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Single and binary adsorption of iron and manganese in synthetic water using activated pumice composites: effect of monovalent and divalent ions, desorption and reuse isotherms

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ABSTRACT

Adsorption performance of Fe and Mn, using three different activated pumice composites at varying doses, pH, and the initial metal conditions, was investigated in the single and binary metal systems. Adsorption performance of Fe was found to be higher than Mn adsorption at all adsorption conditions. Consequently, maximum a 100% and a 64% of Fe and Mn removal was recorded, respectively. Adsorption efficiencies of activated pumice composites using HCl and HNO_3 were found to be close to each other that they were eventually higher than the results of H_2O_2 activated pumice. Removal of Fe or Mn decreased to some extent in the binary system compared with the single system at all activated pumice composites. Adsorption data sets well fitted Langmuir isotherm than Freundlich and Temkin isotherms. The presence of monovalent (Na^+) salt did not significantly change the removal of both Fe and Mn in the single and binary systems, while divalent (Mg^{2+} and Ca^{2+}) salts slightly decreased the removal efficiencies of Fe and Mn. High desorption and reuse efficiencies were obtained when 0.1 N HCl solution was used; however, the adsorption efficiency decreased after first recycling and reuse. In conclusion, adsorption of Fe and Mn using HCl activated pumice composite is a promising low-cost adsorbent in comparison with other low-cost adsorbents.

Keywords: Acid activated pumice; Iron; Manganese; Adsorption; Desorption; Isotherms; Single and binary systems; Surface modification; Reuse

1. Introduction

Heavy metals are mainly non-biodegradable and tend to accumulate in living organisms, causing various diseases [1]. Iron (Fe) and manganese (Mn) are often present in water and wastewaters, and Fe can cause anorexia, oliguria and diphasic shock while Mn can affect nervous and endocrine systems [1–4]. Furthermore, Fe and Mn commonly are also not preferred in potable water due to the unpleasant taste, color, odor and turbidity [1]. As well, levels of iron and manganese can create problems in the desalting plants, which means that there is a need of pretreatment to remove them [5–8].

One of the most suitable and widely used treatment methods for removal of metals is known to be adsorption due to the cost-effective and easy operation [9]. Pumice has been evaluated an effective and a low-cost material having a large porous surface area to remove various pollutants such as dyes [10,11] and metals [12–14]. As reported in a review study on recent investigations on pumice, most of the metals can successfully be adsorbed when pumice is activated or doped with other catalysts [15]. However, there has not been cited any adsorption study yet for the removal of Fe and Mn in the single and binary adsorption systems using activated pumice powder.

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The aim of this study is to evaluate the effect of the acid activation of pumice surface using HCl, HNO_3 and H_2O_2 on the removal of Fe and Mn in the single and binary adsorption systems. The effect of the amount of pumice, pH and initial Fe or Mn concentrations and the presence of monovalent and divalent ions on the adsorption performance was investigated. Desorption and reuse of activated pumices were also evaluated. Langmuir isotherm was found to fit Fe and Mn in both adsorption systems at optimum process conditions than other isotherms' attempts.

2. Materials and methods

2.1. Chemicals

The pumice was obtained from a company extracting pumice in Cappadocia region (Nevşehir city area, Central Anatolia) of Turkey, where a large pumice reserve is present. The particle size of pumice powder ranged from nano to micron (0–125 micron). All chemicals used in the study were purchased from Sigma Aldrich (St. Louis, Missouri, USA) at >99% purity.

2.2. Activation of pumice

The surface of pumice was activated using H_2O_2 (P1), HNO_3 (P2) and HCl (P3). First, 50 g pumice was added to 250 mL solution that contained a volumetric ratio of 1:10 of acid:distilled water. Pumice was stirred in the solutions for 24 h and washed several timesw with distilled water and dried at 105°C for 24 h before adsorption experiments.

2.3. Adsorption experiments

Adsorption experiments were performed in 100 mL flasks. The samples were shaken at 200 rpm speed for 24 h. The effect of activated pumice amount (0.5–2.0 g), the effect of pH (3–8) and the effect of initial metal concentration (10–100 mg/L) on Mn and Fe removal in the single and binary systems were evaluated in this study considering the following steps:

- Adsorption of Fe and Mn in single and binary systems was optimized first at 20 mg/L of each metal.
- To study the adsorption isotherms, 2 g activated pumice composites were put into the flasks containing 100 mL of Fe, Mn or Fe + Mn solution of different initial concentrations (10–100 mg/L).
- To study the effect of salts and ionic strength on the adsorption of the Fe and Mn, 2 g of activated pumice was added to 100 mL solution containing 50 mg/L of Fe or Mn or Fe + Mn with different concentrations of $MgCl_2$, NaCl and $CaCl_2$ solutions (100, 200, 300, 400 and 500 mg/L) and was shaken for 24 h.

At the end, taken samples were centrifuged for 5 min at 4,000 rpm speed before metal analysis. The adsorption removal efficiency was calculated as follows [1,2,4]:

$$\text{Adsorption Efficiency}\,(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \tag{1}$$

where C_0 (mg/L) is the initial metal concentration, and C_e (mg/L) is the metal concentration after 24 h adsorption.

