Remediation of wastewater containing heavy metals using raw and modified diatomite

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Abstract

Diatomite and manganese oxide modified-diatomite (Mn-diatomite) were tested for heavy metal removal from wastewater. Impregnating the diatomite surface with $0.38\,g\,g^{-1}$ of manganese oxide gave a 2.4-fold increase in the adsorbent surface area. Equilibrium studies demonstrated that diatomite has a higher removal capacity for Pb^{2+}, Cu^{2+} and Cd^{2+} from water than untreated diatomite. Furthermore, the adsorption capacity of Mn-diatomite increased by decreasing the quantity of manganese oxides deposited on the surface. Electronic microscopy was carried out to study the effect of heterogeneity, modification and diatomite frustule type on adsorption. Both centric and pennate types of diatomite were present. The scanning micrographs also indicated the birnessite structure of manganese oxides, which is characterised by a platy-like-crystal structure. Adsorption kinetics confirmed the effectiveness of the manganese chemical treatment, which also significantly improved the diatomite filtration properties.
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1. Introduction

Water is considered an important and scarce commodity in many countries around the world. In particular, the contamination of surface and ground water with heavy metals is a concern. Industries such as plating, ceramics, glass, mining and battery manufacturing are considered the main source of heavy metals, e.g. lead, in local water streams. The elevated level of lead and other heavy metals, e.g. cadmium, chromium and mercury, in the local water streams is a major concern to public health.

Within literature, many treatment processes have been proposed for the removal of heavy metals. Chemical precipitation, membrane filtration, ion exchange, alum coagulation and activated carbon adsorption are some of the most commonly used methods for the treatment, and disposal, of metal-containing wastes [1,2]. Adsorption is considered to be a particularly competitive and effective process for the removal of trace quantities of heavy metals [3]. In principle, any solid material with a microporous structure can be used as an adsorbent, e.g. bone and coal char, clays, iron oxides,

synthetic and natural zeolites, molecular sieves and activated carbon. The most important property of any adsorbent is the surface area and structure. Furthermore, the chemical nature and polarity of the adsorbent surface can influence the attractive forces between the adsorbent and adsorbate. The highly developed structure of activated carbon allows wide usage as an adsorption media for a large number of organic and inorganic materials, including trace concentrations of heavy metals. Activated carbon, however, is not suitable in developing countries due to the high costs associated with production and regeneration [4]. The use of alternative low cost materials for heavy metals removal is required. Materials like activated peat and clay [5,6], chitin and chitosan [7,8] have been tested as potential sorbents for heavy metal removal. A comprehensive review has been presented by Bailey et al. [9].

Increasing of the sorption efficiency of low cost natural adsorbents towards heavy metals has also been investigated. The sorption efficiency of chitosan towards V(V) and U(VI) has been greatly increased after modification with oxo-2-glutaric [10]. Karthikeyan and Chaudhuri [11] studied the removal of Hg(II) by coal. After chemical treatment by nitric acid oxidation, H_2O_2 oxidation, CS_2 sulphurisation and impregnation with manganese oxides, the authors reported that the efficiency of the treated coal exceeded

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that of activated carbon. Ground husks modified with EDTA have also shown a high efficiency for removal of Cd(II) and Pb(II) [12]. Moore and Reid [13] showed that manganese-impregnated acrylic fibres were effective for removing radium from natural waters. Brandao and Galembeck [14] also reported that the impregnation of cellulose acetates with manganese dioxide resulted in high removal efficiency of Cu(II), Pb(II) and Zn(II) from aqueous solutions. Sagara et al. [15] prepared a selective ion-exchanger material for Li(I) and Na(I) by dispersing MnO_2 within cellulose gel beads.

Diatomite ($SiO_2 \cdot nH_2O$), or diatomaceous earth, is a soft lightweight rock available in large deposits around the world. This pale coloured sedimentary rock consists principally of silica microfossils of aquatic, unicellular alga varying in shape and size of diatom [16]. Diatomite is highly porous, with its structure containing up to 80–90% voids. It is used in a number of industrial applications, e.g. as a filtration media for various beverages, and inorganic and organic chemicals, and as an adsorbent for pet litter and oil spills [16]. Although diatomite has a unique combination of physical and chemical properties, its use as an adsorbent in wastewater treatment has not been extensively investigated [17–19].

The aim of this work is to examine the effectiveness of local diatomaceous earth (72% SiO_2) for the removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from wastewater. Furthermore, the effect of surface loading with manganese oxide on adsorbent structure and adsorption capacity were investigated.

