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Study on the adsorption of metal ions onto azomethine functionalized magnetic nanoparticles in a single- and competitive-aqueous system

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ABSTRACT

This study evaluates the capability of azomethine functionalized magnetic nanoparticles to selectively remove heavy metal ions from aqueous solution containing complex matrix of contaminants and single contaminant system. The metal ions investigated were Pb^{2+}, Zn^{2+}, Cu^{2+} and As^{3+}. Batch adsorption studies involving the influence of pH and initial metal ion concentrations were assessed to determine the best experimental conditions. The adsorption capacities in a single-component system were higher than that obtained in a competitive adsorption system. The sequence of adsorption in both single and competitive component systems was Pb > Cu > As > Zn. This sequence was against the order obtained for their respective ionic radii in a competitive system. This was attributed to the fact that adsorption did not depend on the ionic radii of metal ions in solution but rather on the textural and functional characteristics of the adsorbent employed in this study. The result of influence of pH and initial metal ions concentration on the competitive removal of metal ions revealed that uptake of metal ions was pH and initial metal ion concentration dependent. Lastly, the removal of heavy metal ions from municipal wastewater demonstrated excellent adsorption efficiency confirming that azomethine functionalized magnetic nanoparticles exhibit good adsorption performance for the sequestering of complex matrix of contaminants.

Keywords: Adsorption; Competitive; Single component; Copper; Zinc; Arsenic; Lead; Wastewater

1. Introduction

The continuous release of substances containing heavy metals into the environment from mining, paint, welding, plating, electronic devices, alloy and cosmetic manufacturing industries is posing dangerous threat to the survival of living organisms. Among the most dangerous contaminants known to exist in wastewater are heavy metals. Heavy metals remain one of the non biodegradable and non-metabolized substances and because of this; they accumulate in the environment and cause severe risk to living organisms [1]. They usually find their way into the food chain through numerous ways and gradually cause harmful effects in organisms throughout their life cycle. A number of harmful effects experienced with heavy metal ingestion include fever, diarrhea, kidney and liver problems, neurological disorder and sometimes death. It is, therefore, important to remove heavy metals from aqueous solutions before their disposal into the environment.

Since the advent of nanotechnology, several efforts have been geared toward synthesizing new nanosized materials that will efficiently cater for these heavy metals in aqueous solutions by preferentially removing them from solution at least to non-toxic levels recommended by regulatory agencies. Recently attention has been tailored towards magnetic nanoparticles (MNPs) because of their unique properties including high contaminant removing capabilities, low cost, high superparamagnetism which

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will aid easy separation from solution and high surface area unlike other materials such as kaolin [2], chitosan [3], ion-exchange resins [4], carbon nanotubes [5], clay [6], activated carbon [7] and titanium dioxide [8] which either has low adsorption capability, separation difficulty or regenerability problems inherent in them. Functionalized MNPs possess even higher removal capacity than bare MNPs because of the presence of functional groups on their surface which enhances the uptake of heavy metals from aqueous solutions. Here, we introduced Schiff base ligand with functional azomethine group, 4-{[(E)-phenylmethylidene] amino}benzoic acid through covalent bonding to the surface of MNPs so as to enhance its capabilities toward heavy metal removal.

Different types of techniques including oxidation [9], ion-exchange [10], coagulation [11], ultrafiltration, adsorption and chemical precipitation [12] have been applied to wastewater for the removal of heavy metal ions to relatively low amount acceptable by regulatory agencies. But adsorption technique is preferred in this study for the removal of contaminants using functionalized MNPs because of its ease of operation; low assemble cost, ability to regenerate adsorbents, broad acceptability and high efficiency.

This study aims at examining the potential of azomethine functionalized magnetic nanoparticles (MNP-Maph) for the effective removal of Pb^{2+}, Zn^{2+}, Cu^{2+} and As^{3+} by adsorption in a single-metal ion system and complex metal ion matrix. Adsorption experiment involving change in pH and initial metal ions concentration were also examined so as to reveal the best experimental condition for adsorption.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical grade and used as received. Nickel (II) chloride hexahydrate and iron (III) chloride hexahydrate, ethanol, ammonia (25%), sodium hydroxide pellet and hydrochloric acid were supplied by Merck (Pty) Ltd., South Africa. Dicyclohexylcarbodiimide (DCC), 4-aminobenzoic acid, tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxylsilane (APTES) were supplied by Sigma-Aldrich (South Africa) while 4-dimethylaminopyridine (DMAP) and benzaldehyde were supplied by SAAR Chem (South Africa) and dimethylformamide (DMF) was supplied by BDH Limited, Poole, England. Analytical grade zinc metal, copper metal and lead metal powders and arsenic (III) standard solution were supplied by Industrial Analytical (Pty) Ltd., South Africa.

2.2. Instruments

Thermo Fisher iCE 3500 flame atomic absorption spectrophotometer (FAAS) was used to determine the concentrations (initial and final) of Cu^{2+}, Pb^{2+}, As^{3+} and Zn^{2+} in solution. The calibration of the instrument was carried out for the determination of these metals by obtaining a calibration plot from standard solutions within concentration range of 0 and 120 mg L^{-1} (depending on the metal ion, five different calibration points with different concentrations were used to plot the calibration curves) at each time of metal ion concentration determination, the initial and final concentrations of Cu^{2+}, Pb^{2+}, As^{3+} and Zn^{2+} were obtained from these calibrations.

