparation of phytogetic magnetic nanoparticles (PMNPs) has already reported by **Ali et al., 2018a, 2018b (Text-SII)**. Various types of instrumentations were used for the execution of adsorption experiments, fabrication and characterization of PMNPs (**Supplementary information, Text-SIII**).

Text-SII

In brief, 50 mL of plant extract (PE) and 50 mL of metal salt (MS) (having 1/1 ratio of Fe⁺² : Fe⁺³) solution were mixed and boiled at 80°C onto magnetic stirrer heater for at-least 60 minutes. The solution pH was maintained at 12 by using 0.1mol/L NaOH solution drop-wise. The formation of PMNPs was confirmed as the mixture color turned from pale green to dark black. After this, black color particles were separated using centrifugation and vacuum filtration techniques. Finally, the black powder was washed/ cleaned completely twice by 50 mL of ethanol solution and then dried in an hot oven at 80°C for at-least 20 minutes (**Ali et al., 2018a,b**).

Text-SIII

Different types of instrumentations including temperature controlled rotary shaker (THZ-92A, China), magnetic stirrer (MS-M-S10, Biobase Biodustry, Shandong Co., Ltd.), Atomic Absorption Spectrometry (Solar M6, Thermo Elemental, USA), thermostatic water bath shaker (Max Q 7000, Thermo Scientific), weighing balance (Sartorius Entris 64-1S, German), centrifuge machine (model C-30BL), pH meter (mV/ORP METTLER TOLEDO), volumetric flasks and Erlenmeyer flasks (JOAN Lab Pyrex Glass Erlenmeyer Flask, Ningbo Yinzhou Joan Lab Equipments, china) were utilized. Furthermore, various types of instruments such as UV-vis spectrophotometer (T80, P.G. Instrument Ltd., UK), Brunauer-Emmet-Teller (BET) analyzer (Micromeritics'ASAP2020), Fourier transforms infrared spectroscopy (FTIR, Bruker Vertex 70), Vibrating sample magnetometer (VSM, VSM600), Scanning Electron Microscope with integrated energy dispersive X-ray system (SEM-EDX, JSM-6610 LV, Japan

Electronics), X-ray photoelectron spectroscopy (XPS, ESCALAB 250, German), X-ray diffractometer (XRD, Philips Electronic Instruments), Thermo-gravimetric analyzer (TGA, NETZSCH TG 209F3), syringe pump and syringe were utilized for the fabrication and characterization of BMMCs.

Text-SIV

Scanning electron microscope (FE-SEM, S-3000N, Hitachi Ltd., Japan) was employed to scrutinize the morphology of the prepared BMMCs from surface to inner core at 5 KV. The fabricated BMMCs were immersed in liquid nitrogen for 2 min, and then freeze-dried at -80°C and 10 Pa for 72 h to obtain a perfect hydrogel skeleton. Chemical composition and functional groups of the prepared BMMCs were explored by FTIR (Bruker Vertex 70), with a resolution of 4 cm⁻¹, scans= 64 and wavelength in the range of 650~4000 cm⁻¹. For FTIR analysis, four types of samples were prepared as: (i) PVA-SA mixture was prepared by homogenously mixing of 4 mL PVA and 1 mL SA solution together, and then dried in a hot oven at 95°C for at-least 4 h. After this, the dried sample was grinded to convert into powder; (ii) PVA-SA-PMNPs mixture was prepared by mixing 4 mL PVA, 1 mL SA, 2 mL PMNPs solution together, and then dried in a hot oven at 95°C for at-least 4 h. After this, the dried sample was grinded to convert into powder; (iii) BMMCs were prepared without incorporating secondary cross-linking agents and freeze dried at -80°C and 10 Pa for 72 h, then these were grinded to convert into powder; and (iv) finally, the BMMCs were prepared by incorporating primary and secondary cross-linking agents and freeze dried at -80°C and 10 Pa for 72h, and then these were grinded to convert into powder. EDX (JSM-6610 LV, Japan Electronics) and XPS (ESCALAB 250, German) was employed to reveal elemental contents and their atomic percentages. Thermal stability of the prepared BMMCs was assessed by the thermo-gravimetric analyzer (TGA, NETZSCH TG 209F3). Material properties and magnetic measurements were conducted by powder XRD (Philips Electronic Instruments) and VSM (VSM600). Material interlayer spacing was estimated based on the Bragg's Law. Freeze dried BMMCs were utilized to accomplish all these analyses. For the micro-meritic studies, the diameter of the prepared BMMCs was determined by vernier caliper (n=100, MNT-150, Shanghai, China). Initially, the shape of the prepared capsules was estimated by measuring aspect ratio of the capsules. The aspect ratio of the prepared capsules was calculated as:

$$\text{Aspect ratio} = \frac{D_{\max}}{D_{\min}} \text{-----} (1)$$

Where, D_{max} (mm/ m/ cm) and D_{min} (mm/ m/ cm) are the maximum and minimum diameter of the prepared capsules, respectively. For this purpose, fifteen (15) prepared BMMCs were selected. The values closer to one (01) illustrated rounder shape, while the values equal to one (01) suggested a perfect sphere shape of the capsules. Moreover, the density (P) and volume (V) of the prepared capsules was determined as:

$$\text{Density, } P \left(\frac{g}{m^3} \right) = \frac{M}{V} \text{-----} (2)$$

$$\text{Volume, } V (m^3) = \frac{4\pi r^3}{3} \text{-----} (3)$$

Where, P, M, V and r are the density (g/m³), weight (g), volume (m³) and radius (mm) of the prepared BMMCs, respectively. For this purpose, fifteen (15) capsules were randomly selected from the prepared BMMCs and the average maximum diameter of the capsules was used, as calculated for the determination of aspect ratio.