2. Experimental

2.1. Adsorbent

Diatomite was obtained through the Natural Resources Authority (NRA), Amman, Jordan. The samples were washed with distilled water to remove fines and other adhered impurities, dried at 100 °C, desiccated and stored in tightly stoppered glass bottles. Surface modification was accomplished by treating the diatomite with manganese chloride and sodium hydroxide [13]. Samples of diatomite (15 g) were immersed in 6 M sodium hydroxide at 90 °C for 2 h. The mixture was then placed in 100 ml of 2.5 M manganese chloride (adjusted to pH 1–2 with hydrochloric acid), at room temperature, for 10 h. The manganese soaked diatomite was filtrated and separated from the supernatant. The solid was then immersed in 6 M sodium hydroxide, at room temperature, for 10 h to precipitate the manganese hydroxide. The excess solution was decanted off and the diatomite left exposed to the air (to facilitate oxidation of manganese hydroxide to form a mixture of hydrated manganese oxides). The sample was then washed with water, dried at 100 °C, desiccated and stored in tightly stoppered glass bottles. In this work, the modified diatomite is referred to as Mn-diatomite. The manganese content of

the samples was determined by atomic absorption spectroscopy (Pye Unican, SP9). Prior to analysis, the samples were immersed in 4 M hydrochloric acid, at 40 °C, to dissolve the deposited oxides. Manganese oxide diatomite samples was prepared, using the aforementioned procedure, with manganese chloride concentrations from 0.20 to 3.50 M.

The effect of chemical modification on the adsorbent was characterised on the basis of surface area using the Sears' method [20], the zinc ion adsorption method [21] and infrared absorption spectra (FT-IR Spectrophotometer, Impact 400, Nicolet). The surface area of diatomite was estimated, according to Sears' method, by weighting 1.5 g of diatomite and acidifying with dilute hydrochloric acid to pH 3–3.5. Sodium chloride (30 g) was then added and the volume made up to 150 ml with distilled water. The solution was titrated with 0.10 M sodium hydroxide and the pH measured throughout. The volume (V) required to increase the pH from 4 to 9 was recorded. The surface area (S) was estimated from the equation [22]:

$$S \, (\mathrm{m^2 g^{-1}}) = 32V - 25 \tag{1}$$

The surface area for Mn-diatomite was estimated according to the Zn^{2+} adsorption method. A 2 g sample was mixed with 25 ml of Zn^{2+} solution (2 M NH_4Cl, 0.1073 M $ZnCl_2$), stirred with a mechanical shaker for 24 h and then allowed to stand overnight. The supernatant solution was analysed for Zn^{2+} content using atomic absorption spectroscopy.

Desorption experiments were carried out to test the stability and irreversibility of the treatment. A 0.6 g of Mn-diatomite (prepared using 2.5 M $MnCl_2$ solution) was added to 400 ml of distilled water and agitated continuously. A 5 ml sample was withdrawn, using a pipette, after 1.5, 2.5, 7 and 22 h. After centrifugation, the samples were analysed for Mn^{2+} content using atomic absorption spectroscopy.

2.2. Adsorbate

Standard Pb^{2+}, Cu^{2+} and Cd^{2+} (1000 mg dm^{-3}) solutions were prepared by dissolving $Pb(NO_3)$, $CuCl_2 \cdot 2H_2O$ and $CdCl_2$ powder, respectively, in distilled water. Diluted solutions were prepared from the stock solutions (1000 mg dm^{-3}). All chemicals used in this work were of analytical reagent grade.

2.3. Scanning electron microscope (SEM) studies

Samples of diatomite and Mn-diatomite were attached to an SEM sampling plug with epoxy resin and dried overnight in an oven at 60 °C. A thin layer of Silpaint was added to provide an electrical ground between the sample and the plug, and the sample was then coated with 30 nm of gold using a sputter coater. The samples were scanned using a JOEL JSM 6400 electron microscope.