2.3. Preparation of nanomaterials

MNPs were synthesized by the coprecipitation method involving $NiCl_2.6H_2O$ and $FeCl_3.6H_2O$ at pH 11.0 under inert atmosphere for 3 h. The obtained MNPs were coated with silica to allow for further functionalization using TEOS. The silica modified MNPs were reacted with APTES to afford amine functionalized magnetic nanoparticles ($MNPs-NH_2$). 4-{[(E)-phenylmethylidene]amino}benzoic acid (100 mg) was covalently bonded to amine functionalized MNPs (200 mg) in the presence of DCC (100 mg) and DMAP (70 mg). After 48 h of stirring, the product obtained, azomethine functionalized magnetic nanoparticles (MNP-Maph) was collected with ethanol and washed thoroughly with deionized water to remove DMF and DCC, respectively, and the crude was separated from solution by using a magnet. The collected crude was oven dried at 100°C for 2 d. Details of the synthesis of Schiff base ligands 4-{[(E)-phenylmethylidene]amino}benzoic acid and the characterization of MNP-Maph have been previously reported by Ojemaye et al. [13].

2.4. Adsorbate preparation

Pure metal ion powder (1 g) of Pb^{2+}, Zn^{2+} and Cu^{2+} was separately dissolved in approximately 100 mL of 5 M nitric acid and made up to 1,000 mL mark in volumetric flasks with deionized water to afford our stock solutions. Working solutions were daily prepared from the stock solutions of As^{3+} purchased from the suppliers.

2.5. Batch adsorption experiment

Two different adsorption experiments were conducted in this study; single-component system and complex metal ion matrix. For the single-component adsorption system, experiment were conducted at pH 5.0 with metal ion concentration ranging from 10 to 100 mg L^{-1}, contact time of 4 h and agitating speed of 200 rpm using 20 mL parts of metal ions at 20°C and 40 mg adsorbent amount. The suspensions were separately filtered with the aid of an external magnetic field after agitation and the filtrates aspirated into FAAS for the final concentrations of each metal ion.

For the complex metal ion matrix, parameters influencing adsorption performance such as the effect of pH, contact time and adsorbent amounts were varied. The experiment involving the effect of pH was carried out at pH values 1–10 by adjusting using 50 mg L^{-1} 20 mL adsorbate concentrations to the desired pH using 0.1 mol L^{-1} HNO_3 or NaOH. The suspension was agitated at 200 rpm, 100 mg adsorbent amount at 20°C for 24 h and separated from aqueous solution at the completion of the allotted time for adsorption by using a bar magnet. The final concentrations of metal ion in the filtrates were determined by aspirating into flame atomic absorption spectroscopy.

The percentage removal and adsorption capacity (q_e) of metal ions were deduced from Eqs. (1) and (2), respectively.

$$\% \text{ Adsorbed} = \left(\frac{C_i - C_{\text{eq}}}{C_i}\right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_i - C_{\text{eq}}}{w}\right) \times V \quad (2)$$

where C_i and C_{eq} are the initial and equilibrium Pb^{2+}, Zn^{2+}, Cu^{2+} and As^{3+} concentration in mg L^{-1}, q_e is the adsorption capacity in mg g^{-1}, w in mg is the mass of the adsorbent and V is the volume of the adsorbate solution used in L.

2.6. Real wastewater analysis

The assessment of MNP-Maph for the removal of Cu^{2+} and Zn^{2+} in municipal wastewater was determined using nine different wastewater samples obtained from three different municipal wastewater treatment facilities in the Eastern Cape region of South Africa. Simulated water of similar initial metal ion concentrations was also prepared and assessed for the simultaneous removal of Cu^{2+} and Zn^{2+}. This was carried out at optimum conditions using 100 mg of adsorbent dose, 50 mL of adsorbate amount at pH 6.0 for 4 h and at a temperature of 20°C. After agitation, the suspensions were filtered magnetically and the filtrates aspirated into FAAS for the final concentration of Cu^{2+} and Zn^{2+}. The final metal ions concentrations were used to determine the percentage adsorption and adsorption capacity for each metal ion using Eqs. (1) and (2), respectively.

3. Result and discussion

3.1. Characterization of adsorbents

The synthesis of MNP-Maph was successfully carried out and the detailed characterization done using various techniques as been described in our earlier reported study [13].

Major distinctive characteristic of this adsorbent is presented in Table 1 for thermal measurement using TGA between MNP-Maph and $MNP\text{-}NH_2$. This result indicates the purity and successful synthesis of MNP-Maph. It can be observed that the introduction of Maph-COOH to $MNP\text{-}NH_2$ to afford MNP-Maph resulted into about 4% weight loss around 620°C–870°C. Also FTIR spectra result (Table 2) showed that C=N str was observed on the spectra of MNP-Maph after functionalization of $MNP\text{-}NH_2$ with Maph-COOH.

Due to the increased removal of metal ions from aqueous solutions by azomethine functionalized MNPs, MNP-Maph, the potential of the functionalized material for the removal of metal ions in a complex matrix system was examined so as to determine the efficiency of MNP-Maph for application in real-life scenarios in which wastewater samples contain complex matrix of contaminants simultaneously in solution. The removal efficiency of MNP-Maph in a single-metal ion system is compared with those obtained in a complex metal ion matrix in the section.

3.2. Single metal ion system adsorption

The removal of metal ions in a single adsorption system was conducted at pH 5.0 at different initial adsorbate concentration ranging from 10 to 100 mg L^{-1}. The limit of detection of these metal ions are as follows: 9.0, 9.0, 5.0 and 3.0 mg L^{-1} for Cu^{2+}, Pb^{2+}, As^{3+} and Zn^{2+}, respectively, using FAAS. As observed in Fig. 1, the removal of metal ions increases as adsorbate concentration increases. This can be ascribed to the fact that as initial adsorbate concentration increases, there is an enhanced equilibrium force required to surmount the resistance of the adsorbent–adsorbate thereby resulting into an increased adsorption capacity [14]. The order of removal of metal ions was noticed to be $Pb^{2+} > Cu^{2+} > Zn^{2+} > As^{3+}$ (Fig. 1).

