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Geogenic arsenic removal through core-shell based functionalized nanoparticles: Groundwater *in-situ* treatment perspective in the post-COVID anthropocene

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GRAPHICAL ABSTRACT

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ABSTRACT

Groundwater, one of the significant potable water resources of the geological epoch is certainly contaminated with class I human carcinogenic metalloid of pnictogen family which delimiting its usability for human consumption. Hence, this study concerns with the elimination of arsenate (As(V)) from groundwater using bilayer-oleic coated iron-oxide nanoparticles (bilayer-OA@FeO NPs). The functionalized (with high-affinity carboxyl groups) adsorbent was characterized using the state-of-the-art techniques in order to understand the structural arrangement. The major emphasis was to examine the effects of pH (5.0–13), contact times (0–120 min), initial concentrations ($10\text{--}150\text{ }\mu\text{g L}^{-1}$), adsorbent dosages ($0.1\text{--}3\text{ g L}^{-1}$), and co-existing anions in order to understand the optimal experimental conditions for the effective removal process. The adsorbent had better adsorption efficiency ($\sim 32.8\text{ }\mu\text{g g}^{-1}$, after 2 h) for As(V) at neutral pH. Adsorption process mainly followed pseudo-second-order kinetics and Freundlich isotherm models ($R^2\sim 0.90$) and was facilitated by coulombic, charge-dipole and surface complexation interactions. The regeneration (upto five cycles with 0.1 M NaOH) and competition studies (with binary and cocktail mixture of co-anions) supported the potential field application of the proposed adsorbent.

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1. Introduction

On the onset of novel coronavirus disease outbreak (COVID-2019), emerging from the etiologic agent severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), surface water might be under high risk of contaminations with discharge of untreated municipal wastewater which hypothetically contain SARS-CoV-2 RNA (Ahmed et al., 2020). Till date number of studies have reported molecular detection of this novel virus in wastewater, which certainly restrict the application of surface water and increase the dependency on groundwater for human consumption and other agricultural activities considering its filtered quality (Ahmed et al., 2020; Lodder and de R. Husman, 2020; Wu et al., 2020). But, nature itself has imposed certain limitations on the overuse/exploitation of resources and this law (Nature's law of limitation) becomes pertinent for groundwater in which naturally present geogenic contaminants (arsenic (As), fluoride (F⁻), antimony (Sb), phosphate (PO₄³⁻), selenium (Se), etc.) limited its application in a new geological epoch (the Anthropocene) where the world faces a new global level of water concern (Kumar et al., 2020; Sanjrani et al., 2019).

Amongst the listed geogenic contaminants, carcinogenic metalloid with the well-known name As has been placed in group 15 of the periodic table and it is known for its toxicity to human beings. Geogenic and anthropogenic are the two primary origin/sources for As entry into groundwater. In the groundwater naturally occurring microorganisms oxidize organic matter and generate hydrogencarbonate and salt of carbonic acid which ultimately enhances the alkalinity of the solution and release As from mineral surfaces. Anthropogenically As and its compounds are widely used (as fertilizers, pesticides, drugs, feed additives and wood preservatives) and finds their entry into groundwater (Henke, 2009; Kumar et al., 2019; Saikia et al., 2017).

In response to these widespread As contamination through various sources, it has been estimated that worldwide > 0.15 billion people have been affected due to poisonous As polluted groundwater consumption/utilization. Any concentration above world health organization (WHO) recommended value of 10 µg L⁻¹ for As causes harmful diseases like, hyperkeratosis, diarrhea, cerebrovascular disease, diabetes mellitus, hypothyroidism, cancer and arsenicosis (Henke, 2009; Jadhav et al., 2015; Sarkar and Paul, 2016). To combat with pernicious As, variety of treatment techniques were proposed and most of them have been summerized in the form of short as well critical reviews by number of researchers (Sanjrani et al., 2019; Kumar et al., 2019; Jadhav et al., 2015; Sarkar and Paul, 2016; Singh et al., 2015). However, use of conventional physicochemical methods has been confined due to excessive-energy consumption and release of hazardous chemicals into the environment. Amid these technologies, adsorption has been considered as one of the favorable techniques because of the ease of operation, easy maintenance, cost-effectiveness, absence of added reagents and applicability as a compact household module or in a community plant (Habuda-Stanić and Nujić, 2015; Shim et al., 2019). Thus, it is a continuing need to recognize effortlessly synthesizable, economically viable, environmentally stable and sustainably regenerable adsorbent for effective and facile removal of As.

Iron-oxide core based NPs i.e., magnetite (Fe₃O₄) (Chowdhury et al., 2011), hematite (α-Fe₂O₃) (Tang et al., 2011), maghemite (γ-Fe₂O₃) (Park et al., 2008), Goethite (α-FeOOH) (Zhang and Stanforth, 2005) and akaganéite (β-FeOOH) (Deliyanni et al., 2003) have been reported to be one of the best adsorbents for As removal due to their easy collecting property with external magnetic response, which enable their multiple time reuse for the adsorption process and thereby reduce the secondary pollution problem. However, their high surface energy, resulted from the strong magnetic field, will cause NPs to agglomerate with each other. This agglomeration will not only reduce the surface energy but also diminishes the available surface area and thereby associated adsorption capacity as well as in dynamic flow system (i.e., fixed-bed columns) it could result in pressure drops. The aggregated and structurally unstable NPs finally leach into an aqueous

medium. These leached NPs require sophisticated instrumentation facilities to separate out from the drinking water source such as groundwater aquifer after their application (Dutta et al., 2020; Zaid et al., 2020).

Hence, in order to increase functionality and biocompatibility as well as to reduce surface energy, unstability and chemical activity (i.e., air oxidation), the surface of the NPs needs to be grafted/functionized with organic molecules/inorganic layer (Harris et al., 2015). Compared to inorganic ones, coating of organic molecules would increase the potential applications of NPs by preserving their magnetic property and also by aiding the ensemble of reactive functional groups (hydroxyl, carboxyl, amino and aldehyde groups) (Wu et al., 2008). In previous studies authors tried to directly coat iron oxide NPs with alginate biopolymer, however it could not prevent aggregation of iron NPs mainly because alginate polymeric backbone is more conformationally limited (Sreeram et al., 2004; Ma et al., 2007). Hence, recently extensive organic groups containing materials, also known as covalent organic frameworks (COFs) have been applied for the functionalization of the iron based NPs (Liu et al., 2017; Leus et al., 2018). However, several associated challenges such as, complex fabrication/synthesis procedure, less stability and generation of anonymous toxic breakdown products restrict their applications for the groundwater purification.

Oleic acid (OA), containing C18 tail with a central single cis-double bond (forming a kink), is very well known surfactant to stabilize the magnetic NPs due to its higher affinity towards the surface of Fe₃O₄, compared to previously reported fatty acid (i.e., stearic acid) (Goswami et al., 2011; Yang et al., 2010). In addition to providing stability, the OA coated iron oxide nanoparticles (OA-IONPs) have been reported as the potent and moderate biofilm inhibiting agent against gram-positive and gram-negative bacteria, respectively (Velusamy et al., 2016). However, the long aliphatic hydrocarbon chain of OA would render the NPs to be immiscible in an aqueous suspension and thereby reduce the interaction of NPs with the pollutants (As as the model pollutant) and ultimately decrease the adsorption efficiency (Wang et al., 2003; Gage et al., 2013). To circumvent this limitation, further iron oxide NPs need to be coated with the double layer of OA. This practice not only increase the hydrophilicity but it also retain magnetization of the coated NPs and increase the available functional groups on the surface of the final adsorbent.