2.4. Desorption and reuse study

To study the desorption and reuse of spent activated pumice composites, adsorption experiments were performed in 50 mL flasks using 50 mg/L of Fe and/or Mn concentrations and shaken at 200 rpm speed for 24 h using 1 g of activated pumice at room temperature. Later, spent activated pumice was collected and centrifuged for 5 min at 4,000 rpm speed. After that it was washed several times with distilled water and finally dried at 105°C. Three reagents were used to activate spent activated pumices to be: (i) distilled water, (ii) 0.1 N HCl (50 mL), (iii) 0.5 N HCl (50 mL) and (iv) 1 N HCl (50 mL). After that, reactivated pumice was used for adsorption experiments of reuse at abovementioned conditions. At the end, taken samples were centrifuged for 5 min at 4,000 rpm speeds before metal analysis. The desorption efficiency was calculated as follows [16,17]:

$$\text{Desorption Efficiency}\,(\%) = \frac{q_{\text{des}}}{q_{\text{ads}}} \times 100 = \frac{C_{\text{des}}}{C_{\text{ads}}} \times 100 \tag{2}$$

where q_{des} (mg/g) is the desorption capacity, and q_{ads} (mg/g) is the adsorption capacity. C_{ads} (mg/L) is the metal concentration of the adsorbed onto pumice ($C_0 - C_e$ from Eq. (1)), and C_{des} (mg/L) is the metal concentration of the desorbed from pumice after 24 h.

2.5. Analysis

To obtain surface properties of the pumice composites, they were submitted to scanning electron microscopy (SEM) energy-dispersive X-ray (EDX) analyzer (FEI-QUANTA FEG 250) and Fourier transform infrared spectroscopy (FTIR) (Bruker VERTEX 70 ATR) analysis. SEM-EDX was operated at 5 kV accelerating and 3 spot at a constant magnification of 20,000×. FTIR was obtained in the range of 400–4,000 cm^{-1}.

Fe and Mn analysis were performed with Merck test kits (Fe-114761 and Mn-114770) using UV–Vis spectrophotometer (Schimadzu UV-2401 PC) at λ = 562 nm and λ = 448 nm wavelengths with calibration curve.

The pH was monitored using a pH meter (WTW pH 315i). The pH at the point of zero charge (pH_{pzc}) of activated pumice composites were determined according to literature [17]. Briefly, 50 mL of 0.01 M NaCl solution was adjusted to the value varying between 2 and 12 by adding 0.1 M HCl or NaOH solutions. Then, 0.15 g of pumice added the solutions at different initial pH values and left for 48 h at room temperature. After 48 h, the final pH values are measured. The pH_{pzc} was determined from the curve as $pH_{final} - pH_{initial}$ vs. $pH_{initial}$.

3. Results and discussion

3.1. Characterization of surface pumice composites

SEM of pumice and acid activated pumice composites is demonstrated in Fig. 1. It can be clearly seen that pumice has porous and rough surface (Fig. 1(a)), and its surface shape did not notably change after activation procedures (Figs. 1(b)–(d)). EDX spectra showed that oxygen and silisium are the major elements due to the origin of pumice characteristics that mainly contain 58.4% O, 29.5% Si, 6.7% Al, 1.4% K, 3.9% Na and 0.2% Fe. It was reported elsewhere that the main components of pumice are SiO_2, Al_2O_3 and K_2O

[10,18,19]. Those characteristics did not significantly vary with the activation procedures applied in this study.

FTIR spectra of surface activated pumices are given in Fig. 2. It is seen that three main peaks at 1,020, 780 and 455 cm^{-1} in the FTIR spectra are displayed to vary from pumice to surface activated pumices. The strongest peak at ~1,020 cm^{-1} could be the Si–O–Si symmetric stretching vibration due to the groups of $(SiO_4)_2$ [20]. The transmittance at 1,020 cm^{-1} shows an enhancing intensity with the surface activation. Transmittance intensities were obtained to be 81.9%, 79.3%, 77.0% and 72.6% for activated pumice, P1, P2 and P3, respectively. The peaks at ~780 cm^{-1} could be a vibration of Si–O–Si bond [10,19,21]. Furthermore, the vibration of Si–O–Si bond intensity is the highest one at the HCl activated pumice. Intensities of activated pumice, P1, P2 and P3 composites were observed as 89.1%, 87.3%, 85.0% and 83.0% at 455 cm^{-1}, respectively. Other small peaks observed at ~1,600 and ~3,400 cm^{-1} are also owed to the bending vibration of H–O–H bond and asymmetric stretching vibration of H–O bond in adsorbed water molecules, and those peaks are same in all activated pumice composites [20,22].

3.2. Effect of activated pumice amounts

As shown in Fig. 3, the removal of Fe was found to be ~100% at all amounts used of P2 and P3 composites while it was nearly observed at 100% using 1.5 g of P1 composite in the single system. Nearly the same removal of Mn was observed using all activated pumice composites in the single Mn adsorption system. However, a rather lower removal efficiency was obtained using P1 composite. In the case of binary adsorption systems, both Mn and Fe removals slightly decreased. Anyhow, Mn and Fe removals increased with increasing amount of activated pumice composites. The removal of both Fe and Mn was higher using P2 and P3 composites than P1 composite. Nevertheless, a gradually increasing removal trend of Mn and Fe being 53.4% and 66.0% for P1; 79.9% and 71.6% for P2 and 93.1% and 98.5% for P3 was observed using 2 g of each composite correspondently. In a previous study, the removal of Fe was reported to increase from 72.7% to 87.8% using acid activated montmorillonite varying from 2 to 6 g/L [23].