3.3. Adsorption of metal ions in a competitive system

3.3.1. Effect of pH

The solution pH is a major deciding factor that controls adsorption process especially heavy metal ions removal because it affects ion speciation and surface charge. The effect of pH on competitive adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+} and As^{3+} by MNP-Maph from aqueous solution was evaluated

Table 1
Thermal decomposition characteristics of functionalized magnetic nanoparticles

Adsorbents	Temperature (°C)			
	100°C–120°C	120°C–350°C	350°C–600°C	620°C–870°C
$MNP\text{-}NH_2$ (% weight loss)	3.469	6.904	7.8	–
MNP-Maph (% weight loss)	1.107	6.521	7.8	3.806

Table 2
Major FTIR adsorption bands of synthesized materials

Adsorbents and ligand	FTIR bands					
	O–H Str	$–CH_2$ Str	C=N Str	C–N Str	Si-O Str	Fe–O Str
MNP	3,600	–	–	–	–	530
$MNP\text{-}NH_2$	–	–	–	1,280	1,100	530
Maph-COOH	3,500	2,900	1,550	1,285	–	–
MNP-Maph	–	2,900	1,600	1,300	1,100	530

from pH values 1–10 using 100 mg adsorbent, 50 mL each of adsorbate metal ion concentrations and 20°C (Fig. 2). The effect of pH indicates that the adsorption of all metal ions in solution increases as pH increases, the adsorption of As^{3+} was observed to decrease slowly at pH > 8.0 unlike that of other metals which was observed to be steady from pH > 7.0. The point of zero charge, pH_{pzc} is a parameter which gives information about the surface charge of the adsorbent. The pH_{pzc} of this adsorbent has been reported to be 5.8 in our previous study [13]. When pH value of adsorption is lower than that of the pH_{pzc}, the surface charge of the adsorbent will be positive and vice versa [15]. A decrease in the removal of metal ions was observed at lower pH values signifying that competition for adsorption took place at this pH. This is as a result of the presence of H^+ at lower pH values which competes with the metal ions in solution for space on the surface of the adsorbent for binding and the precipitation of the metal ions to their hydroxides at pH values greater than 5.8. Also, the calculated ksp values of the metal ions, Cu^{2+}: 4.8×10^{-20}, Pb^{2+}: 1.43×10^{-20}, As^{3+}: 1.38×10^{-19} and Zn^{2+}: 1.17×10^{-17} indicate that hydrolysis of metal ions was mainly responsible for their removal from aqueous solution and at higher pH values, pH greater than 5.8, precipitation occurred as a result of the complexation of the inner sphere but for outer sphere, there is a weaker interaction between adsorbent and metal ions.

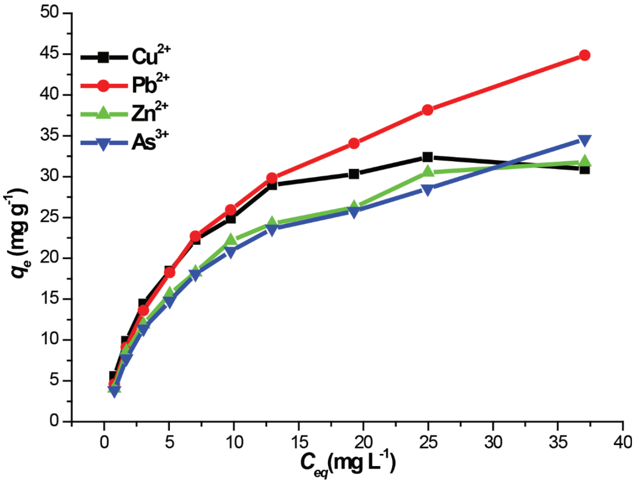

Fig. 1. Adsorption of Cu^{2+}, Pb^{2+}, Zn^{2+} and As^{3+} in a single metal ion system by MNP-Maph at pH 5.0, 4 h, 20°C, adsorbent dose of 40 mg and 200 rpm.

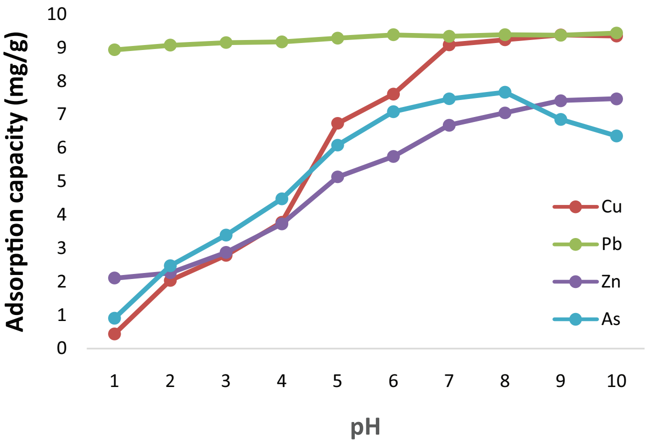

Fig. 2. Effect of pH in a competitive adsorption system at 20°C, adsorbent dose of 100 mg, 50 mg L^{-1} adsorbate solution and 200 rpm for the removal of Cu^{2+}, Pb^{2+}, Zn^{2+} and As^{3+} by MNP-Maph.

Therefore, the order of competitive removal of metal ions was $Pb^{2+} > Cu^{2+} > As^{3+} > Zn^{2+}$. This trend has been previously reported by other studies [16,17]. For subsequent experiments on the competitive removal of metal ions from solution in this study, pH 6.0 was adopted.