Considering the significant properties such as non-toxicity and antibacterial activity of the OA, first time this surfactant fabricated iron oxide NPs were used as an adsorbent for an eco-efficient removal of geogenic As from simple and complex water matrices. The specific objectives were: (i) synthesis and characterization (before and after sorption) of bilayer-OA@FeO NPs for As(V) removal; (ii) to examine the effects of system variables for the development of critical understanding about the optimal experimental conditions required for the effective As(V) removal; (iii) to determine the sorption capacity and reaction rate, carry out the mathematical modeling of isotherms and kinetics, respectively; (iv) to comprehend the sorption mechanism (v) to identify the potential reutilization efficiency of sorbent; and (vi) to carry out the competition study with binary and cocktail mixtures of co-anions for understanding the feasibility of the adsorbent towards field applications.

2. Experimental segment

2.1. Reagents and materials

The main precursors for the synthesis of iron oxide NPs, FeCl₂.4H₂O (98 % purity) and FeCl₃.6H₂O (97 % purity) were purchased from Loba chemie and Merck specialties LTD., respectively and used as such without further purification. All other solvents (methanol and acetone) and reagents/chemicals (oleic acid and ammonia) were procured from Finar Ltd. All reagents used were of analytical reagent (AR) grade. To prepare As stock solution (100 mg L⁻¹), 0.422 g of sodium arsenate

dibasic heptahydrate salt ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, > 98 %, Hi-Media, Mumbai, India) was dissolved in 100 mL of MQ water. By suitable dilution of this stock, different working solutions of arsenic (within the concentration range of 10–150 $\mu\text{g L}^{-1}$) were prepared and used for the subsequent adsorption study. High purity deionised water (18.2 M Ω cm^{-1} , ELGA PURELAB Flex 3 system) was used for all the experimental study.

2.2. Synthesis and characterization of bilayer-OA@FeO NPs

Bilayer-OA@FeO NPs were chemically synthesized via simple co-precipitation method as adapted by (Liu et al., 2006). Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed with appropriate amount of the water in 1:2 ratio and stirred vigorously for 1–2 h at 80–100 °C temperature. After the solution becomes colloidal dark yellow colored, 20 mL ammonia solution was added drop-wise until the development of black precipitates. The further drop-wise addition of OA (10 mL) was to form a layer around nanoparticles to avoid their agglomeration caused due to high surface energy. The obtained precipitates were washed meticulously with methanol/acetone to remove unreacted residues of OA and to increase the magnetization property of the finally synthesized adsorbent. The dried Bilayer-OA@FeO NPs (adsorbent) was stored in an air tight container for further characterization and adsorption study (Fig. S1).

The surface morphology of adsorbent was characterized by field-emission scanning electron microscopy (FE-SEM) (JEOL JSM7600 F). The elemental analysis of the adsorbent was measured by an energy-dispersive spectrophotometer (Oxford, Model INCA Energy 250 EDS), attached to FE-SEM. Fourier Transform Infrared (FT-IR) spectra of the adsorbents were chronicled (within the range of 4000 to 400 cm^{-1}) using Spectrum Two FTIR spectrophotometer (PerkinElmer) to recognize the functional groups culpable for As(V) adsorption. X-ray diffraction (XRD) spectrum was recorded using the Bruker AXS – Germany (D8 Discover) diffractometer in the range of 10–80° to identify the compound, the characteristics of the crystal structure and the size of nanoparticles. Brunauer-Emmett-Teller (BET) surface area and pore-size distribution of coated NPs were calculated by N_2 adsorption-desorption isotherm technique at low-temperature (77 K) with Micromeritics ASAP 2020 gas adsorption apparatus (Micromeritics, USA). Degassing was performed under the flow of nitrogen gas at 200 °C temperature for 1 h. In order to ascertain the stability of adsorbent against temperature, thermogravimetric analysis (TGA) was performed using a PerkinElmer thermogravimetric analyzer (TGA 4000). The point of zero charge (pH_{ZPC}) of the Bilayer-OA@FeO NPs was examined according to the method proposed by (Dutta et al., 2020).

2.3. Adsorption experiments

The adsorption experiments of As(V) onto synthesized adsorbent (bilayer-OA@FeO NPs) were conducted in a batch mode at laboratory-scale. The effect of different parameters on As(V) adsorption by the synthesized stable NPs was estimated, including pH (5.0–13.0), the concentration of adsorbent (0.1–3.0 g L^{-1}), the initial concentration of As (10–150 $\mu\text{g L}^{-1}$) and contact time (0–120 min). At predetermined time intervals, portions of the solution (3 mL) were extracted and filtered using 0.2 μm , Ø 25 mm Axiva nylon non-sterile syringe filters (SFNY25 RB). The residual As concentration was measured using a Graphite Furnace Atomic Absorption Spectrophotometer (GF-AAS) (PerkinElmer). Quality control and method validation measures along with the LoD of the instrument used for As analysis are provided in section 2.1 of the Supplementary File. The percent of As adsorption (R %) and the equilibrium sorption capacity of bilayer-OA@FeO NPs (q_e) was calculated and evaluated.

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{W} \quad (2)$$

where q_e ($\mu\text{g g}^{-1}$) is the equilibrium sorption capacity of bilayer-OA@FeO NPs for As(V), C_i and C_e ($\mu\text{g L}^{-1}$) are the initial and equilibrium concentrations of sorbate in the solution, V (L) is the sample volume, W (g) is the mass of bilayer-OA@FeO NPs.

2.4. Kinetic study and isotherm modeling

2.4.1. Adsorption kinetics

The adsorption rate is deliberated as the preeminent regulating factor for the numerical reckoning of removal efficiency. For the kinetic study, 0.1 g of bilayer-OA@FeO NPs was added to 100 mL of As(V) working solutions with variable initial concentrations and placed on a rotary shaker (250 rpm) (REMI-RIS24+, Mumbai India) at 298 ± 2 K for 2 h period. After predetermined time intervals (0, 15, 30, 45, 60, 75, 90 and 120 min), three mL of sample was collected and measured as described in the section 2.3. The rate limiting steps were delineated by fitting pseudo-first-, second- order and simple Elovich rate model Eqs. (3–5 respectively) (Mukherjee et al., 2020; Pan et al., 2017).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

Where q_t ($\mu\text{g g}^{-1}$) is the sorption capacity of bilayer-OA@FeO NPs for As(V) at definite time t , k_1 (min^{-1}) and k_2 ($\text{g } \mu\text{g}^{-1} \text{min}^{-1}$) are the rate constants for pseudo-first-, second- order kinetic sorptions, respectively. α ($\mu\text{g g}^{-1} \text{min}^{-1}$) and β ($\mu\text{g g}^{-1}$) are Elovich parameters and belong to the initial sorption rate and the extent of surface coverage, respectively. The values of Elovich constants (β and α) were determined from the slope $\frac{1}{\beta}$ and intercept $\frac{1}{\beta} \ln(\alpha\beta)$ of the linear plot of q_t vs. $\ln t$.