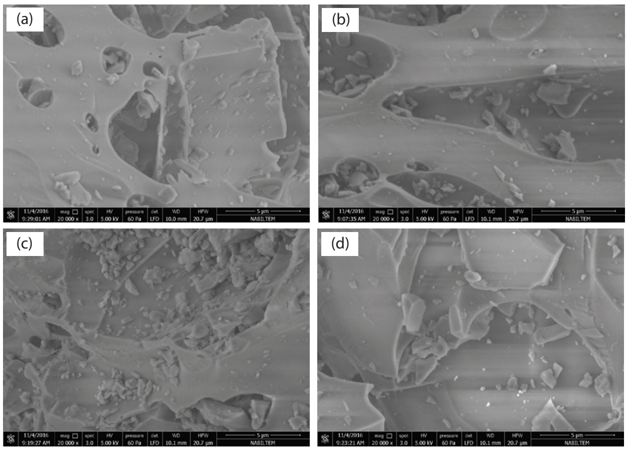

Fig. 1. SEM results of: (a) pumice, (b) H_2O_2 activated pumice, (c) HNO_3 activated pumice and (d) HCl activated pumice.

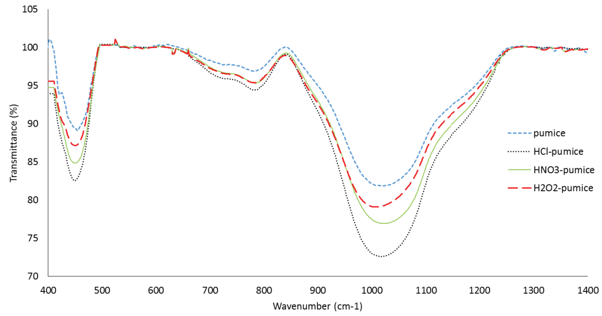

Fig. 2. FTIR spectra of pumice and three different activated pumices.

3.3. Effect of pH

pH is one of the most important factors influencing the efficiency of adsorption process due to affecting both the surface charge of the adsorbent and the bonding-formation of metals. Both Fe and Mn removals were found to be lower at acidic conditions than the alkaline conditions in both single and binary systems (Figs. 4(a) and (b)). On the other hand, higher Fe and Mn removals were reported with increasing pH from 2 to 8 using untreated activated carbon and tannic acid modified activated carbon [24]. It is stated that the low metal adsorption at very low pH values arises from the competition between H^+ protons and metals on the active sites of adsorbent [25,26]. Removal of Fe and Mn increased with increasing solution pH up to 8. Fe removal using P2 and P3 activated pumice composites was observed to be nearly the same while Fe removal using P1 was found to be lower than other composites used in the single system (Fig. 4(a)). In the case of Mn removal, maximum efficiency was obtained using P3 activated pumice composite (Fig. 4(a)). Accordingly, the performance order of composites used for Mn removal was found to be P3 > P2 > P1. Although the same results for both metals were observed in the binary adsorption systems (Fig. 4(b)), the adsorption capacity of Fe and Mn decreased for all activated pumice composites compared with the single systems. The adsorption capacities of both Mn and Fe were calculated to be 1.62 and 9.00 mg/g in the single adsorption system, and 1.03 and 7.23 mg/g in the binary adsorption system, respectively, when P3 composite was used.

The pH_{pzc} of activated pumice composites affects the metal removal efficiency. This means that when the solution of pH is lower than pH_{pzc}, the surface of composite is positively charged and this leads to decrease the adsorption of cationic metals. When the solution of pH > pH_{pzc}, the surface of composite is negatively charged, and this leads to increase the adsorption of cationic metals. Higher adsorption removal of metals can be favored above the pH_{pzc} of composites. The pH_{pzc} of pumice was found at 6.12 in the literature [27]. Similar result was observed in this study that the pH_{pzc} of pumice was found to be 5.61 and it is changed to 6.60, 3.97 and 3.79 using P1, P2 and P3, respectively. This high pH_{pzc} value of P1 leads to decrease the Fe and Mn adsorption capacity when the pH of solution