2.4. Adsorption isotherms

The adsorption capacity for diatomite and Mn-diatomite was determined by adding 0.05 g of adsorbent, of particle size range 300–500 μm, to 50 cm^3 of solution of varying concentration (0–300 mg dm^{-3} for Pb^{2+}, 0–200 mg dm^{-3} for Cu^{2+} and 0–90 mg dm^{-3} for Cd^{2+}). Pb^{2+} adsorption isotherms were studied at increased concentrations due to the high capacity of diatomite and Mn-diatomite for the ion. The adsorbate solution was adjusted to pH 4 using sodium hydroxide. The suspensions of adsorbent and solution were sealed and equilibrated in an orbital shaker at 23 ± 1 °C for 3 days. A 10 cm^3 sample of the solution was removed, centrifuged and the metal concentration analysed. Control samples containing adsorbate solution only were also prepared. Pb^{2+} and Cd^{2+} ions were analysed using differential pulse polarography (626 Polarecord, Metrohm, E 505 Metrohm Herisau). Cu^{2+} ions were analysed using atomic absorption spectroscopy. The adsorption capacity of diatomite samples loaded with different quantities of manganese oxides was estimated by equilibrating 0.05 g of adsorbent with 50 cm^3 of a 200 mg dm^{-3} Pb^{2+} solution for 3 days. The quantity of Pb^{2+} adsorbed was estimated from the difference between the equilibrium and initial concentrations.

2.5. Filtration rate

The filtration rate of diatomite and Mn-diatomite was determined using a suction filtration method. A 3 g sample was mixed with 50 ml of distilled water and filtered. After the initial water had been filtered from the sample, a further 100 ml was added and the filtration time recorded. The filtration rate was determined according to the method proposed by Bazhal et al. [23] for diatomite:

$$V_F = \frac{W_F}{Ft} \tag{2}$$

where V_F is the filtration rate (ml m^{-2} s^{-1}); W_F the volume of the filtrate (ml); F the effective filter paper surface (m^2), and t is the filtration time (s).

3. Results and discussion

3.1. Characterisation of natural diatomite

Diatomite frustules are mainly divided into two categories; centric (discoid) and pennate (elongated to filiform). Fig. 1 shows an electron micrograph of diatomite with magnification in the order of 1960. The plate indicates both centric and pennate types of diatom. The centric diatom has a radius of approximately 10 μm, while the length of the pennate shape is greater than 20 μm. It can be inferred from the scanning micrograph that diatomite has a large void volume, in addition to its highly porous structure. The high porosity
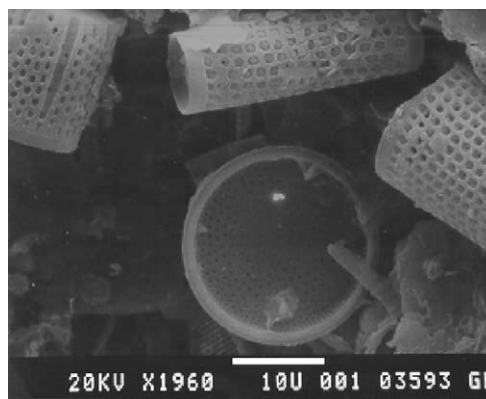

Fig. 1. Scanning electron micrograph of diatomite (magnification 1960×).

of this material was one of the main reasons for choosing it as a potential sorbent for heavy metals.

The Natural Resources Authority provided the X-ray diffraction chemical analysis of diatomite. Table 1 summarises the main oxides that form Jordanian diatomite. The analysis shows that SiO$_2$ is the main component (72.5%) and the metal oxides (Al$_2$O$_3$, Na$_2$O and Fe$_2$O$_3$) are the main minor constituents. Processes of diatomite purification are mainly carried out by eliminating metal oxides (Al$_2$O$_3$ and Fe$_2$O$_3$) and concentrating the silica content [24]. The chemical composition of Jordanian diatomite is similar to sources found in other countries [25]. As well as the unique metal oxides constituents, diatomite has a high surface area. The surface area of natural diatomite used in this study is approximately 33 mg g^{-1}.

3.2. Characterisation of Mn-diatomite

The quantity of manganese oxide loaded on the diatomite surface depends on the nature of the surface, the solution acidity and the duration of the treatment. In this study, the loading on the surface of the diatomite was estimated to be approximately 0.38 g g^{-1}. The surface area of Mn-diatomite calculated by the Zn^{2+} adsorption method was estimated to