3.3.2. Effect of time

In Fig. 3, the removal capacity of MNP-Maph for all heavy metals was evaluated as a function of time in a competitive system. It was observed that Cu^{2+}, Pb^{2+} and Zn^{2+} adsorption by MNP-Maph rose linearly with a rapid removal in about 45 min. This was not so for As^{3+} as adsorption and desorption was noticed in the first 10 min followed by a linear rise thereafter. Although the removal efficiency was observed to be maximum within 45 min and in this order $Cu^{2+} > Pb^{2+} > As^{3+} > Zn^{2+}$ for all metal ions, adsorption experiment for all other parameters was conducted in the duration of 4 h to ensure an effective removal performance of MNP-Maph. Yayayuruk et al. [18] also reported findings similar to the findings in the present study.

3.3.3. Metal ion adsorption at the same initial concentration

The simultaneous uptake of metal ions in a complex matrix involving equal amount of metal ions was conducted at pH 6.0. The percentage uptake of all metal ions except As^{3+} decreases as initial metal ion concentration increases (Fig. 4). Also Fig. 4 shows the uptake of metal ions as a function of initial metal ion concentration. It can be observed that as the initial metal ion concentration increases, an increase in the adsorption capacity of the metal ions was noticed. In both situations, Pb^{2+}

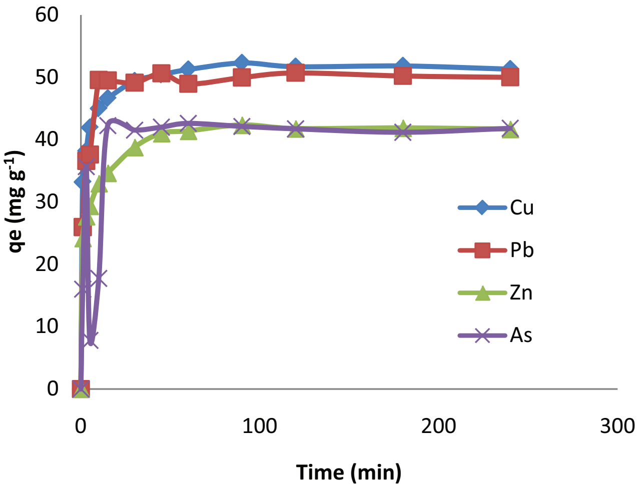

Fig. 3. Effect of time in a competitive adsorption system at 20°C, adsorbent dose of 100 mg, 50 mg L^{-1} adsorbate solution and 200 rpm for the removal of Cu^{2+}, Pb^{2+}, Zn^{2+} and As^{3+} by MNP-Maph.

was observed to have the highest uptake and Zn^{2+} having the lowest uptake across all concentrations. The adsorption capacity was in the sequence of Pb^{2+} (1.72 to 13.12 mg g^{-1}) > Cu^{2+} (1.80 to 12.00 mg g^{-1}) > As^{3+} (1.51 to 11.91 mg g^{-1}) > Zn^{2+} (1.45 to 11.11 mg g^{-1} (Fig. 4). Previous studies on the competitive adsorption of metal ions have reported that the adsorption capacity of metal ions in a complex mixture of contaminants is determined by the ionic radii of the metal ions in solution [19]. Ionic radii of metal species is inversely proportional to their adsorption maximum, the smaller the ionic radii of a metal specie, the higher its adsorption capacity and on the other hand, the greater the ionic radii, the lower and weaker the adsorption capacity of the metal specie [20]. The ionic radii of the metal ions studied in this report is in the sequence Pb^{2+} (4.01 Å) < As^{3+} (4.17 Å) < Cu^{2+} (4.19 Å) < Zn^{2+} (4.30 Å). The trend of adsorption of the metal ions obtained in this study was slightly different from the sequence obtained for their ionic radii; results similar to this have been reported in previous studies [21,22]. Although several studies have reported many investigations involving the competitive removal of metal ions in a complex matrix where similar trend was observed between adsorption capacity and ionic radii of metal ions in solution [23, 24], the removal of metal ions from aqueous solution may sometimes depend majorly on the textural and functional properties of the adsorbent used [25] as also observed in this study.

3.4. Metal ion adsorption at different initial concentration

The adsorption of metal ions in a competitive system is influenced by many factors, among which are the ratio of metal ions in a complex matrix of contaminants, the properties of the adsorbent materials and the nature of the metal ions. Herein, we consider the effect of initial metal ion concentration of competing metal ions in solution for the adsorption of a specific metal in aqueous solution by keeping its concentration at 25 mg L^{-1} and varying competing metal ion concentrations from 10 to 50 mg L^{-1}.

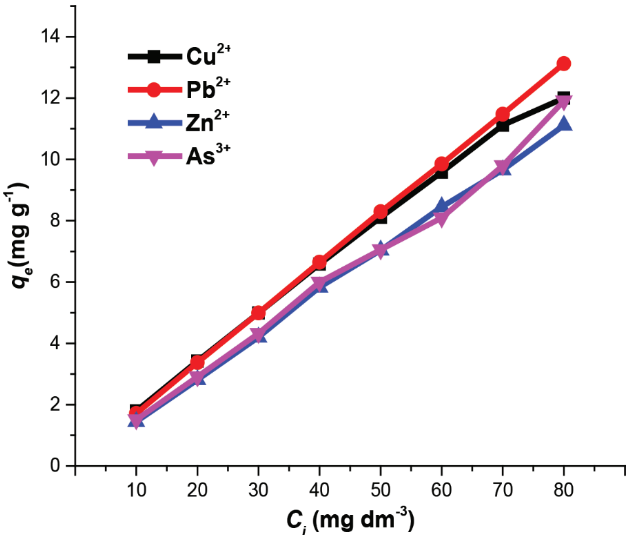

Fig. 4. Adsorption capacity of Cu^{2+}, Pb^{2+}, Zn^{2+} and As^{3+} by MNP-Maph at the same initial metal ion concentration at pH 6.0, 20 mL adsorbate amount and 4 h.