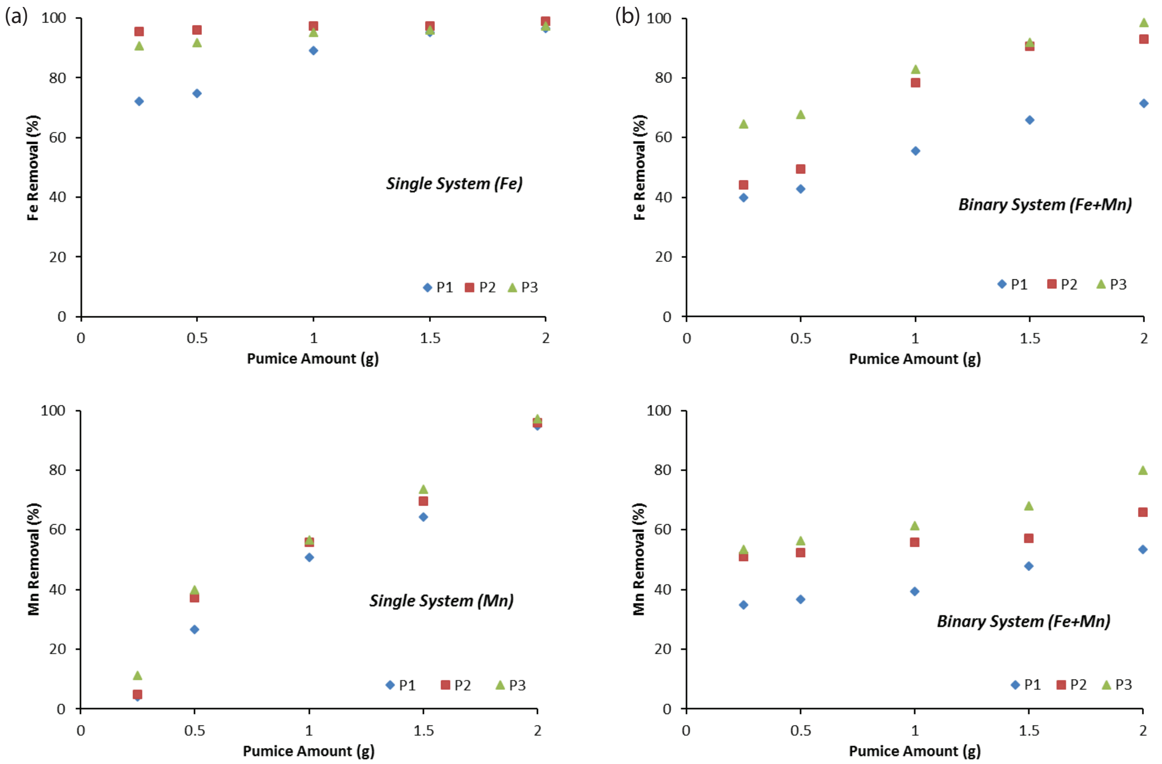

Fig. 3. Effect of pumice amount using P1, P2 and P3 in the (a) single and (b) binary adsorption systems (initial Fe or Mn concentration: 20 mg/L, pH: 7; time: 24 h).

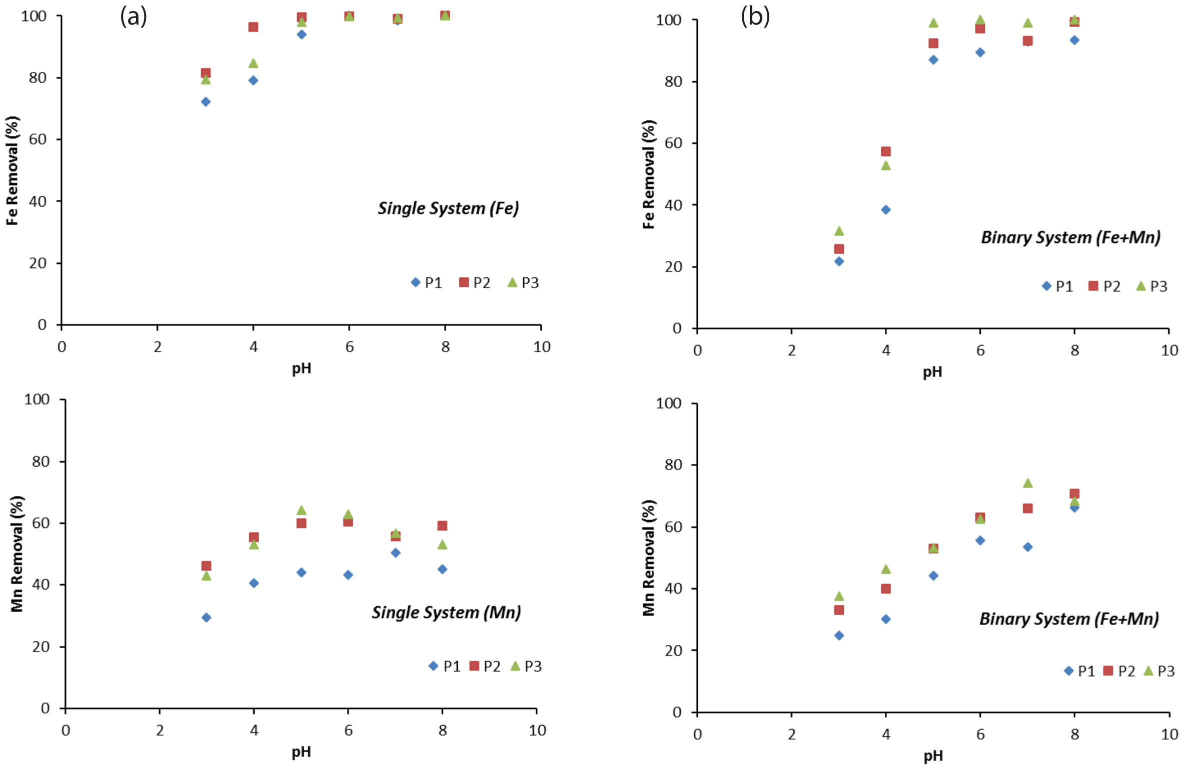

Fig. 4. Effect of pH using P1, P2 and P3 in the (a) single and (b) binary adsorption systems (initial Fe or Mn concentration: 20 mg/L, pumice concentration: 2 g; time: 24 h).