However, these commonly used kinetic rate models were not able to recognize the potential diffusion mechanism hence, the kinetic data were also examined by using the following equation based intraparticle diffusion model (proposed by Weber-Morris) (Raval et al., 2016).

$$q_t = K_{id}t^{1/2} + I \quad (6)$$

Where, K_{id} ($\mu\text{g g}^{-1} \cdot \text{min}^{-1/2}$) and I ($\mu\text{g g}^{-1}$) are the intraparticle diffusion rate constants.

2.4.2. Equilibrium sorption isotherm modeling and statistical interpretation

Adsorption isotherms depict the nature of the solid-solution interaction and furnish inclusive information on the adsorption efficiency of the studied sorbent (Raval et al., 2016). Bilayer-OA@FeO NPs (0.1 g L^{-1}) was equilibrated with the aqueous solutions of As(V) by agitating for 120 min at 250 rpm. The commonly used two parameter isotherm models were selected to examine the equilibrium sorption data.

Langmuir isotherm is routinely practiced to determine the equilibrium state connection between the functioning sites on the adsorbents' surface and concentration of sorbate molecules in the medium. It considers homogenous type of the sorption with cipher interaction between sorbed ions/molecules. The Langmuir equation is presented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (7)$$

where K_L (L g^{-1}) is constant and q_m ($\mu\text{g g}^{-1}$) is the Langmuir single-layer maximum sorption capacity. Both the parameters $1/q_m$ and K_L were determined from the slope and intercept, respectively, of the linear plot of C_e/q_e vs. C_e .

The main characteristic of the Langmuir equation is a non-dimensional constant called the equilibrium/separation constant which is

well-defined by following equation:

$$R_L = \frac{1}{(1 + K_L \cdot C_0)} \quad (8)$$

The R_L value showed the type of the adsorption: $R_L = 0$ means irreversible type of the adsorption; $0 < R_L < 1$ considers energetically favorable sorption; $R_L = 1$ denotes linearity of the adsorption process and $R_L > 1$ depicts unfavourable adsorption.

Freundlich isotherm presumes that the sorption process takes place onto the adsorbent with heterogeneous surfaces. The linearized form of Freundlich equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where K_F ($\mu\text{g}^{1-1/n} \text{L}^{1/n}/\text{g}$) and $1/n$ are the isotherm constant and heterogeneity exponent relating to the extent of sorption and adsorption intensity, respectively. Both the parameters K_F and n were calculated from the intercept and slope, respectively, of the linear plot of $\log q_e$ vs. $\log C_e$.

Temkin isotherm model is applied to take into account of heat of sorption for all interacting ions/molecules in the layer, which proportionally decreases with increasing surface coverage. The linear form of Temkin isotherm equation is expressed as:

$$Q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (10)$$

where R = universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), b_T (kJ mol^{-1}) and A_T (L g^{-1}) are the Temkin isotherm constants, associated with the binding energy and heat of sorption and calculated from the slope and intercept of the linear plot of Q_e versus $\ln C_e$, respectively.

The Dubinin–Radushkevich (D–R) isotherm is a semi-empirical model. It is usually applied to represent the sorption mechanism of contaminant with an information of Gaussian energy dissemination onto a heterogeneous surface. The linear form of D–R isotherm equation is:

$$\ln q_e = \ln Q_m - K_d \varepsilon^2 \quad (11)$$

Where Q_m ($\mu\text{g g}^{-1}$) is the calculated sorption capacity, K_d ($\text{mol}^2 \text{kJ}^{-2}$) is D–R constant and it is associated with mean free-energy of adsorption. It is often considered to be the most important constant of the D–R isotherm model because its value can be used to calculate free-energy change. ε is Polanyi potential, related to the equilibrium concentration of adsorbate (C_e) via equation-13:

$$E = \frac{1}{\sqrt{2K_d}} \quad (12)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

Optimization process is indispensable in order to identify the suitable kinetic and isotherm models to the obtained experimental results. For the present study, correlation coefficient of determination (R^2) was performed for data optimization process. The isotherm model with obtained R^2 value much closer to unity is estimated to offer the best-fit with the experimental data. However, sometimes because of the inherent bias arising from linearization, non-linear regression was applied to ascertain substitute isotherm parameter sets. Hence, Chi-square test (χ^2) was also carried out for the current study (Kundu and Gupta, 2006; Raval et al., 2017). The mathematical equation for the sum of squares can be represented as:

$$\chi^2 = \sum \frac{(q_{e(\text{exp})} - q_{e(\text{cal})})^2}{q_{e(\text{cal})}} \quad (14)$$

Where, $q_{e(\text{exp})}$ ($\mu\text{g g}^{-1}$) is experimental data based equilibrium capacity; $q_{e(\text{cal})}$ ($\mu\text{g g}^{-1}$) is the model based calculated equilibrium capacity.

2.5. Studies to confirm the potentiality of the bilayer–OA@FeO NPs

2.5.1. Desorption and regeneration studies

To carry out the desorption/regeneration of the applied/utilized adsorbent, the bilayer–OA@FeO NPs were separated with an external magnetic field application after completion of the adsorption cycle and redispersed into alkaline solution (50 mL) and agitated for 120 min at normal room temperature (298 ± 2 K). After regular time interval, the remaining concentrations of metalloid arsenate were determined by GF–AAS. Considering the lower removal efficiency of As(V) at alkaline condition (refer Fig. 3(c)), NaOH was selected as a desorbing agent for regeneration of both the biosorbents. The suitable concentration of NaOH used for desorption–regeneration cycle was determined from the preliminary experiments with 0.1 and 0.5 M NaOH solutions. These regenerated nanoparticles were washed with DI water and ethanol for many times and dried in an oven ($@323$ K) to reutilize in a new adsorption–desorption–regeneration cycle.

2.5.2. Competition studies

To determine the effectiveness, field-scale capability and selectivity of the synthesized adsorbent (bilayer–OA@FeO NPs) towards As, the competition studies in presence of common anionic co-contaminants (F^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) were performed in a batch mode. In the concentration range of $0.1\text{--}5 \text{ mmol L}^{-1}$, solution of the mentioned co-existing anions were added to As(V) solution with initial concentration of 100 ppb, individually (in a binary mixture) and combinely (cocktail mixture). The mixture was agitated with optimum amount of sorbent for predefined time intervals and the remaining As concentration was measured using previously mentioned model of GF–AAS.