Table 1
Chemical composition of natural diatomite

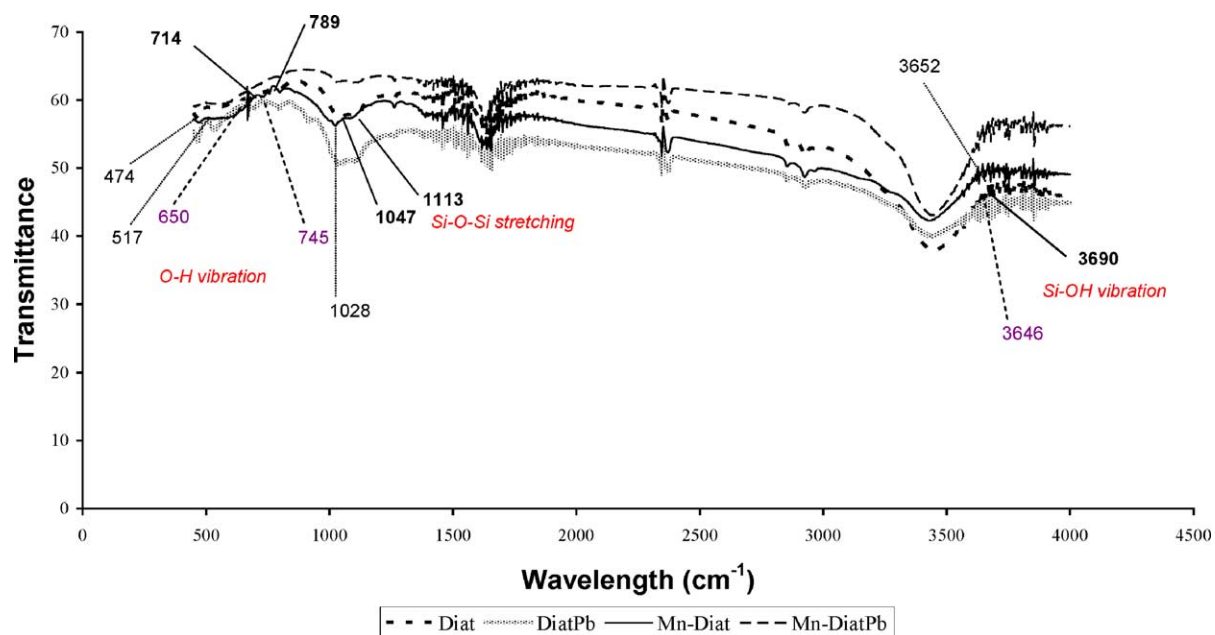| Oxide	Composition[a] (%)
SiO$_2$	72.50
TiO$_2$	–
Al$_2$O$_3$	11.42
Fe$_2$O$_3$	5.81
MnO	–
MgO	0.25
CaO	1.48
Na$_2$O	7.21
K$_2$O	0.69
P$_2$O$_5$	–
LOI[b]	–

[a] XRF analysis.
[b] Loss on ignition.

Fig. 2. FT-IR spectra of: diatomite, Mn-diatomite, adsorbed diatomite with lead and Mn-diatomite with lead. Experimental conditions: 0.05 g diatomite; 50 ppm metal ion concentration; temperature = 23 °C, particle size = 300–500 μm and pH = 4.

be approximately $80 \, m^2 \, g^{-1}$. This method was developed for manganese oxide surfaces, and depends on the presence of surface hydroxyl groups (OH^-) for estimating the surface area.

Understanding the mechanism of heavy metal ion adsorption onto a modified and solid oxide surface is essential for a full understanding of the removal of heavy metal ions from industrial wastewater. Fourier transform infrared (FT-IR) was used to evaluate the mechanism involved. FT-IR offers some indication of the ability of the heavy metals to react with the silanol groups which spread over the diatomite surface. Fig. 2 shows the FT-IR spectra of diatomite, Mn-diatomite adsorbed diatomite and Mn-diatomite with lead. The vibration of the Si–OH bond results in a band at $3700 \, cm^{-1}$, together with a doublet, due to O–H deformation, at approximately $800 \, cm^{-1}$.

The main adsorption bands of diatomite occurs at 3690, 1047, 1113, 910, 789 and $714 \, cm^{-1}$. After modification with manganese oxides, the aforementioned bands completely disappeared, which can be attributed to chemical interactions between the oxides and the silanol groups on the diatomite surface. The broad band at $3652 \, cm^{-1}$ in the modified diatomite spectrum represents the OH stretch of interlayer molecules and framework hydroxyl groups. The band at $1028 \, cm^{-1}$ is attributed to the deformation of Mn^{3+}–OH bonds. The most important peaks present in the IR spectrum of modified diatomite are 517 and $474 \, cm^{-1}$, which correspond to Mn–O stretching modes of the octahedral layers in the birnessite structure.