Furthermore, the density of the prepared capsules was measured by calculating its weight both on wet and dry basis. In addition, theoretical average water content/ swelling ratio (SR) of the prepared BMMCs was also estimated by:

$$\text{Water content/ Swelling ratio (\%)} = \frac{(W-D)}{W} \times 100\% \text{-----(4)}$$

Where, W and D are the average weight (g) of the prepared BMMCs on wet and dry weight basis, respectively as calculated by digital analytical weighing balance (Sartorius Entris 64-1S, German).

Text-SV

Sorption isotherm Models

The following equations of these models were used to fit the experimental data:

Langmuir Model

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max} C_e} + \frac{1}{q_{\max}}$$

Where, q_e (mg/g) and C_e (mg/L) are the amount adsorbed and concentration of the metals ions in solution at equilibrium.

The $q_{\max}$ (mg/g) and K_L (L/mg) are the monolayer sorption capacity of the adsorbent and Langmuir equilibrium constant relating to the free energy of the adsorption. The Langmuir model is based upon the assumption of monolayer adsorption process where pollutant sorbed onto the homogenous sites of the adsorbents without any interaction between sorbed ions. The values of the Langmuir equilibrium constant or dimensionless constant/ separation factor (K_L) were determined by the following equation:

$$K_L = \frac{1}{1 + bC_e}$$

Where, b (L/mg) is another Langmuir constant related to binding energy of the pollutants onto the active sites of the adsorbent. The values of $q_{\max}$ give hint about active sites while b about driving force at equilibrium. The values of $q_{\max}$ and b were determined from slope and intercept of a straight line by plotting graph $1/C_e$ vs $1/q_e$. The favorability of the sorption isotherm depends upon on the K_L value. If $K_L > 1$ sorption isotherm is unfavorable, if $K_L = 1$ sorption isotherm is liner, if $K_L = 0$ sorption is irreversible isotherm and if $0 < K_L < 1$ then sorption is favorable.

Freundlich Model

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log k_f$$

Where, k_f (mg/g) and n are the empirical constants/ Freundlich constants, related to adsorption capacity and adsorption intensity of the adsorbent. The Freundlich isotherm model is based upon the assumption of heterogeneous adsorption process where pollutant sorbed onto the miscellaneous sites of the adsorbents with different binding energy. The values of n and k_f were calculated from intercept and slope of the graph plotted $\log C_e$

vs $\log q_e$. Moreover, the value of $1/n$ varies with the heterogeneity of the material. The value of $1/n$ between 0 and 1 showed that the adsorption of pollutant onto the surface of adsorbent was favorable at experimental conditions.

Temkin Model

$$q_e = \left(\frac{RT}{B_T}\right) \log C_e + \left(\frac{RT}{B_T}\right) \log K_T$$

Where, K_T (L/g) is the equilibrium binding constant presenting maximum binding energy. B_T (KJ/mol) is the constant related to the heat of adsorption. R is the ideal gas constant (8.314J/mol. K). T is the temperature in Kelvin. The values of K_T and B_T were determined from the intercept and slope of graph plotted $\log C_e$ vs q_e ,

Dubinin-Radushkevich model

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$

Where, q_e (mg/g) is the quantity of the CV ions adsorbed on per unit weight of adsorbent, q_m (mg/g) is the maximum sorption capacity, β (mol²/J²) is the activity coefficient related to average sorption energy per mole of adsorbate and ε is the Polanyi potential. The values of q_m and β were estimated from intercept and slope of the straight line plotted ε^2 vs $\ln q_e$. While, the values of ε were calculated by using this formula:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$

In addition, the values of sorption mean free energy (E) gives hint about nature of adsorption i.e. physical or chemical and it can be calculated by using this formula:

$$E = \frac{1}{\sqrt{(2\beta)}}$$

Sorption Kinetics Models

The sorption kinetics was calculated by the following equations:

Pseudo-First-Order Kinetic

$$\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.303}$$

Where, q_t (mg/g) is the adsorption capacity at time (t). while k_1 (min⁻¹) is the Pseudo first order rate constant for the kinetic model and it can be measured from the slope of straight line plotted t vs $\log(q_e - q_t)$, For calculating q_t and q_e , the following equations were employed:

$$q_e = \frac{(C_o - C_e)}{m} V$$

$$q_t = \frac{(C_o - C_t)}{m} V$$

Where, C_o (mg/L) is the initial concentration of MG dye in solution. While, the C_e (mg/L) and C_t (mg/L) are the concentration of MG dye at equilibrium and time (t).