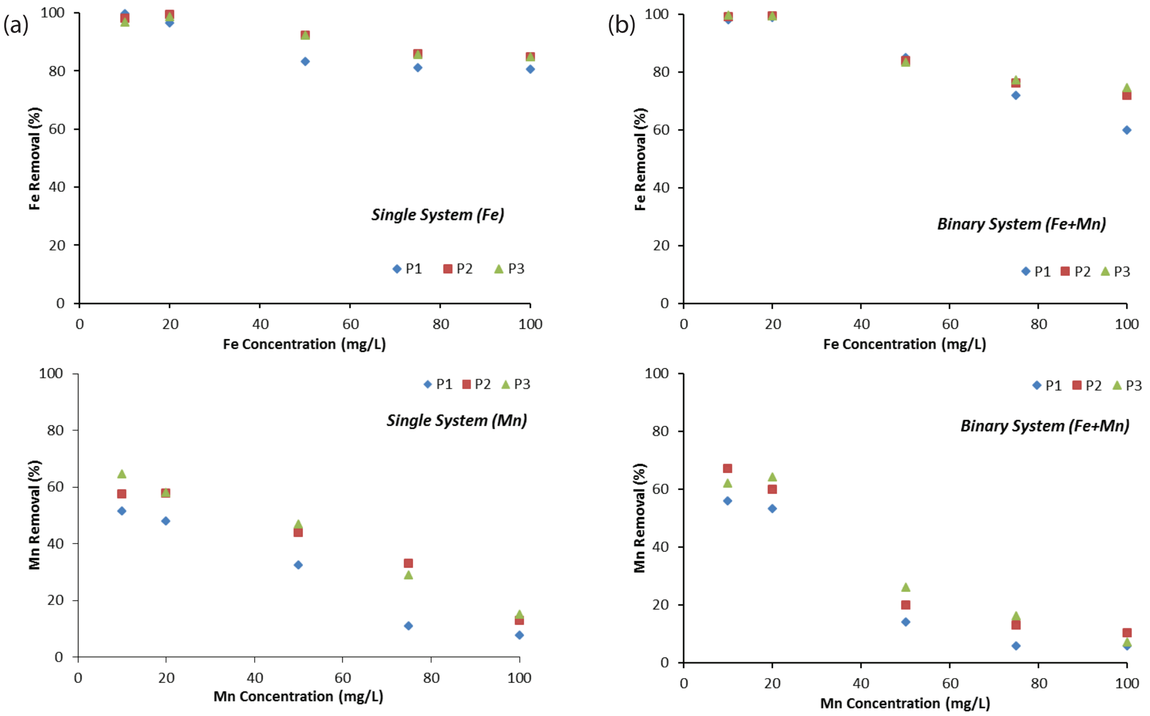

Fig. 5. Effect of initial Fe or Mn concentration using P1, P2 and P3 in the (a) single and (b) binary adsorption systems (pH: 7, pumice concentration: 2 g; time: 24 h).