Fig. 3 shows that the diatomite frustules are completely modified by the manganese oxide treatment. The modified diatomite silica structure is of 'birnessite' type, which is characterised by platy crystals [26].
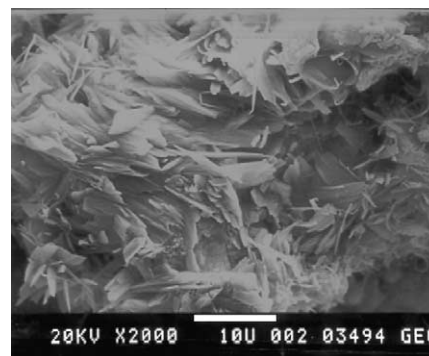

Fig. 3. Scanning electron micrograph for Mn-diatomite (magnification 2000×).

3.3. Stability of modified adsorbent (Mn-diatomite)

It has previously been reported that structural Mn^{2+} can be desorbed from the surface during adsorption of heavy metals [27,28]. Therefore, the stability of the manganese oxides deposited on the diatomite surface was examined. The results for desorption of Mn^{2+} ions from the surface into solution are summarised in Table 2. The results indicate that a small quantity of Mn^{2+} (0.02–0.04 ppm) can leave the

Table 2
Desorption of Mn^{2+} from Mn-diatomite surface

Time (h)	Mn^{2+} (ppm)
1.5	0.02
2.5	0.03
7.0	0.04
22.0	0.04

surface after agitation for 22 h. The low desorption of Mn^{2+} from the surface reflects the strong interaction between the diatomite and the manganese oxides, hence adding more stability and value to the modified adsorbent.

3.4. Adsorption capacity for heavy metals: adsorption isotherms

The batch isotherm studies were conducted under slightly acidic conditions (pH 4) for two main reasons. First, heavy metals normally start to precipitate (by forming metal oxides and hydroxides) under alkaline conditions. In the concentration range studied, heavy metals are expected to precipitate at $pH \geq 8$, therefore, a slightly acidic solution ensures that adsorption on diatomite and on Mn-diatomite is restricted to divalent ions rather than to highly absorbable metal hydroxide species. In addition, heavy metals are usually found in a cationic form in wastewater. Second, diatomite powder is slightly unstable in higher pH conditions. It is known that silica containing materials precipitate (dissolve) when exposed to alkaline solution. Moreover, it was found that the filtration quality is improved at acidic pH (pH < 4), with the material showing gel features under alkaline conditions. Thus, conducting the experiments at pH 4, ensures the presence of the divalent form of the ions and preserves the chemical stability of the diatomite. It is worth mentioning that, coating with manganese oxides improves the chemical strength of diatomite, therefore, avoiding the problem of gel formation. This can be considered as one of the advantages of chemical coating, or modification.

The use of mathematical modelling and representation of adsorption data is well studied, and forms the basis of any feasibility study on a potential new adsorbent. The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm; graph of the amount adsorbed against the equilibrium concentration, at a specific temperature. The nature of the interaction between the adsorbate and adsorbent, i.e. favourable or unfavourable, can be determined from the isotherm shape. The Langmuir isotherm has been applied to many adsorption systems including organic [29] and inorganic adsorbates [18]. The model is applicable in cases where only one molecular layer of adsorbate is formed at the adsorbent surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration; this corresponds to complete coverage of the adsorbent surface by a monomolecular layer of adsorbate, which remains constant even at higher adsorbate concentrations. The Langmuir equation can be presented by the well-known equation [30]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L}C_e \qquad (3)$$

where C_e and q_e are the solution ($mg\,g^{-1}$) and surface concentrations ($mg\,dm^{-3}$) for the adsorbate, respectively, and K_L and a are the isotherm constants for a particular
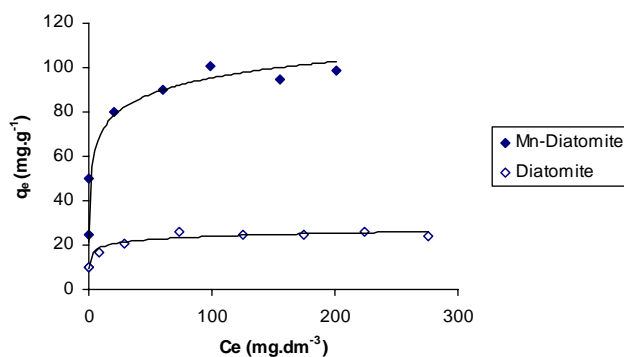

Fig. 4. Adsorption isotherm Pb^{2+} on diatomite and Mn-diatomite. Experimental conditions: mass = 0.050 g; volume of solution = 50 ml; $T = 23\,°C$; equilibrium time = 21 h; pH (initial) = 4.

solute–solvent combination. K_L can be obtained from the interception of a plot of C_e/q_e versus C_e. The constant, a, is related to the energy of adsorption. The essential characteristics of the Langmuir equation can also be expressed in terms of a dimensionless factor, R_l [29]:

$$R_l = \frac{1}{1 + K_L C_0} \qquad (4)$$

where C_0 is the highest initial dye concentration ($mg\,dm^{-3}$). The magnitude of the factor indicates the nature of the interaction and the isotherm type; unfavourable ($R_l > 1$), linear ($R_l = 1$), favourable ($0 < R_l < 1$), or irreversible ($R_l = 0$).