3.4.1. Competitive adsorption of Pb^{2+} in the presence of Cu^{2+}, Zn^{2+} and As^{3+}

The effect of the presence of other metal ions on the selective adsorption of Pb^{2+} was evaluated by fixing its concentration at 25 mg L^{-1} while varying the concentration of other competing ions between 10 and 50 mg L^{-1}.

Fig. 5 indicates that the removal of all competing ions in solution decreases as initial metal ion concentration increases. The percentage adsorption of Pb^{2+} with a fixed initial concentration decreases from 79.42% to 56.40% as the initial metal ion concentration of other species in solution increases from 10 to 50 mg L^{-1}. The percentage removal of Cu^{2+} showed to be the highest among the metal ion in solution across all concentration from 82.52% to 59.48%. This observation showed that there is an increase in competition for binding on the active site on the adsorbent as a result of the presence of other competing ions in solution making Pb^{2+} removal not to be the highest. This same observation was also noticed for Zn^{2+} and As^{3+} removal with both metal ions having their own fair share of percentage adsorption from 64.01% to 29.89% and 69.56% to 39.25%, respectively, as the initial metal ion increases.

The order of metal ion removal when Pb^{2+} was fixed at a particular concentration and other metal ions were varied was observed to be $Cu^{2+} > Pb^{2+} > As^{3+} > Zn^{2+}$.

3.4.2. Competitive adsorption of Cu^{2+} in the presence of Pb^{2+}, Zn^{2+} and As^{3+}

The influence of the presence of varying concentration of other competing ions on the removal of Cu^{2+} was conducted at pH 6.0 using 100 mg dose of adsorbent and 20°C. The adsorption of Cu^{2+} gradually decreases as the concentration of other competing ions (Fig. 6) increases. The percentage removal of Cu^{2+} ion was observed to be the highest among metal ions in solution with percentage adsorption efficiency ranging from 88.66% to 57.30% as the concentration of other

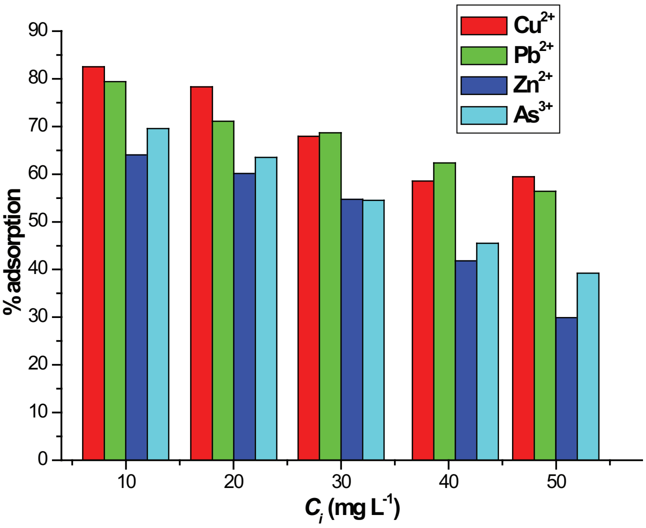

Fig. 5. Multi-component adsorption of Pb^{2+} at constant concentration of 25 mg L^{-1} and varying concentrations of Cu^{2+}, Zn^{2+} and As^{3+} (conditions: pH 6.0, 100 mg adsorbent dose, 4 h, 20°C and 200 rpm).

competing ions increases from 10 to 50 mg L^{-1}. The percentage removal of other competing ions in solution with the exception of As^{3+} also decreases as their metal ion concentration increases. This trend could be ascribed to the presence of competing ions jostling for binding on the active site of the adsorbent. Observation similar to this was reported by Oyetade et al. [25], Kavand et al. [26], Swayampakula et al. [27]. The percentage removal of Pb^{2+} and Zn^{2+} across all initial concentration is in the range of 80.77%–50.74% and 58.91%–22.60%, respectively. The removal of As^{3+} did not result into a significant decrease as its concentration increases; as a result this was not influenced by a change in concentration. The order of removal of competing ions can be observed to be $Cu^{2+} > Pb^{2+} > As^{3+} > Zn^{2+}$.

3.4.3. Competitive adsorption of Zn^{2+} in the presence of Cu^{2+}, Pb^{2+} and As^{3+}

The competitive removal of Zn^{2+} at a fixed concentration (25 mg L^{-1}) in the presence of varying amount (10–50 mg L^{-1}) of other ions was conducted at pH 6.0 for 4 h by using 100 mg adsorbent dose and at 20°C (Fig. 7). The percentage removal of Zn^{2+} was observed to increase as the initial concentration of competing ions increases. Although the removal efficiency of Zn^{2+} was not seen to be the highest, the affinity of Zn^{2+} by MNP-Maph was still noticeable even at higher concentrations of other metal ions. This same observation was noticed for other metal ions in solution with Cu^{2+} having the highest removal efficiency across all temperatures. The trend for the uptake of metal ions at fixed initial Zn^{2+} concentration is in the order $Cu^{2+} > Pb^{2+} > As^{3+} > Zn^{2+}$.

3.4.4. Competitive adsorption of As^{3+} in the presence of Cu^{2+}, Pb^{2+} and Zn^{2+}

The effect of the presence of varying concentration of other metals ions on the removal of As^{3+} from aqueous solution was conducted at pH 6.0, for 4 h by using 100 mg adsorbent dose and at 20°C (Fig. 8). The uptake of As^{3+} was observed to decrease as the initial concentration of other ions in solution increases. Although the As^{3+} uptake was not the highest in the adsorption process, the uptake was still very high with percentage removal going from 70.35% to 30.95% with its removal efficiency decreasing as the initial metal ion concentration of other competing metal increases. Cu^{2+} again showed higher removal efficiency compared with all other ions in solution. The removal of Cu^{2+} and every other ion in solution decreases as their initial concentration increases from 10 to 50 mg L^{-1}. The order of removal can be found to be $Cu^{2+} > Pb^{2+} > As^{3+} > Zn^{2+}$.