Pseudo-Second Order Kinetic Model

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

$$h = k_2(q_e)^2$$

Where h (mg.g⁻¹.min⁻¹) is the initial adsorption rate constant, q_t (mg/g) is the adsorption capacity at time (t). while k_2 (min⁻¹) is the Pseudo second order rate constant for the kinetic model and it can be measured from the slope of straight line plotted t vs t/q_t ,

Adsorption and desorption were also discovered by using Elovich's kinetic model.

Elovich's Kinetic Model

$$q_t = \frac{1}{\beta \ln \alpha \beta} + \frac{1}{\beta \ln t}$$

Where, α (mg.g⁻¹.min⁻¹) and β (g/mg) are the adsorption and desorption rate constants. The values of α were calculated by the ratio of q_e/t . whereas the value of β was measured from the slope of graph plotting between $\ln t$ vs q_t .

To check the diffusion mechanism between MG dye and 3-MPA@PMNPs, Weber and Morris kinetic equation was used as.

$$q_t = k_{ipd} t^{0.5}$$

Where, k_{ipd} (mg.g⁻¹.min^{-0.5}) is the intraparticle diffusion rate constant and can be calculated from the slope of the straight line of $t^{0.5}$ vs q_t . Finally to confirm the film diffusion mechanism, liquid film diffusion kinetic model was employed to experimental data and the applied equation is given below:

$$\ln(1 - F) = -k_{fd} t$$

Where, k_{fd} (g/mg) is the film diffusion rate coefficient. F is the fractional attainment of equilibrium and can be measured by q_t/q_e . The values of k_{fd} were calculated from the slope of the straight line of graph plotted between t vs $\ln(1-F)$.

Thermodynamic study

Thermodynamic parameters i.e. change in free energy ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol) and entropy ΔS° (kJ/mol) were estimated by:

$$\Delta G^{\circ} = -RT \ln K_D$$

$$\ln K_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$

Where, ΔG° (kJ/mol) is the change in free energy, ΔH° (kJ/mol) is the enthalpy, ΔS° (kJ/mol) is the entropy, R is the universal gas constant (8.314 J/mol.K), T is the temperature (K) and K_D is the distribution coefficient and the value of K_D was calculated by the ratio of q_e/C_e . The values of ΔS° and ΔH° were measured from the slope and intercept of the straight line plotted against $1/T$ vs $\ln K_D$.

Text-SVI

Measurement of Point of Zero Charge

The point of zero charge pH (pHPZC) of the prepared bio-magnetic capsules was calculated using pH drift method as employed by **Ali et al., 2018a**. Briefly, 20 mL of NaCl (0.005 mol/L) solution was added into several 50mL bottles of polystyrene. Initial pH (pHi) values of NaCl solutions were adjusted from 2-13 using drop-wise 0.1mol/L solution of HCl and NaOH. Thereafter, 10 mL of NaCl (0.005 mol/L) solution was further added into each bottle to bring total volume up-to 30mL. The solution (pHi) values were again noted carefully and 0.500 g of bio-magnetic capsules were added in each bottle, which was tightly and instantly covered. The suspensions were shaken at 25°C for 48 h. Thereafter, the suspensions were vacuum-filtered through a 0.22µm filter paper and final pH (pHf) values of the supernatant liquid were noted. The value of pHPZC was estimated by plotting graph between pHi versus (pHf-pHi). In fact, the value of pHPZC is the point where the two curves i.e standard pH (pHi vs pHi) and pHi vs (pHf-pHi) intersect each other.

Text-SVII

q_e (exp.): Experimental q_e (mg/g); q_e (cal.): Calculated q_e (mg/g); I: Intercept; C_o : Initial concentration of the pollutant (mg/L); h: initial adsorption rate constant ($\text{mgg}^{-1}.\text{min}^{-1}$); k_1 & k_2 : equilibrium rate constants for Pseudo-first and Pseudo second order kinetic models (min^{-1}); R^2 : Regression coefficient; α = adsorption rate constant; β = desorption rate constant; K_{fd} = Film diffusion rate constant (g/mg); k_{ipd} = intraparticle diffusion rate constant ($\text{mgg}^{-1}.\text{min}^{-0.5}$)

Text-SVIII

q_{max} : maximum monolayer adsorption capacity of adsorbent; b: constant related to binding energy; K_L : dimensionless constant; n: adsorption intensity; K_f : empirical constants relative adsorption capacities of the adsorbent; K_T : the equilibrium binding constant presenting maximum binding energy; B_T : constant is related to the heat of adsorption; E: average energy; β : activity coefficient; ϵ Polanyi potential

Text-SIX

Key: ΔG° : Change in free energy; ΔH° : enthalpy; ΔS° : entropy

Fig. S1 Size mesurment of the prepared BMMCs