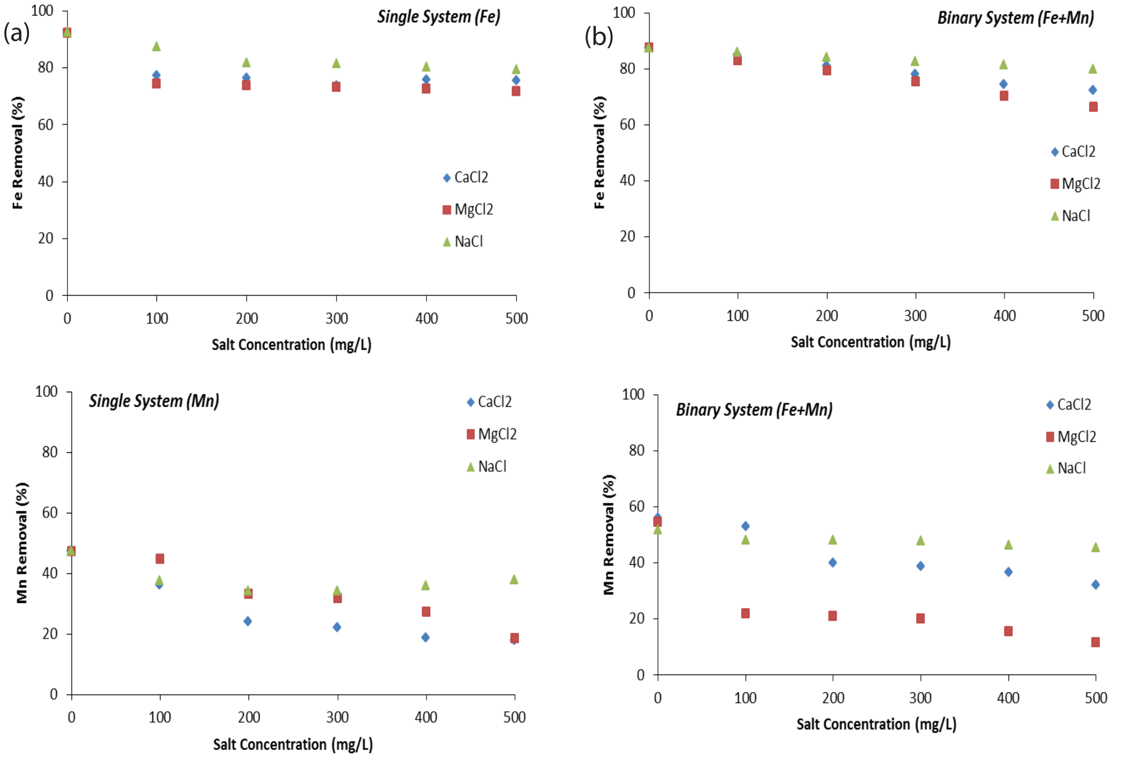

Fig. 6. Effect of salts on Fe and Mn removal using P3 in the (a) single and (b) binary adsorption systems (initial Fe or Mn concentration: 50 mg/L, pH: 7, pumice concentration: 2 g; time: 24 h).

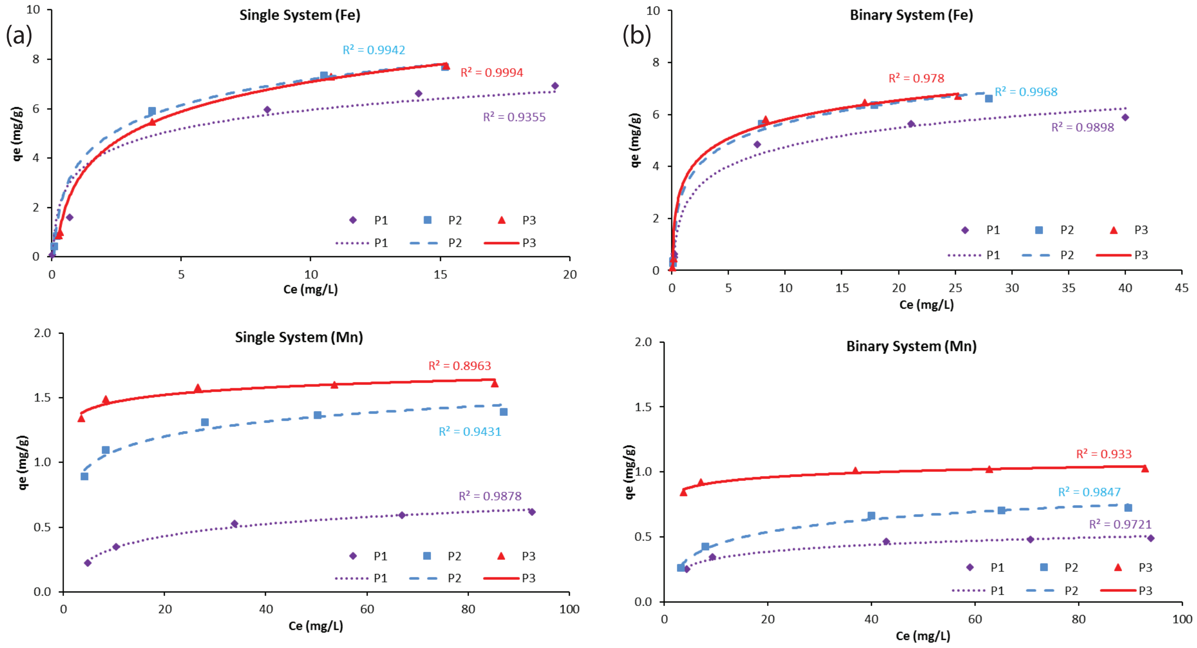

Fig. 7. Langmuir isotherm using P1, P2 and P3 in the (a) single and (b) binary adsorption systems (pH: 7, pumice concentration: 2 g; time: 24 h).

was lower than the pH_{pzc} value (pH_{pzc} = 6.60). The lower pH_{pzc} value of P2 and P3 could gain an advantage that high removal efficiencies of Fe and Mn can be obtained in a wide range of pH values (≥4).

3.4. Effect of initial metal concentrations

Increasing initial metal concentration caused to decrease the removal of the metals due to the saturation of active sites on the activated pumice composites as seen in Fig. 5. Fe removal slightly decreased, whereas the Mn removal was much affected by initial Mn concentration varying in the range of 10–100 mg/L. The removal efficiencies ranged from 96.8% to 84.8% for Fe and 64.5% and 14.7% for Mn using P3 at 10 and 100 mg/L, respectively. Both Fe and Mn removals were found to be lower in the binary system than the single adsorption system after an initial concentration of Fe and Mn being 20 mg/L. Mn removal was influenced more than that of Fe removal, comparing the single and binary systems.