3. Results and discussion

3.1. Characterization of bilayer–OA@FeO NPs

Fig. 1(a–f) represents the FE–SEM microphotographs and EDS spectra of the bare FeO NPs and bilayer–OA@FeO NPs, before (c, d) and after (e, f) equilibrating with the solution of As ($100 \mu\text{g L}^{-1}$). The elemental composition of uncoated and coated NPs before their removal application is presented in Table S1. The SEM–EDS images of the bare FeO NPs clearly revealed the existence of aggregated particles, resulting from the high surface energy of naked NPs and occurrence of Fe (72.19 wt%) as the major element together with C, O and Cl as other components (Fig. 1(a, b)). After coating of NPs with OA-bilayer, the separated particles can be obtained as observed in Fig. 1(c). Through bilayer coating OA may form shell around each core of the FeO NPs (refer Fig. S2). This would resulted in an increase of the NPs size, but at the same time more separated particles can provide individual binding surface for the pollutants. The EDS spectra for bilayer–OA@FeO NPs (Fig. 1 (d)) indicated the mass variation of major element (Fe = 53.47 wt%) along with the change of minor elements like, C, O and N which provides an evidence for successful functionalization of NPs with OA. However, due to low concentration of As(V) solution ($100 \mu\text{g L}^{-1}$) was used to equilibrate with the adsorbent, the retained element could not be observed in the EDS spectrum of bilayer–OA@FeO NPs after adsorption (Fig. 1(f)). The obtained outcomes are in good agreement with the earlier reported results where authors have speculated the textural changes of synthesized nanocomposite adsorbent due to heterogeneous dispersion of magnetic NPs onto supporting polyaniline hollow microsphere surface (Dutta et al., 2020).

FT–IR spectra of bare iron oxide nanoparticles (FeO NPs), oleic acid (OA) and bilayer–OA@FeO NPs are shown in Fig. 2(a). The spectrum of bare FeO NPs exhibited strong bands in $1000\text{--}500 \text{ cm}^{-1}$ regions. According to (Ma et al., 2007) the spectrum of magnetite (Fe_3O_4) nanoparticles represented band at 570 cm^{-1} , whereas for maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles the broad band has been observed within the region of $520\text{--}610 \text{ cm}^{-1}$. In present study, the characteristic Fe–O

Fig. 1. SEM microphotographs and SEM-EDS analysis of bare FeO NPs (a, b); bilayer-OA@FeO NPs before (c, d) and after (e, f) equilibrating with aqueous solution containing $100 \mu\text{g L}^{-1}$ of As(V) solution.

vibrations of magnetic iron oxide can be confirmed with the band observed at 545 cm^{-1} (for both uncoated and coated nanoparticles). In the FT-IR spectrum of bare FeO NPs, the broad bands observed at 3153 and 1622 cm^{-1} were related to $-\text{OH}$ stretching and bending vibrations, respectively. This was mainly because, during synthesis of nanoparticles in an aqueous medium their surfaces were covered with the hydroxyl groups. The bilayer-OA coated FeO NPs showed bands at 2925 and 2854 cm^{-1} . These were respectively, attributed to the asymmetrical (ν_{as}) and symmetrical stretching vibrations (ν_{s}) of $-\text{CH}_2$ groups. Presence of these two bands further confirmed the successful coating of OA with FeO NPs. In-plane scissoring (δ_{s}), a characteristic vibrational band for $-\text{CH}_2$ groups, has also been observed for nanoparticles after coating with the OA surfactant at 1423 cm^{-1} wavenumber.

In the spectrum of OA the sharp peak can be observed at 1705 cm^{-1} , which is due to the presence of polar head group associated with the $\text{C}=\text{O}$ bond asymmetric vibration. However, after monolayer coating, where the $-\text{COO}^-$ groups of OA connected with the Fe atoms, this band weakened and then shifted the stretching frequency to a lower value. Previous studies have reported that the bilayer OA coated iron oxide nanoparticles showed characteristic stretching vibrations of $-\text{C}=\text{O}$ at

1700 cm^{-1} region (Yang et al., 2010; Liu et al., 2006; Maity and Agrawal, 2007). Similar vibrations of $\text{C}=\text{O}$ bond at 1705 cm^{-1} were observed in the spectrum of bilayer-OA@FeO NPs, which confirm the successful synthesis of bilayer-OA coated FeO NPs.

As shown in Fig. 2(b), the XRD pattern of bilayer-OA@FeO NPs indicates characteristic features of oleic impregnated iron oxide nanoparticles, which showed several distinct peaks at $(2\ 2\ 0)$, $(3\ 1\ 1)$, $(4\ 0\ 0)$, $(4\ 2\ 2)$, $(5\ 1\ 1)$ and $(4\ 4\ 0)$. All these diffraction planes corresponding to the 2θ values of $\sim 30.5^\circ$, 36° , 43.5° , 54° , 57.8° , 64° , respectively, are related to the Fe_3O_4 crystal structure (Baharuddin et al., 2018). The appearance of different peaks at above mentioned 2θ values also confirmed the successful coating of the Fe_3O_4 nanoparticles with OA and thereby prevent their further oxidation, as without coating Fe_3O_4 would get oxidized to $\gamma\text{-Fe}_2\text{O}_3$ and showed the peaks at $(1\ 1\ 3)$, $(2\ 1\ 0)$ and $(2\ 1\ 3)$. Similar observations were also recorded by other researchers in the coating of Fe_3O_4 with oleic acid (Liu et al., 2006).

Fig. 2(c) illustrates the N_2 adsorption-desorption isotherm (type IV) of the bilayer-OA@FeO NPs. The BET and Langmuir surface area of the adsorbent was determined to be 6.53 and $124.82 \text{ m}^2 \text{ g}^{-1}$, respectively. The total pore volume of the bilayer-OA@FeO NPs was found to be $0.0163 \text{ cm}^3 \text{ g}^{-1}$. The average pore size is calculated from the single-

Fig. 2. Characterization validation of the synthesized bilayer-OA@FeO NPs using FT-IR spectra (a), XRD pattern (b), nitrogen (N_2) adsorption-desorption curve (c) and TGA analysis (d).

point adsorption total volume for the coated nanoparticles. The pore size distribution (Fig. S3) indicates that most of the mesoporous is around 1.7–4.0 nm. The BET surface area and pore size distribution support the fact that coated NPs have a micro-mesoporous structure. Similarly, in the previously reported core-shell nanocomposite adsorbent (Fe(0)@Fe oxide and Mn(0)@Mn oxide) authors have obtained the similar porous characteristics (Panda et al., 2020).

It is essential to study the thermal stability of the functionalized adsorbent in order to interpret how morphological changes influence the adsorption capacity of coated NPs. The quantitative evidence for the coating of OA onto iron oxide NPs was also provided by TGA (Lan et al., 2007). The weight losses of bare FeO NPs and bilayer-coated OA@FeO NPs were analyzed within the temperature range of 50–750 °C at a heating rate of 10 °C min and results are presented in Fig. 2(d). The TGA was carried out under inert (nitrogen) atmosphere which causes reduced oxidation of bare and OA coated NPs.