Adsorption isotherms of Pb^{2+}, Cu^{2+} and Cd^{2+} onto diatomite and Mn-diatomite are shown in Figs. 4–6. The adsorption isotherms take the form of a typical 'H', or 'high capacity', isotherm, according to 'Giles' classification [31], or Type-2 Class L (Langmuir Type), according to the classification of adsorption isotherms in solution [32]. Similar isotherms for heavy metal adsorption onto peat were reported by Allen and Brown [30]. As shown, the quantity of metal adsorbed increases with increasing metal concentration until a maximum adsorption (Q) is established. Furthermore, the isotherms show that adsorption capacity of
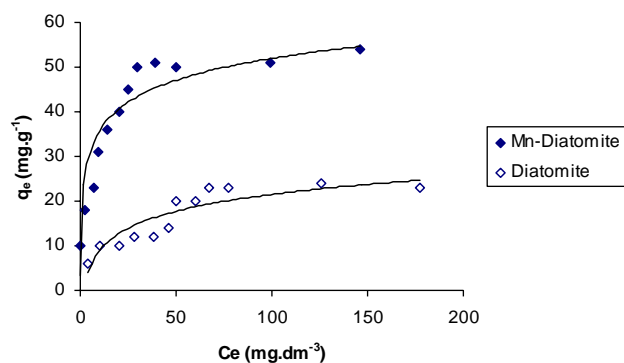

Fig. 5. Adsorption isotherm Cu^{2+} on diatomite and Mn-diatomite. Experimental conditions: mass = 0.050 g; volume of solution = 50 ml; $T = 23\,°C$; equilibrium time = 21 h; pH (initial) = 4.
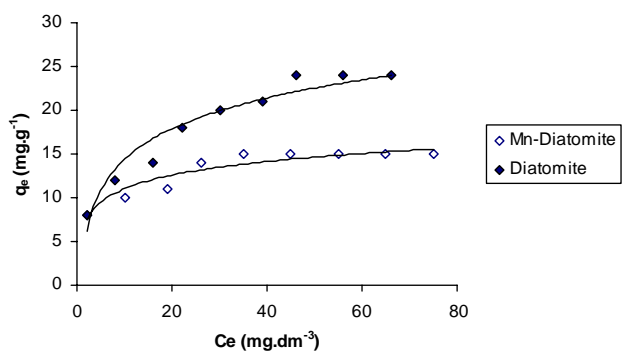
Fig. 6. Adsorption isotherm Cd^{2+} on diatomite and Mn-diatomite. Experimental conditions: mass $= 0.050$ g; volume of solution $= 50$ cm^3; $T = 23$ °C; equilibrium time $= 21$ h; pH (initial) $= 4$.

Fig. 7. Effect of manganese oxides loading on Pb^{2+} adsorption onto Mn-diatomite. Experimental conditions: adsorbent mass $= 0.050$ g; pH (initial) $= 4$; equilibrium time $= 20$ h; initial concentration $= 200$ mg dm^{-3}.

diatomite is greatly improved by modification with manganese oxides. Adsorption of heavy metals onto Mn-diatomite decreases in the order: $Pb^{2+} > Cu^{2+} > Cd^{2+}$. Similar adsorption behaviour on manganese oxides was reported by Gadde and Laitinen [33] and Murray [34]. The preferential adsorption of Pb^{2+} ions onto diatomite, Mn-diatomite and manganese oxides could be attributed to the electronegativity of the correspondingly heavier ions [30]. Metals of higher electronegativity are expected to have higher affinities; Pb^{2+} ions have a higher electronegativity when compared with Cu^{2+} and Cd^{2+} [35].

The maximum adsorption capacity (Q) reported in Table 3, demonstrates the higher capacity of Mn-diatomite for Pb^{2+}, Cu^{2+} and Cd^{2+} removal as compared with untreated diatomite. The adsorption capacities for diatomite are 24.9, 27.6 and 16.1 mg g^{-1} adsorbent for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively, while values of 99.0, 57.6 and 27.9 mg g^{-1} are obtained for Mn-diatomite.