3.5. Effect of ionic strength

Natural water and wastewater usually contain salt (ionic strength) which is to cause the electrostatic interaction between solution and surface of the activated pumice, eventually the salt ions compete with metal ions [28–30]. Three different salts as NaCl, $MgCl_2$ and $CaCl_2$ were investigated in this study to influence adsorption of Fe and Mn removals. The results are shown in Fig. 6. Removal of Fe and Mn decreased with increasing the salt concentration. A decreasing Mn removal with an increasing ionic strength was observed to be higher than the Fe removal in both single and binary adsorption systems. It was also observed that there is more competition between Mn and salt ions than that of between Fe and salt ions. The removal of Fe and Mn slightly decreased with Na^+ than the divalent metals (Mg^{2+} and Ca^{2+}) in accordance with the literature [29,31]. In addition, Tunç and Duman [32] reported that Na^+ is indifferent ion and Mg^{2+} and Ca^{2+} are the potential determining cations to affect the negative zeta potential of pumice [30]. They found that the higher negative zeta potential of pumice was obtained in the presence of NaCl to vary between 10^{-1} and 10^3 M. Additionally, the effect of $MgCl_2$ and $CaCl_2$ on the zeta potential of pumice was reported to be similar [32]. In this study, the salt concentration used varied from 10^{-2} to 10^{-3} M. Thus, the higher negative surface of pumice could tolerate the negative effect of salt addition (NaCl). However, Mg^{2+} and Ca^{2+} were adsorbed on the surface of pumice and changed the surface charge of pumice. Finally, that leaded to decrease the adsorption removal efficiencies of Fe and Mn. The degree of interaction increased with the increase of the salt concentrations between 100 and 500 mg/L, and was found to be in the order of $Mg^{2+} > Ca^{2+} > Na^+$. It can be concluded that the activated pumice composite is suitable for the removal of Fe and Mn in aqueous media with a lower salt concentration (<200 mg/L) [33].

3.6. Adsorption isotherms

Langmuir, Freundlich and Temkin isotherms were evaluated to assess the adsorption kinetics of Fe and Mn in the single and binary systems. Because low regression coefficients were observed for Freundlich and Temkin isotherms, only Langmuir isotherms of activated pumices are given in Fig. 7. Langmuir isotherm was often reported to fit the adsorption data of different pollutants using pumice [12,34,35]. Fitting Langmuir isotherm of Fe or Mn adsorption at a high

Table 1
Comparison of Fe and Mn adsorption capacities according to Langmuir isotherm

Adsorbent	Initial concentration (mg/L)	q_{max} (mg/g)	Reference
Fe removal			
HCl-activated pumice	10–100	9	This study
Zeolite	300–1,000	7.4	[1]
Zeolite	20–400	6.6	[37]
TAAC	–	2.8	[25]
Activated carbon	–	14.6–46.4	[42]
Granular activated carbon	–	3.6	[40]
Bentonite	0–400	21	[43]
Kaolinite	100–250	11.2	[36]
Acid-activated kaolinite	100–250	12	[36]
Montmorillonite	100–250	28.9	[36]
Acid activated montmorillonite	100–250	30	[36]
Clinoptilolite	0–500	5.9–7.6	[41]
Bentonite	0–500	4.1	[41]
Chabazite	0–500	5.5	[41]
Zaccagnaite	0–200	9.4	[44]
Mn removal			
HCl-activated pumice	10–100	1.62	In this study
Clinoptilolite	–	7.69	[45]
Clin–Fe	–	27.1	[45]
Granular activated carbon	–	2.55	[40]
Clinoptilolite	100–400	4.22	[39]
Zeolite	20–400	2.42	[37]
Na montmorillonite	–	3.22	[38]
TAAC	–	1.73	[25]
Activated carbon	–	0.51–16.4	[42]
Zaccagnaite	0–200	30.69	[44]
Manganese coated sand	–	0.164–0.868	[46]

Note: Clin-Fe: Clinoptilolite-Fe; TAAC: Tannic acid immobilised activated carbon.

regression coefficient than the other isotherm was explained due to the monolayer coverage on the surface of activated pumice.

Although Fe adsorption capacity was not significantly changed using three activated pumice composites, the adsorption capacity of Mn yielded 2.4 times higher using HCl activated pumice than H_2O_2 activated pumice composite use in the single adsorption system. Similar trend was observed in the binary adsorption system (a 2.2 times higher Mn adsorption capacity was observed using P3 compared with P1). This enhanced adsorption removal was also shown in the literature using acid activated clays [36]. Maximum adsorption capacities of Fe and Mn were observed using P3 in both adsorption systems. Fe and Mn adsorption capacities were found to be 9.00 and 1.62 mg/g in the single system while they were calculated as 7.23 and 1.03 mg/g in the binary system. These results indicated a higher capacity of activated pumice composites than the results of zeolite and tannic acid immobilized activated carbon as reported by Motsi et al. [25,37]. They found a 6.61 mg/g of Fe adsorption capacity while Mn adsorption capacity was reported to be 2.42 mg/g using natural zeolite. Furthermore, Üçer et al. [24] reported that Fe and Mn adsorption capacities were 2.80 and 1.73 mg/g, respectively, using tannic acid immobilized activated carbon. Mn adsorption capacity was also obtained as 3.22 mg/g using montmorillonite, 4.22 mg/g using clinoptilolite and 2.55 mg/g using granular activated carbon [38–40]. Fe adsorption capacity was calculated between 6.6 and 7.4 mg/g using natural zeolite [1,37].

Although Mn adsorption capacity of activated pumice was found to be lower than all other adsorbents reported in the scientific literature (Table 1), pumice could be evaluated to be more economical one [15]. As compared with the literature (5.9–7.6 using clinoptilolite, 5.5 mg/g using chabazite, 4.1 mg/g using bentonite, 11.2 mg/g using kaolinite) [36,41], Fe adsorption capacity of pumice was found to be higher than the range given in the literature except the results of montmorillonite adsorbent.