In case of the bare FeO NPs the mass loss was observed in two stages. The first weight loss (3.1 %) occurred within the temperature range of 110 °C was probably due to the $-OH$ group of H_2O molecules which was functionalized on the external surface of magnetic NPs. Whereas, for the coated NPs the first mass loss was almost double (5.9 %), compared to uncoated one, mainly because of the evaporation of solvent traces, used for the washing of NPs during synthesis stage and also due to the removal of water molecules. After 110 °C temperature the continuous mass loss of bare NPs was attributed to the phase transfer of the magnetic nanoparticles. The sudden mass loss observed in case of uncoated NPs at around 550–560 °C specified the deterioration of magnetic NPs. The coated NPs contain chemically and physically bound primary and secondary layers of OA, respectively surrounding iron core. Hence, the second mass loss was observed in two sub-stages, where first one (II(A)) was assigned to the decomposition of the hydrophobically interacted OA layer (110–200 °C) and second (II(B)) was attributed to the decomposition of the chemically bound OA layer (110–250 °C). For the bilayer-coated OA@FeO NPs, the first mass loss

was accounted for removal of solvents (ethanol/acetone) after a gradual loss of H_2O , a major weight loss started after 200 °C at which the degradation beyond 300 °C corresponds to decomposition of coating molecules (Patil et al., 2014). After the complete decomposition of OA the enduring substance is mainly magnetic FeO NPs. The percentage of OA in the bilayer coated FeO NPs was 14.3 wt%, which can be easily revealed from the TGA curve.

3.2. Removal of As(V) under different operating conditions

Effects of adsorbent mass on As(V) removal at 120 min contact time and $100 \mu g L^{-1}$ of initial metalloid concentration was studied and the acquired results are illustrated in Fig. 3(a) in terms of As(V) removal percentage (%) and in relation of adsorbed amount at equilibrium stage (q_e). It was perceived from Fig. 3(a) that with increasing amount of bilayer-OA@FeO NPs from 0.1–3 g L^{-1} the removal percentage of As(V) increases from 2.67 to 21.1 %. This increased removal efficiency was mainly ascribed to the higher ratio of accessible active sites (due to separated particles) to sorbate concentration. However, beyond 1 g L^{-1} dosage there is not much increase observed in arsenate removal efficiency ($\leq 1\%$ change) which might be due to saturation of the unoccupied sites. Although the removal % of As(V) increased (2.67–21.1%) with increase of bilayer-OA@FeO NPs dose (0.1–3 g L^{-1}), the equilibrium sorption capacity (q_e) decreased from 31.0–8.16 $\mu g g^{-1}$ with increasing amount of adsorbents as depicted in Fig. 3(a). This declined sorption capacity of geogenic contaminant was attributed to the overlapping/aggregation of vacant adsorption sites at higher amount of sorbent. According to this obtained results, 1 g L^{-1} is considered as an optimal sorbent dose and all succeeding experiments were performed with that particular amount of bilayer-OA@FeO NPs.

Determination of the effect of reaction time is an essential parameter in order to identify the rapid and economical adsorption process to achieve the sustainability goal of the Anthropocene epoch. Hence, the sorption of As(V) by bilayer-OA@FeO NPs was measured at varying

Fig. 3. As(V) adsorption by bilayer-OA@FeO NPs. Plot of the effects of different adsorbent dosages (a), initial adsorbate concentrations and contact time (b), pH_{ZPC} of adsorbent (c) solution pH (d) and illustration of hypothetical sorption mechanisms (e). Solution volume: 100 mL; temperature: 298 ± 2 K.

contact times from 0–120 min with altered As concentrations ($10\text{--}150 \mu\text{g L}^{-1}$). The obtained results in terms of As(V) removal percentage (%) and adsorbed amount ($\mu\text{g g}^{-1}$) are plotted in Fig. 3(b) and Fig. S4, respectively. At equilibrium, the removal capacity of As(V) at 10 and $150 \mu\text{g L}^{-1}$ was 47.8 % and 17.6 %, respectively (Fig. 3(b)). It is noted that As(V) removal percentage was lower at the higher initial concentration, because at enhanced sorbate concentration the inadequate number of available adsorption sites got saturated onto bilayer-OA@FeO NPs as shown in Fig. 3(b). With increasing initial metalloid concentrations from $10\text{--}150 \mu\text{g L}^{-1}$, the amount of adsorption of As(V) was increased from $4.5\text{--}23.4 \mu\text{g g}^{-1}$ at room temperature (Fig S3). This rising adsorption capacity of toxic metalloid arsenic at higher initial adsorbate concentration was because of the high driving force to transfer the mass of elevated concentration of As(V) in the solution. For different initial As concentrations, equilibrium was attained in almost 120 min.

The magnetic sorbents, adsorb metalloid (As) via surface complexation with the help of functional groups present on their surfaces which usually undergo protonation or deprotonation reactions under variable pH conditions (Zhu et al., 2009). In the literature it was already expounded that the As(V) mainly exists as oxo-anions (H_2AsO_4^- ,

HASO_4^{2-} and AsO_4^{3-}), within the pH order of 3–11 (Sanjrani et al., 2019; Henke, 2009; Sarkar and Paul, 2016). Considering the importance of sorbents' surface charge and pH dependency of As(V) adsorption from earlier literature, first we have examined the pH_{ZPC} of bilayer-OA@FeO NPs and then investigated the effects of pH on As(V) adsorption via synthesized sorbent (bilayer-OA@FeO NPs) within 5.0–13.0 pH range. The relevant results are depicted in Fig. 3(c, d).

The pH_{ZPC} of the bilayer-OA@FeO NPs was 7.3 (Fig. 3(c)). At low pH, protonation of the accessible functional groups ($-\text{COO}^-$) favours the binding of the anionic arsenic species. This resulted in the higher adsorption capacity at $\text{pH} < \text{pH}_{\text{ZPC}}$ (lower pH) (Fig. 3(d)), which might be due to coulombic forces/electrostatic attraction and hydrogen bonding (Fig. 3(e)). At higher pH ($\text{pH} > \text{pH}_{\text{ZPC}}$) (Fig. 3(d)), surface of the adsorbent becomes less positively charged, which resulting in a reduction of arsenate adsorption (via electrostatic repulsion forces) as presented in Fig. 3(e). Similar observations were previously reported by other researchers, where they have applied magnetic nanoparticles for the removal of As(V) (Chowdhury et al., 2011; Chowdhury and Yanful, 2010). However, a strong permanent dipole, created by the covalent bonding of relatively electronegative oxygen atom with carbon atom,

Fig. 4. Kinetics analysis of As(V) adsorption onto bilayer-OA@FeO NPs by linear plots of pseudo-first-order (a), pseudo-second-order (b), Elovich (c) and intraparticle diffusion rate equations. Adsorbent dose: 1 g L⁻¹; solution volume: 100 mL; pH: 7.0 ± 0.2; temperature: 298 ± 2 K.

can still favourably interact with anions (H_2AsO_4^-) present in the solution via charge-dipole/ion-dipole interactions and assisted the adsorption of As(V). In addition, the formation of an inner-sphere surface (As-Fe) complexes via ligand exchange mechanism also contributes in the removal process (refer Fig. 3(e)) (Boddu et al., 2008; Kumar and Jiang, 2016).