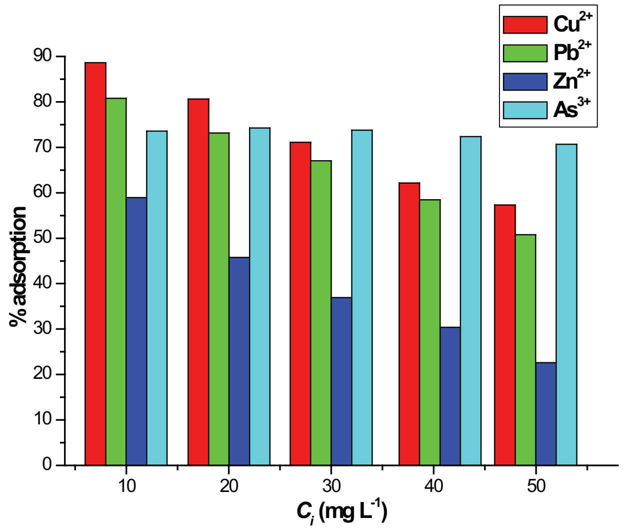

Fig. 6. Multi-component adsorption of Cu^{2+} at constant concentration of 25 mg L^{-1} and varying concentrations of Pb^{2+}, Zn^{2+} and As^{3+} (conditions: pH 6.0, 100 mg adsorbent dose, 4 h, 20°C and 200 rpm).

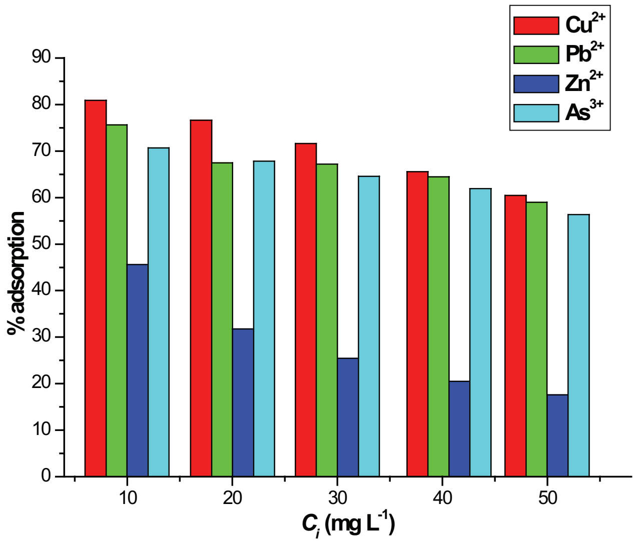

Fig. 7. Multi-component adsorption of Zn^{2+} at constant concentration of 25 mg L^{-1} and varying concentrations of Cu^{2+}, Pb^{2+} and As^{3+} (conditions: pH 6.0, 100 mg adsorbent dose, 4 h, 20°C and 200 rpm).

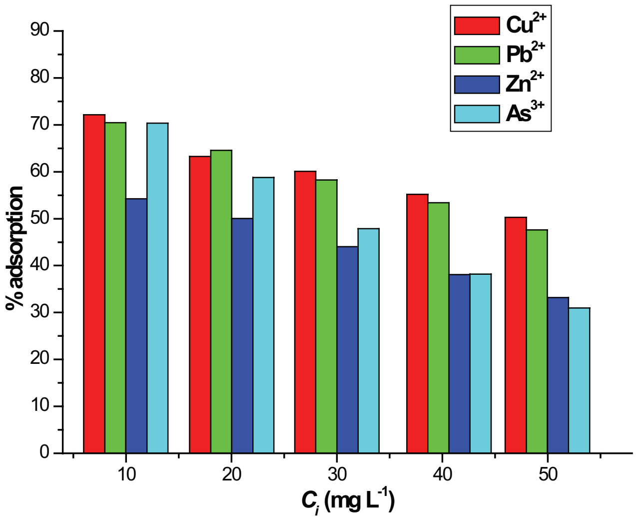

Fig. 8. Multi component adsorption of As^{3+} at constant concentration of 25 mg L^{-1} and varying concentrations of Cu^{2+}, Pb^{2+} and Zn^{2+} (conditions: pH 6.0, 100 mg adsorbent dose, 4 h, 20°C and 200 rpm).

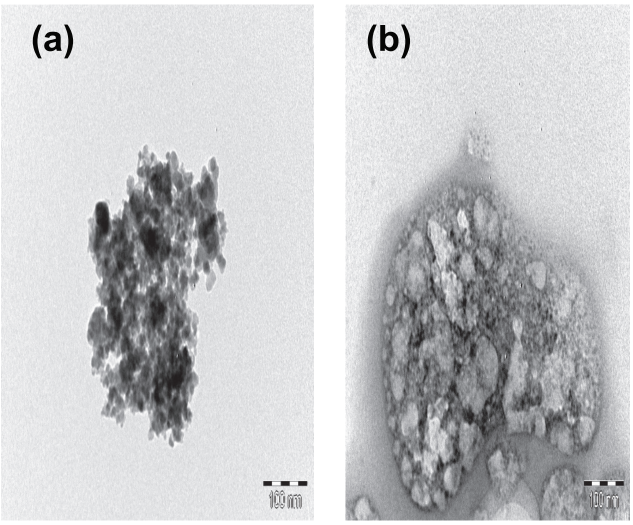

Fig. 9. TEM images of MNP-Maph (a) before and (b) after adsorption.