Table 3 further shows that the metal uptake data agrees strongly with the Langmuir model. The model shows correlation coefficients of greater than 0.99 for all systems studied. This supports the theory that the number of sites on the diatomite surface is limited and the heavy metals form a monomolecular layer on the surface at maximum capacity. This also agrees with the observation that adsorption from an aqueous solution usually forms one layer on the adsor-
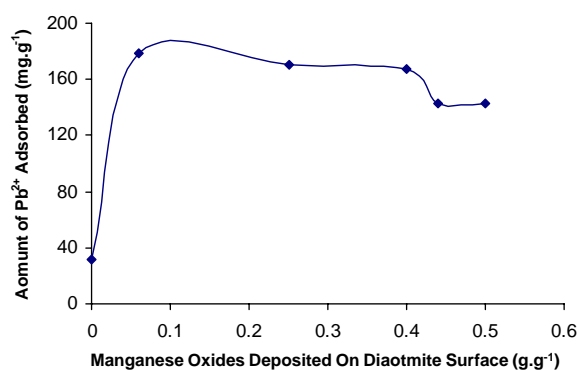
Table 3
Langmuir isotherm constants for adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} onto diatomite and Mn-diatomite

Metal	Q (mg g^{-1})	a (dm^3 mg^{-1})	K_L (dm^3 g^{-1})	R_l ($\times 10^{-3}$)	r^2
Diatomite					
Pb^{2+}	24.94	1.04	25.91	0.13	0.997
Cu^{2+}	27.55	0.04	1.03	4.8	0.940
Cd^{2+}	16.08	0.22	3.56	2.8	0.993
Mn-diatomite					
Pb^{2+}	99.00	0.52	51.28	0.065	0.998
Cu^{2+}	55.56	0.18	9.88	0.51	0.996
Cd^{2+}	27.86	0.10	2.64	4.2	0.979

bent surface [36]. Moreover, multilayer formation does not normally occur with metal adsorption. According to the R_l values detailed in Table 3, the adsorption behaviour of the three metals is extremely favourable ($R_l \ll 1$), tending to be a weakly irreversible adsorption ($R_l = 0$). Adsorption onto Mn-diatomite is more favourable as compared with diatomite, as indicated by R_l values for the former being lower. The higher 'a' value for Pb^{2+}, as compared with Cu^{2+} and Cd^{2+}, indicates that the Pb^{2+} ion has a higher adsorption energy, and as a result attains adsorptive capacities comparable with the ultimate capacity of the adsorbent.

Improvement in diatomite performance following modification could be attributed to an increase in surface area, as well as the resultant surface charge offered by the formation of the manganese oxides on the diatomite surface. Manganese oxides surface charge in solution is normally higher than other oxides, e.g. SiO_2, TiO_2 and Al_2O_3, due to the large acidity constant of the manganese oxide surface. This means that the surface ionises at a low pH and carries a net negative charge greater than that of other oxides [37]. If SiO_2 is assumed to be the main active centre for adsorption on diatomite, then the surface charge for diatomite and Mn-diatomite, at pH 4, is 0 and -40 μC cm^{-2}, respectively [34]. The high negative surface charge of Mn-diatomite makes the process the chemisorption, or 'nonexchangeable' adsorption type [38].

The effect of concentration of manganese oxide deposited on the surface on adsorption ability was investigated. As shown in Fig. 7, modification improves the performance of diatomite for heavy metal removal. Moreover, diatomite performance is better at lower loading (<0.4 g g^{-1} diatomite) of manganese oxides. The highest removal is achieved using diatomite loaded with 0.06 g manganese oxides per gram diatomite. At higher loading, diatomite efficiency levels off. This can be attributed to distribution of manganese oxides on all areas of the diatomite; both macro-and micropores. With lower loading (on a surface containing both macro and micropores), a large modified surface area is retained, however, higher quantities of coating may lead to complete blockage

Table 4
Adsorption capacities (mg g^{-1}) of natural adsorbents for Pb^{2+}, Cu^{2+} and Cd^{2+}

Adsorbent	Pb^{2+}	Cd^{2+}	Cu^{2+}
Diatomite	24.94	16.08	–[a]
Mn-diatomite	99.00	27.86	–
Zeolite [9]	155.4	84.3	–
Zeolite [42]	–	–	6.74
Clay [41]	58	16.5	–
Chitosan [10]	796	558	–
Activated carbon (authors, unpublished work)	22	13	–

[a] No results reported in literature.

of the micropores. The latter results in a lower surface area, and consequently a reduced number of active sites. Other researchers have reported that heavy metal sorption on modified sorbents increases by decreasing the surface loading [39,40].