3.3. Adsorption kinetics and modeling analysis

The frequently used rate models (pseudo-first- and second- order) were used to ascertain the suitability of the sorption reaction between representative adsorbate (As(V)) and applied sorbent (bilayer-OA@FeO NPs). The respective kinetic plots are presented in Fig. 4(a, b) and statistically calculated parameters/constants from intercept (q_e (cal)) and the slope (k_1 , k_2) of these plots are mentioned in Table 1. The closer values of experimental data ($q_{e(\text{exp})}$) pertaining to the applied sorbent towards rate model-based calculated values ($q_{e(\text{cal})}$) for the pseudo-second-order kinetic model confirmed its better applicability (refer Table 1). In addition, the best fits of the linear regression of the pseudo-second order rate model show the R^2 values of 0.968 for As(V) adsorption on BOA@FeO NPs. At the same time, the lower value of sum of square error function (χ^2) for the data of second-order rate model confirms its applicability (refer Table 1). These findings clearly implied that the sorption kinetics of As(V) onto stable NPs followed pseudo-second order model more closely, which provides an indirect assumption of chemisorption mediated rate limiting steps. For the applied adsorbent, the higher values of K_1 compared to the values of K_2 , determine the significance of initial concentrations of As(V). This result confirms the near pseudo-equilibrium stage of the studied batch system.

Further, Elovich kinetic equation which typically describes the chemisorption interaction between the sorbate and sorbent was used to model the sorption data of As(V) onto bilayer-OA@FeO NPs. The Elovich rate constants (α and β) were calculated from the slope and

Table 1

Parameters for pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models for the sorption of As(V) onto bilayer-OA@FeO NPs (Adsorbent dose: 1 g L⁻¹; solution volume: 100 mL; pH: 7.0 ± 0.2; temperature: 298 ± 2 K).

Kinetic models and associated rate constants		Initial As(V) concentration ($\mu\text{g L}^{-1}$)				
		10	30	70	100	150
Pseudo-first-order	$q_{e(\text{exp})}$ ($\mu\text{g g}^{-1}$)	4.52	8.71	15.2	23.7	23.4
	$q_{e(\text{cal})}$ ($\mu\text{g g}^{-1}$)	13.0	13.6	26.7	24.6	53.1
	k_1 (min^{-1})	0.045	0.037	0.039	0.044	0.055
	R^2	0.81	0.76	0.87	0.88	0.91
	χ^2	76.4				
Pseudo-second-order	$q_{e(\text{cal})}$ ($\mu\text{g g}^{-1}$)	4.00	11.9	24.2	27.0	34.4
	k_2 ($\text{g } \mu\text{g}^{-1} \text{min}^{-1}$)	0.0005	0.002	0.001	0.003	0.001
	R^2	0.48	0.97	0.86	0.99	0.94
	χ^2	37.6				
Elovich	α ($\mu\text{g g}^{-1} \text{min}^{-1}$)	0.15	0.46	0.82	7.41	1.52
	β ($\mu\text{g g}^{-1}$)	0.47	0.34	0.20	0.22	0.13
	R^2	0.92	0.95	0.89	0.96	0.94
Intra-particle diffusion	K_{id} ($\mu\text{g g}^{-1} \text{min}^{-1/2}$)	0.60	0.784	1.524	1.338	2.234
	I ($\mu\text{g g}^{-1}$)	-1.95	0.78	-0.75	10.1	0.90
	R^2	0.94	0.97	0.92	0.92	0.91

intercept of the straight lines of Fig. 4(c) and mentioned in Table 1. The squared correlation coefficients (R^2) obtained by Elovich equation were much relevant to those obtained from pseudo-second-order and higher than pseudo-first-order rate models. Based on R^2 values, the suitability order of the kinetic rate models for sorption of AS(V) on bilayer-OA@FeO NPs adsorbent was: pseudo-second order ≥ Elovich >

pseudo-first order. Siddiqui and Chaudhry (2019) reported the similar results for the adsorptive removal of arsenic from an aqueous solution onto $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ nanoparticles (Siddiqui and Chaudhry, 2019).

In order to recognize the possible diffusion mechanism the experimental kinetic results for the adsorption of As(V) onto bilayer-OA@FeO NPs were examined with the Weber–Morris model and the results are plotted in Fig. 4(d). With multilinearity correlation, the plot confirmed the adsorption process of model geogenic contaminant (As(V)) onto proposed adsorbent in three consecutive steps/mechanisms (film, particle and external surface adsorption). The first step, often regarded as film diffusion is the mobilization of As from the solution to the outer-most surface of the coated nanoparticles by process of diffusion. This step was very sharp as shown in figure, mainly because initially large number of As molecules were available to transport to the adsorbent surface. The internal diffusion was the second step in which As molecules transported from surface of the NPs into interior sites. Due to the inter-connected layers of OA, this stage was very rapid. This can be explicable as the connected tails might provide channels to transport metalloid, As(V), into the interior portions of the adsorbent. The final and/or equilibrium stage approaches when the intra-particle diffusion begins to slow down. This was because of lower concentration of As(V) in solution phase and sorption of As(V) molecules from the active sites into the interior pores/sites. The intraparticle diffusion constants have been calculated using the Weber–Morris linear equation and are presented in Table 1 together with the other studied rate constants. The negative value ($-1.95 \mu\text{g g}^{-1}$) of intercept for the lower initial adsorbate concentration ($10 \mu\text{g L}^{-1}$) confirmed the inefficient boundary layer control. Also the plots for different As(V) concentrations were not originated from the zero which suggested the concurrent type of the adsorption mechanism together with the intraparticle diffusion.

3.4. Adsorption isotherms study

The adsorption isotherms for the removal of As(V) onto bilayer-OA@FeO NPs were evaluated using the frequently used

Table 2

Parameters for Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherms for the sorption of As(V) onto bilayer-OA@FeO NPs (Adsorbent dose : 1 g L^{-1} ; solution volume : 100 mL; pH: 7.0 ± 0.2 ; temperature : $298 \pm 2 \text{ K}$; adsorption time : 120 min).

Isotherm Models	Isotherm Parameters	Value for Adsorbent
Langmuir Isotherm	$q_m (\mu\text{g g}^{-1})$	32.8 ± 0.54
	$K_L (\text{L g}^{-1})$	0.72 ± 0.04
	R_L	$0.26 \text{ \& } 0.83 \text{ (for } 10 \text{ \& } 150 \mu\text{g L}^{-1})$
	R^2	0.93 ± 0.01
	χ^2	1.06 ± 0.03
Freundlich Isotherm	$K_F (\text{L g}^{-1})$	1.80 ± 0.07
	n	1.82 ± 0.003
	$1/n$	0.55 ± 0.001
	R^2	0.99 ± 0.002
	χ^2	0.27 ± 0.01
Temkin Isotherm	$A_T (\text{L g}^{-1})$	0.30 ± 0.01
	$b_T (\text{kJ mol}^{-1})$	0.17 ± 0.004
	R^2	0.92 ± 0.004
	χ^2	2.40 ± 0.08
	χ^2	9.06 ± 0.01
D-R Isotherm	$Q_m (\mu\text{g g}^{-1})$	17.1 ± 0.51
	K_d	15.2 ± 0.33
	$E (\text{kJ mol}^{-1})$	0.18 ± 0.002
	R^2	0.73 ± 0.01
	χ^2	9.06 ± 0.01

two-parameter isotherm models as shown in Fig. 5(a–d) and the obtained sorption parameters/constants are presented in Table 2. For the determination of felicitousness and aptness of the model parameters, statistical hypothesis tests (correlation coefficient (R^2), chi-square test (χ^2)) were performed and their obtained values are mentioned in the same table together with isotherm parameters. The extent of the goodness of fit function (R^2) were high and relatively comparable for all the studied isotherm models (Table 2).