3.5. TEM result of adsorbent after adsorption

The test to ascertain the adsorption of metal ions on the surface of the adsorbent was carried with the use of transmission electron microscopy (TEM) (Fig. 9). The result obtained showed that a spherical shaped material was synthesized with little or no aggregation (Fig. 9(a)) but after adsorption, the spherically shaped material was observed to show a rock-like shaped nano-adsorbent (Fig. 9(b)). This result indicate that adsorption of metal ions to the surface of the adsorbent has taken place.

3.6. Analysis of municipal wastewater

The assessment of MNP-Maph for the removal of Cu^{2+} and Zn^{2+} in municipal wastewater was determined using nine different wastewater samples obtained from three different municipal wastewater treatment facilities in the Eastern Cape region of South Africa. Simulated water of similar initial metal ion concentrations was also prepared and assessed for the simultaneous removal of Cu^{2+} and Zn^{2+}.

Table 3
Analytical data for municipal wastewater samples at pH 6.0, 200 rpm, 20°C, 100 mg of adsorbent, 50 mL of adsorbate for 4 h

Metal ion	Wastewater treatment plants	C_i (mg L^{-1})	C_{eq} (mg L^{-1})	Mass (g)	Volume (mL)	% Adsorbed
Cu^{2+}	Simulated water	10.02	1.08	0.105	0.05	89.22
	Adelaide					
	Influent	10.21	1.78	0.100	0.05	82.57
	After aeration	9.37	1.69	0.101	0.05	81.96
	Effluent	10.64	1.93	0.113	0.05	81.86
	Berlin					
	Influent	9.76	1.82	0.100	0.05	81.35
	After aeration	9.50	1.89	0.108	0.05	80.11
	Effluent	9.42	1.93	0.103	0.05	79.51
	Seymour					
	Influent	10.54	2,02	0.101	0.05	80.83
	After aeration	10.01	1.96	0.100	0.05	80.42
	Effluent	9.84	1.86	0.100	0.05	81.10
Zn^{2+}	Simulated water	10.00	1.88	0.105	0.05	81.20
	Adelaide					
	Influent	9.90	2.97	0.100	0.05	70.00
	After aeration	9.55	2.75	0.101	0.05	71.20
	Effluent	8.96	2.59	0.113	0.05	71.09
	Berlin					
	Influent	10.13	2.96	0.100	0.05	70.78
	After aeration	10.79	3.16	0.108	0.05	70.71
	Effluent	11.24	3.26	0.103	0.05	71.00
	Seymour					
	Influent	11.60	3.35	0.101	0.05	71.12
	After aeration	11.33	3.15	0.100	0.05	72.20
	Effluent	10.61	2.94	0.100	0.05	72.29

Although the initial metal ion concentration of Cu^{2+} and Zn^{2+} in the wastewater samples was within 10 mg L^{-1}, the initial As^{3+} concentration was found to be within 1 mg L^{-1}, attempt to spike the As^{3+} concentration, will alter the adsorbent metal ion binding affinity, ionic configuration and metal speciation of the samples, thereby influencing the real adsorption efficiency of other metal ions in solution. Hence, we conducted competitive adsorption on the real wastewater samples by MNP-Maph for Cu^{2+} and Zn^{2+} sequestering only since their initial concentrations are within measureable amounts. The removal efficiencies of Cu^{2+} and Zn^{2+} in all the water samples were observed to be greater than 80% and 70%, respectively (Table 3) as it is in the case of simulated water. This result, therefore, indicates that MNP-Maph is a promising adsorbent for the uptake of metal ions in a complex contaminant matrix going by the result obtained in this study. Also, the adsorption method employed in this study is efficient enough when employed to municipal wastewater for the simultaneous removal of contaminants.

4. Conclusion

Investigation into the competitive removal of heavy metal ions from aqueous solution by MNP-Maph was conducted through some batch adsorption experiment. Two adsorption component systems, single and competitive systems were assessed to know the extent and trend of the uptake of heavy metal ions.

The uptake of metal ions in a single-component system was considerably high with adsorption in the sequence Pb > Cu > Zn > As while in the competitive adsorption system, the sequence of uptake was from Cu > Pb > As > Zn in all but one of the systems studied. The removal efficiencies of metal ions in a competitive system were low compared with the result obtained in a single-adsorption system; this is because in a competitive adsorption system, there is a strong competition for binding onto the surface of the active site on MNP-Maph irrespective of their initial metal ion concentration.

Attempt made to employ MNP-Maph for the removal of Cu^{2+} and Zn^{2+} from municipal wastewater, a typical complex contaminant matrix suggested that removal efficiencies for Cu^{2+} and Zn^{2+} were considerably high with more than 80% and 70% uptake observed, respectively. This, therefore, demonstrates the suitability of MNP-Maph to sequestially remove divalent and trivalent metal ions from wastewater in real-life situations confirming the adsorptive potentials of MNP-Maph for future applications.

Conflict of interest

The authors wish to declare that there is no conflict of interest regarding the publication of this manuscript.

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References

[1] F. Ge, M. Li, H. Ye, B. Zhao, Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles, J. Hazard. Mater., 211–212 (2012) 366–372.

[2] X. Zhang, S. Lin, X. Lu, Z. Chen, Removal of Pb (II) from water using synthesized kaolin supported nanoscale zero-valent iron, Chem. Eng. J., 163 (2010) 243–248.

[3] R. Laus, V.T. De Fávere, Competitive adsorption of Cu(II) and Cd(II) ions by chitosan crosslinked with epichlorohydrin-triphosphate, Bioresour. Technol., 102 (2011) 8769–8776.