3.5. Comparison of diatomite ability to remove heavy metals with other adsorbents

Numerous types of adsorbents have been tested for their ability to remove heavy metals. Studied adsorbents include organic materials, such as peat and chitosan, and inorganic, such as zeolite and clay [9]. To assess the performance of diatomite and Mn-diatomite, as potential low-cost sorbents for heavy metals, a comparison should be made with other reported results. As diatomite is inorganic in nature, mainly a mixture of inorganic oxides, adsorbent performance should be compared to adsorbents of similar origin. There is no published data on the capacity of natural diatomite towards heavy metals. The sorption capacity of zeolite and clay towards Pb^{2+} and Cd^{2+} are compared to that of diatomite and Mn-diatomite. Table 4 details the results, together with data for the sorption efficiency of chitosan, an organic-origin sorbent. Few literature research papers reported on the adsorption capacity of Cu^{2+}. Gupta and Torres [43], and Kadirvelu et al. [44], reported on the affinity of fly ash and activated carbon towards Cu^{2+}, respectively. In both cases the percentage removal rate was given and no adsorption isotherms were conducted. Therefore, no results could be included in Table 4.

It should be noted, however, that the adsorption capacity for heavy metals is highly dependent on the experimental conditions, e.g. pH, solution temperature, metal concentration, competing ions and adsorbent particle size. The conditions of adsorption experiments are not always reported in detail, therefore, the sorption capacities reported in Table 4 should be considered as an example of adsorbent effectiveness under specific experimental conditions.

As shown in Table 4, diatomite has a comparable capacity to natural silicate sorbents, i.e. clay, however, the adsorption capacity is much lower than zeolite. After surface modification, diatomite shows a higher efficiency than clay.

It is interesting to note that sorbents of organic-origin have an extraordinary capacity for heavy metals. The capacity of chitosan for Pb^{2+} is 30 times higher than diatomite and five times that of zeolite. It is worth mentioning that adsorption capacity is not the sole factor for evaluating the performance of natural sorbents. Filtration quality is another important factor. In fact, inorganic sorbents have better filtration characteristics than other organic-origin sorbents. Thus, zeolite and diatomite may show better performance in filtration systems than chitosan, which has less mechanical strength. It is interesting to mention that the capacity of diatomite and Mn-diatomite for heavy metals exceeds that of commercially activated carbons. This may be due to the fact that activated carbon gave a pH$_{ZPC}$ at 7.2 which strongly indicates that F-400 has a net positive surface charge (as equilibrium pH < pH$_{ZPC}$) during the adsorption process. As a result cationic heavy metal ions are repulsed from the surface. The high capacity of Mn-diatomite for heavy metals, as well as its good filtration characteristics, make it a favourable choice for use in column operations, where filtration is an important factor.

3.6. Effect of surface modification on filtration properties

Filtration quality is an important property of adsorbents used in water treatment, as most adsorption purification processes utilise filtration. The filtration rate of diatomite and Mn-diatomite, estimated using Eq. (2), is 1.53 and 68.57 ml m^{-2} s^{-1}, respectively. The increase in filtration rate is mainly due to the formation of manganese oxides on the surface. Bazhal et al. [23] showed that surface modification of diatomite with Ca(II), Al(III) and Sn(IV) ions resulted in an increased filtration rate as the cations have a high coagulation capacity, which gives a marked aggregation of the particles. Hence, it would appear that modification with manganese oxides has changed the colloid-chemical properties of diatomite and increased aggregation of the particles, which results in a higher filtration rate. Moore and Reid [13] reported an increase in filtration rates for acrylic fibres after modification with manganese oxides.

4. Conclusions

- Diatomite and manganese oxides modified diatomite are effective adsorbents for removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from solution at pH 4.
- Metal sorption capacity of diatomite is considerably improved after modification. This improvement in diatomite performance is attributed to an increase in surface area after coating, as well as the resultant surface charge due to the formation of manganese oxides on the diatomite surface.
- Adsorption capacity of diatomite increases with decreasing quantity of manganese oxides deposited. The performance is highest at a loading of 0.06 g oxide g^{-1} di-

atomite, after which adsorption capacity decreases to a constant value.

- Filtration quality of diatomite is significantly increased after modification with Mn-oxides. Improvements in filtration quality widen the applicability of diatomite in filtration systems.

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