3.7. Desorption and reuse of pumice composite

HCl solutions were used as desorption agent in this study as reported to be more effective desorption agent than the H_2SO_4 solutions when the using Cr adsorption with pumice [23]. Also, it is found that desorption of Cu is much higher in HCl solutions than the HNO_3 solutions using chitosan as an adsorbent [47]. Desorption of Fe and Mn from the pumice composites was evaluated using four desorption media as explained in section 2.3. The highest desorption was achieved when 1 N HCl solution was used for this purpose. Increasing of HCl normality did not change or slightly decrease the desorption efficiency. The maximum desorption efficiencies are 91.1% and 88.0% for Fe and Mn using HCl activated pumice, respectively (Fig. 8). Desorption in distilled water (41%–52% for Fe and 39%–63% for Mn using different activated pumices) was observed to be lower than HCl desorbed solutions. Although the Fe and Mn removals slightly decreased, an 81.0% and 44% of Fe and Mn removals were obtained, respectively, when HCl activated pumice was reused (Table 2). Fe adsorption was observed to be more affected than Mn adsorption. It is concluded that HCl activated pumice is more suitable when pumice is reused for adsorption of Fe and Mn.

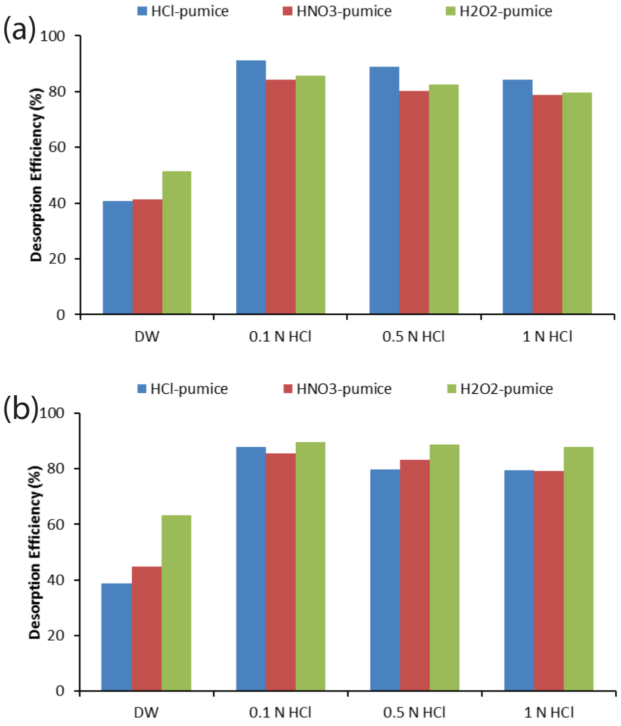

Fig. 8. Desorption efficiency using different desorption agents (a) for Fe and (b) for Mn removal.

4. Conclusion

Three types of acids were evaluated to activate the surface of pumice to remove Fe and Mn from synthetic water. Desorption and reuse of pumice were also evaluated. The effect of monovalent and divalent ions on the adsorption efficiency was investigated. Three widely used isotherms were used to fit the adsorption data. The results of this study are outlined below:

- Removal of Fe and Mn increased with increasing pumice amounts and varying pH of the solutions.
- Fe and Mn removals were affected by activation acid. HCl and HNO_3 acids were noted more effective ones than H_2O_2 in the single metal adsorption system. In the case of binary system, higher Fe and Mn removals were obtained using HCl activated pumice composite. Removal efficiencies of Fe and Mn were obtained in the order of HCl > HNO_3 > H_2O_2.
- N HCl solution was also observed to be suitable for desorption.

Table 2
Desorption and reuse efficiencies (%) using HCl solutions (initial Fe or Mn concentration: 50 mg/L, pumice: 1 g, pH: 7, time: 24 h)

Pumice		DW		0.1 N HCl[a]		0.5 N HCl[a]		1 N HCl[a]	
Composite	A	D	R	D	R	D	R	D	R
Fe removal (%)									
HCl-pumice	92.8	40.7	50.4	91.1	81.0	88.8	81.3	84.1	77.4
HNO_3-pumice	92.0	41.3	52.1	84.3	79.9	80.2	79.4	78.7	74.7
H_2O_2-pumice	82.6	51.4	49.4	85.7	74.8	82.4	74.9	79.8	77.8
Mn removal (%)									
HCl-pumice	46.6	38.7	30.5	88.0	44.0	79.8	40.4	79.3	41.5
HNO_3-pumice	44.1	44.7	37.1	85.4	33.8	83.3	32.8	44.7	25.8
H_2O_2-pumice	32.2	63.4	15.1	89.5	25.0	88.8	25.5	87.8	27.4

[a] Desorption agents.

Note: DW: distilled water, A: adsorption efficiency, D: desorption efficiency, R: reuse adsorption efficiency.

- When HCl activated pumice was reused after desorption, an 81.0% and 44% of Fe and Mn removals were obtained, respectively.
- Monovalent and divalent ions affected the adsorption efficiency to be in the order of $Mg^{2+} > Ca^{2+} > Na^+$ for the salt concentrations varying between 100 and 500 mg/L.
- Langmuir isotherm fitted the adsorption data of both Fe and Mn at the highest correlation.

In conclusion, HCl acid activated pumice can be recommended to be more suitable and economic material for the removal Fe and Mn in both the single and binary adsorption systems.

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