The maximum monolayer sorption capacity (q_m) of $32.8 \pm 0.5 \mu\text{g g}^{-1}$ was for As(V) onto the surface of bilayer-OA@FeO NPs. The sorption capacity of present bilayer-OA@FeO NPs adsorbent, prepared

Fig. 5. Adsorption isotherm analysis of As(V) onto bilayer-OA@FeO NPs by linear plots of Langmuir (a), Freundlich (b), Temkin (c) and Dubinin–Radushkevich (d) empirical isotherm models. Adsorbent dose: 1 g L^{-1} ; solution volume: 100 mL; pH: 7.0 ± 0.2 ; temperature: $298 \pm 2 \text{ K}$; adsorption time: 120 min.

Table 3
The comparison of various operational parameters and monolayer sorption capacity (mg g^{-1}) of different magnetic nanoparticles to remove As(V) with bilayer-OA@FeO NPs adsorbent.

Sr. No.	Adsorbent	pH	pH _{zpc}	Diameter (nm)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Equilibrium contact time	Initial concentration (mg L^{-1})	Dose (g L^{-1})	Maximum sorption capacity (mg g^{-1})	Approx. removal cost ($\text{\$ kg}^{-1}$)	References
1.	Magnetite	6.5	6.5	10^5	0.890	< 2 days	75	0.1	25.6	0.16	(Giménez et al., 2007)
2.	Hematite	7.3	6.7	25×10^4	0.381	< 2 days	75	0.1	31.3	0.20	(Giménez et al., 2007)
3.	Goethite	7.5	6.8	25×10^4	2.009	< 2 days	75	0.1	12.1	0.23	(Giménez et al., 2007)
4.	Maghemite NPs	7.0	8.3	11–23	41–49	120 min	1	1	4.64	0.26	(Park et al., 2008)
5.	Nano zero valent iron supported on activated carbon	6.5	7.4	< 100	69.4	72 h	2	1	12	2.83	(Zhu et al., 2009)
6.	MnFe ₂ O ₄ nanoadsorbents	2–6	–	12	–	1 h	0.1	2.5	2.13	1.89	(Parsons et al., 2009)
7.	Iron-doped activated micro/nano fibers	6.5–7.5	–	100–500	790–1140	24 min	< 20	5	5	3.48	(Gupta et al., 2010)
8.	Fe ₃ O ₄ - γ -Fe ₂ O ₃ NPs	6.5	–	20–40	60	180 min	2	0.5	4.75	3.64	(Chowdhury et al., 2011)
9.	Stearic acid functionalized Fe ₃ O ₃ NPs	6.5	–	10	–	80 min	0.1–0.5	0.25	10.5	2.41	(Goswami et al., 2011)
10.	Activated carbons modified with iron hydro (oxide) NPs	6–8	8.6	3–36	632–1101	100 min	0.025–1.5	0.75	1.64–1.73	2.34	(Viteira-Rodriguez and Rangel-Mendez, 2013)
11.	Fe-hydroxalate supported magnetite NPs	9.0	–	50	1.5	60 min	0.025–1.5	5	1.28	1.73	(Türk and Alp, 2014)
12.	Bilayer-OA@FeO NPs	7.0	7.3	20–40	6.53	120 min	0.1	1	0.032	2.34	This study

by chemical co-precipitation, was compared with the other magnetic nanoparticles reported in contemporary literature (Table 3). Another important constant (K_L) of monolayer isotherm which is related to the sorption energy was found to be $0.72 \pm 0.04 \text{ L g}^{-1}$. R_L (separation factor) values (0.26 to 0.83) were between the range of 0–1 for different initial As concentrations ($10\text{--}150 \mu\text{g g}^{-1}$) which further confirm the favorable adsorption process of modeled pollutant onto applied adsorbent. The Freundlich isotherm, which assumes multilayer coverage of adsorbate over a well distributed heterogeneous adsorbent surface, simulated the experimental data very well with the R^2 value of 0.99 and χ^2 value of 0.27. It has been reported that favorable adsorption was indicated when the values of '1/n' obtained from Freundlich isotherm were between 0.1–1 (Verma and Singh, 2019). In the present work, the value of '1/n' was found to be in the suggested range (0.55 ± 0.001) indicated that arsenate can favourably adsorbed onto bilayer-OA@FeO NPs.

By comparing the values of goodness of fit (R^2) and standard error (χ^2) of the isotherm models on the experimental data, the Freundlich > Langmuir > Temkin models gave higher R^2 and the lower error χ^2 values. Therefore, it is conceivable to consider that the adsorption of As(V) occurs by the formation of consecutive multilayer/monolayer coverages and difference in heat of adsorption onto proposed adsorbent (bilayer-OA@FeO NPs) (Wang et al., 2018).

The thermodynamic transfer of the free energy of solute to the external surface of the adsorbent can be calculated from the D–R constants (numerical derivation of ϵ and E). The E values (0.18 kJ mol^{-1}) of arsenate metalloid indicated that the adsorption process is controlled by physisorption (see Table 2). Similar findings were reported by other researchers, where the mean energy of adsorption was in the range of $0.18\text{--}0.96 \text{ kJ mol}^{-1}$ and physisorption dominates chemisorption over the entire equilibrium concentration range (Yildirim and Bulut, 2019).

3.5. Potential application study

3.5.1. Regeneration and reusability of the bilayer-OA@FeO NPs

The possible reutilization efficiency, essential to determine the robustness, of the applied adsorbent towards As(V) removal was estimated by performing desorption experiments under alkaline environment. It was found that the synthesized adsorbent can be successfully regenerated up to consecutive five desorption/regeneration cycle with application of 0.1 M NaOH as a desorbing agent (Fig. 6(a)). From Fig. 6(a), it has been observed that the As(V) removal efficiency was 14.8 % for bilayer-OA@FeO NPs after fifth cycle which was only 5.6 % less than that obtained with the fresh adsorbent (20.4 %). At higher pH, strong competition between hydroxyl anions and complexed ligands causes desorption of adsorbed As(V). The obtained results are in line with the previously published work where alkaline solution has been reported as the favorable regenerant for desorption of anionic (negatively charged) geogenic contaminants from bio-nano polymer based composite adsorbents because of the high affinity of the complexed metal oxides for hydroxyl anions (Dutta et al., 2020). The results clearly demonstrate that the engineered adsorbent (bilayer-OA@FeO NPs) could be sustainably regenerated with NaOH treatment and reutilized multiple times for the management of geogenic contaminants to provide potable water for the human development which is considered to be one of the prime challenges of the Anthropocene era.