[4] L. Wang, L. Yang, Y. Li, Y. Zhang, X. Ma, Z. Ye, Study on adsorption mechanism of Pb (II) and Cu (II) in aqueous solution using PS-EDTA resin, Chem. Eng. J., 163 (2010) 364–372.

[5] W. Yang, P. Ding, L. Zhou, J. Yu, X. Chen, F. Jiao, Preparation of diamine modified mesoporous silica on multi-walled carbon nanotubes for the adsorption of heavy metals in aqueous solution, Appl. Surf. Sci., 282 (2013) 38–45.

[6] N.C. Dias, P.A. Steiner, M. Cristina, B. Braga, Characterization and modification of a clay mineral used in adsorption tests, J. Miner. Mater. Charact. Eng., 3 (2015) 277–288.

[7] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse - an agricultural waste, Water Res., 36 (2002) 2304–2318.

[8] M.O. Ojemaye, O.O. Okoh, A.I. Okoh, Performance of $NiFe_2O_4$-SiO_2-TiO_2 magnetic photocatalyst for the effective photocatalytic reduction of Cr (VI) in aqueous solutions, J. Nanomater., 2017 (2017) 1–11.

[9] H.S. El-desoky, M.M. Ghoneim, R. El-sheikh, N.M. Zidan, Oxidation of Levafix CA reactive azo-dyes in industrial wastewater of textile dyeing by electro-generated Fenton's reagent, J. Hazard. Mater., 175 (2010) 858–865.

[10] I.J. Vassilis, Ion exchange and adsorption fixed bed operations for wastewater treatment - Part I : modelling fundamentals and hydraulic analysis, J. Eng. Studies Res., 16 (2010) 29–41.

[11] A.Y. Zahrim, N. Hilal, Treatment of highly concentrated dye solution by coagulation/flocculation-sand filtration and nanofiltration, Water Res. Ind., 3 (2013) 23–34.

[12] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arab. J. Chem., 4 (2011) 361–377.

[13] M.O. Ojemaye, O.O. Okoh, A.I. Okoh, Adsorption of Cu^{2+} from aqueous solution by a novel material; azomethine functionalized magnetic nanoparticles, Sep. Purif. Technol., 183 (2017) 204–215.

[14] I.A.A. Hamza, B.S. Martincigh, J.C. Ngila, V.O. Nyamori, Adsorption studies of aqueous Pb(II) onto a sugarcane bagasse/multi-walled carbon nanotube composite, Phys. Chem. Earth, 66 (2013) 157–166.

[15] L. Lin, X. Xu, C. Papelis, T.Y. Cath, P. Xu, Sorption of metals and metalloids from reverse osmosis concentrate on drinking water treatment solids, Sep. Purif. Technol., 134 (2014) 37–45.

[16] L.G. Lv, G. Tsoi, X.S. Zhao, Uptake equilibria and mechanisms of heavy metal ions on microporous titanosilicate ETS-10, Ind. Eng. Chem. Res., 43 (2004) 7900–7906.

[17] M. Abdel, G. Al-zhrani, S.A. Kosa, Simultaneous removal of copper (II), lead (II), zinc (II) and cadmium (II) from aqueous solutions by multi-walled carbon nanotubes, C. R. Chim., 15 (2012) 398–408.

[18] O. Yayayuruk, A.E. Yayayuruk, C. Kocak, S. Kocak, Lead and copper removal using Kula volcanics from environmental waters, Sep. Sci. Technol., 52 (2017) 2777–2787.

[19] S.B. Chen, Y.B. Ma, L. Chen, K. Xian, Adsorption of aqueous Cd^{2+}, Pb^{2+}, Cu^{2+} ions by nano-hydroxyapatite: single- and multi-metal competitive adsorption study, Geochem. J., 44 (2010) 233–239.

[20] D. Hillel, Environmental Soil Physics, 1st ed., Academic Press, San Diego, CA, 1998. Available at: https://dewagumay.files.wordpress.com/2011/12/environmental-soil-physics.pdf.

[21] P. Srivastava, B. Singh, M. Angove, Competitive adsorption behavior of heavy metals on kaolinite, J. Colloid Interface Sci., 290 (2005) 28–38.

[22] A. Sdiri, T. Higashi, R. Chaabouni, F. Jamoussi, Competitive removal of heavy metals from aqueous solutions by

montmorillonitic and calcareous clays, Water Air Soil Pollut., 223 (2011) 1191–1204.

[23] Y.H. Li, Z. Ding, Z. Luan, Y. Zhu, C. Xu, D. Wu, B. Wei, Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes, Carbon, 41 (2003) 2787–2792.

[24] R. Sitko, E. Turek, B. Zawisza, E. Malicka, E. Talik, J. Heimann, A. Gagor, B. Feist, R. Wrzalik, Adsorption of divalent metal ions from aqueous solutions using graphene oxide, Dalton Trans., 42 (2013) 5682–5689.

[25] O. Oyetade, V. Nyamori, B. Sreekantha, B.S. Martincigh, Adsorption of Selected Pollutants from Aqueous Solutions onto Modified Carbon Nanotubes, University of KwaZulu-Natal, Durban, 2015.

[26] M. Kavand, T. Kaghazchi, M. Soleimani, Optimization of parameters for competitive adsorption of heavy metal ions (Pb^{+2}, Ni^{+2}, Cd^{+2}) onto activated carbon, Korean J. Chem. Eng., 31 (2014) 692–700.

[27] K. Swayampakula, V.M. Boddu, S.K. Nadavala, K. Abburi, Competitive adsorption of Cu(II), Co(II) and Ni(II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent, J. Hazard. Mater., 170 (2009) 680–689.