3.5.2. Effect of co-existing anions

It has been very well-known that As is naturally present in the groundwater, which is considered to be one of the significant drinking water sources in the contemporary time, along with the other common geogenic cationic (i.e., Ca^{2+} , Mg^{2+} and Fe^{2+}) and anionic (i.e., F^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , CO_3^{2-} and SiO_4^{4-}) species (Leus et al., 2018). These differently charged species (anions/cations) may have synergistic and/or antagonistic effects on the adsorption of As. Hence, As(V) adsorption by bilayer-OA@FeO NPs (1 g L^{-1}) was examined in the presence of

Fig. 6. Adsorption/desorption percentage of arsenic, in five regeneration cycles using 0.1 M NaOH regenerant (a) and arsenic removal percentage in presence of common co-contaminants (in binary and cocktail mixture) (b). Adsorbent dose: 1 g L⁻¹; pH: 7.0 ± 0.2; temperature: 298 ± 2 K (Note: the As removal % was set as 100 % without competing anions).

other counter-anions, i.e., F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ and their cocktail mixture, at different concentrations (0.1, 1 and 5 mmol L⁻¹) and the obtained results are depicted in Fig. 6(b). From the plotted results, it was observed that the As(V) removal was least affected in the presence of Cl⁻, SO₄²⁻ and NO₃⁻ ions whereas, more significantly reduced with the common co-contaminants i.e., F⁻, PO₄³⁻. The substantial reduction in the removal efficiency of arsenate in presence of F⁻ and PO₄³⁻ was mainly because of the smaller size/highest electronegativity of the F⁻ ions and structural similarity between arsenate and phosphate which create strong competition amongst them for the available binding sites (–COOH group) present on the bilayer-OA@FeO NPs. Wang et al. (2014) also reported that presence of phosphate significantly deteriorate the adsorption of arsenate onto magnetic nanoparticles impregnated chitosan beads (MICB) adsorbent (Wang et al., 2014). The potential of adsorbent to remove the As(V) in presence of other competitive ions was considerably good and the antagonism of the common anions follows the order of: Cl⁻ < SO₄²⁻ < NO₃⁻ < F⁻ < PO₄³⁻.

To simulate the actual environmental condition, further experiments were performed using cocktail mixture of the major geogenic anions (H₂AsO₄⁻, F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) under the same experimental conditions and the acquired results are plotted in Fig. 6(b). Results confirmed that present adsorbent can remove As(V) (22.0 % and 17.9 %) in presence of cocktail mixture of the contaminants with lower concentrations (0.1 and 1 mmol L⁻¹). However, at higher concentration (5 mmol L⁻¹) of other anions, the removal efficiency of bilayer-OA@FeO NPs towards As(V) was markedly reduced up to 8.4 %. This might be due to the formation of unknown complexes in the cocktail mixture as well as competition of other anions towards accessible sorption sites on the surface of the adsorbent.

3.6. Sorption mechanism of As(V)

In order to comprehend the plausible sorption mechanism of As(V), which is usually present in the form of oxoacids/inorganic acids (arsenic or arsenous acid), as well as the leverage of stabilizing agent (OA) on the magnetic NPs' adsorption properties, comparative characterizations were performed. The surface of the adsorbent became protonated and positively charged when the solution pH was ≤ 7.3, the isoelectric point of the sorbent, which was beneficial to adsorption because As(V) was adsorbed as anionic species via coulombic forces/electrostatic attraction. At higher pH (pH ≥ p*H*_{ZPC}), the negative charge prevails on the surface of the adsorbents which resulting in a reduction of As(V) sorption (via electrostatic repulsive forces). However, a strong permanent dipole can still favourably interact with anions via charge-dipole/ion-dipole interaction. In addition, the surface complexation, film diffusion/absorption and intraparticle diffusion of adsorbates into the sorbent play vital role in the adsorption process.

Comparing the SEM-EDS spectra of synthesized adsorbent in the presence and absence of As(V), it was noticed that after loading of the

geogenic contaminant onto adsorbent surface, the clearly separated particles became invisible and represented changes in their surface morphology (refer Fig. 1(e)). In the present study, bilayer-OA@FeO NPs showed the presence of –COOH and –CO= at ~1423 and ~1705 cm⁻¹ regions (refer Fig. 2(a)). These groups were mainly responsible for the adsorption of As(V). XRD analysis of adsorbent gave an idea about the crystalline nature of the bilayer-OA@FeO NPs. Following As(V) sorption, the metalloid loaded adsorbent had the structural similarities. However, two identical peaks at 2θ values of ~43.5° and 54°, have changes in the shape/intensity which could be attributed to the formation of precipitates of ferric arsenate (FeAsO₄) (refer Fig. 2(b)).

Based on the above analyses, the probable sequestration of As(V) onto proposed adsorbent (bilayer-OA@FeO NPs) can be elucidated by the electrostatic attraction/repulsion, coulombic interaction, ion-dipole/charge-dipole interaction, intra-particle diffusion and inner-sphere complex formation (Monodentate–mononuclear and/or bidentate–binuclear) mechanisms (refer Fig. 3(e)). The proposed sorption mechanism is in agreement with previously reported results where it has been very-well documented that the inner-sphere complexes are mainly responsible for the sorption of As(V) onto various iron-based adsorbents (Henke, 2009; Dutta et al., 2020).

4. Conclusions

The bilayer OA@FeO NPs (core-shell) adsorbent was successfully synthesized and first time practiced for the sequestration of toxic As(V) from the aqueous environment. Compared to bare FeO NPs, the bilayer-coated OA@FeO NPs exhibited properly separated particles which leading to the high uptake capacity for As(V). After coating of NPs, the band observed at ~1705 cm⁻¹ wavenumber confirmed the existence of secondary layer of OA (physisorbed) on the surface of the chemiadsorbed primary layer. By enabling the formation of polar shell, secondary layer of OA makes the hydrophilic surface containing the large number of –COOH groups available for the adsorption. The maximum sorption capacity (~32.8 μg g⁻¹) for As(V) was obtained at neutral (7.0) pH with 1 g L⁻¹ dosage of bilayer-OA@FeO NPs in 120 min of reaction time. As(V) adsorption on proposed adsorbent followed pseudo-second order rate model and well described by three step intraparticle diffusion process. The isotherm studies demonstrated that As(V) adsorption on sorbent followed the Freundlich > Langmuir > Temkin models with higher R² and lower χ² values, suggesting the formation of consecutive multilayer/monolayer coverages. The potential to regenerate the adsorbent was excellent upto 5 cycles with 0.1 M NaOH. Furthermore, the adsorbent showed an efficient As(V) removal efficiency from the binary and cocktail mixture of the co-contaminants. The acquired results clearly validate the sustainable utilization of bilayer-OA@FeO NPs as a promising adsorbent for removing metalloid contaminant from the water. Further research is required to study the efficiency of proposed adsorbent on the real

groundwater in the complex water system together with bacterial consortium. These findings would open a new research directions in the development of an effortless adsorbent material suitable for As(V) removal, which can also inhibit the growth of gram-positive/negative bacteria via *in-situ* application of the adsorbent.

CRedit authorship contribution statement

Nirav P. Raval: Data curation, Formal analysis, Investigation, Methodology, Software, Writing - original draft, Validation. **Manish Kumar:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

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