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Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash

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ABSTRACT

Recently because of increasing of the environmental awareness and demands, several attempts were carried out for the conversion of by-products of natural materials, especially agricultural wastes, to highly sorption capacity materials. In recent years, attention has been focused on the utilization of unmodified or modified agro-residues as sorbents for removal of pollutants. Various modifications have been reported to enhance sorption capacities for heavy metals. The present study deals with the adsorption equilibrium of iron, manganese, lead and arsenic ions from aqueous solutions on copolymer of Al⁺³, Si⁺⁴ and Fe⁺³ using batch techniques. The influence of various parameters, such as agitation time, sorbent mass and pH of sorbate solution were investigated. Under this study the maximum adsorption capacity of iron and aluminum copolymer impregnated with silica (PAIFeCISi) for lead, iron, manganese and arsenic are found to be 416, 222, 158, 146 mg/g, respectively.

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1. Introduction

Activated silica or sodium silicate is one of the four basic types of coagulants aids beside pH adjusters, clay and polymers which increase the stability of coagulant and can unite with the positively charged aluminum or with iron flocs, resulting in a larger, denser lamellar floc that settles faster and enhances enmeshment [1].

Coagulation is one of the most important steps during the conventional water treatment train. Salts and prehydrolysed salts of aluminum and iron were used as coagulants in water and waste water treatment. Because of superior efficiency and relatively low cost of these materials compared with traditional coagulant alum, copolymer of aluminum and iron impregnated with active silica were favorable in addition to the following features: very fast hydrolysis, promote rapid settling rates, extremely efficient in cold water, give low soluble residual aluminum, consume less alkalinity, very little effect on pH, increase stability of coagulant and denser compacted sludge [2,3].

The presence of heavy metals like iron, manganese, lead and arsenic and some anions such as nitrate and fluoride in aquatic systems is a very earnest problem and related to the prevalence of some diseases like renal failure, liver cirrhosis, hair losses, cancer and chronic diseases; heavy metals are dangerous for living organisms because of their stability, toxicity and tendency to accumulating in the environment.

The main methods used for arsenic removal from contaminated water sources are coagulation/direct filtration, ion exchange, adsorption on iron oxides or on activated alumina, iron-oxide coated sand and reverse osmosis. These methods usually require a preliminary oxidation step, for the transformation of As(III) to As(V), in order to achieve efficient arsenite removal. As(III) oxidation is usually performed by the addition of chemical reagents, such as, potassium permanganate, hydrogen peroxide or ozone [4,5].

Different methods can be used for removing lead including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption. Ion exchange and adsorption are the most common and effective processes for this purpose [6].

The main conventional treatment methods available for iron and manganese removal fall into six main categories, which are: (a) aeration, followed by sand filtration, (b) chemical oxidation, followed by filtration, (c) filtration with special filter medium, which acts as ion exchanger, (d) combination of manganese oxide and diatomaceous earth for sorption–filtration, (e) conventional treatment combined with lime softening and (f) use of sodium silicate, phosphate or polyphosphates as sequestering agents [7].

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Table 1

Experimental conditions of Pb, Mn, Fe and AS ions adsorption by PAIFeCISi copolymer at temperature 27 \pm 3 $^\circ$ C.

Conditions	Parameter					
	Pb	Fe	Mn	As		
(a) Agitation time						
Mixing Time (min)	1-10	1-10	1-10	1-10		
рН	8.5	8.5	8.5	8.5		
Dose (mg/L)	70	28	28	14		
(b) Adsorbent dose						
Mixing Time (min)	5	5	5	5		
рН	8.5	8.5	8.5	8.5		
Dose (mg/L)	1-100	1-70	1-70	1–28		
(c) pH value						
Mixing Time (min)	5	5	5	5		
pH	6–9	6-9	6–9	6-9		
Dose (mg/L)	70	28	28	14		

Many researchers used the rice husk ash to remove heavy metals from waste water [8–14]; but this work is concerned with impregnation of activated silica derived from rice husk ash with iron and aluminum inorganic polymer to prepare copolymer which is responsible for the removal of heavy metals from waste water.

The objectives of this study are to produce rice husk ash (RHA) from rice husk (RH), sodium silicate and poly aluminum ferric chloride silicate (PAIFeCISi) based on silica as well as the characterization of the new materials using FTIR, NFTIR and XRD.

2. Experimental

Table 2

All chemicals used are of commercial grade except sodium hydroxide is an analytical grade product. Distilled water was used to make all solutions.

Rice husk ash (RHA) was prepared by burning of rice husk (RH) for 2 h at 650 °C without treatment. Sodium silicate was prepared by the reaction of RHA samples with sodium hydroxide with a SiO₂/NaOH molar ratio of 1:2 in reflux at 100 °C for 1 h or until no silica residue to select optimal condition. The solutions of sodium silicate are designated as SSi. RHA samples and dry sodium silicate were characterized by elemental analysis using ionic chromatography, X-ray diffraction (XRD) and Fourier transform infra red (FTIR) and near Fourier transform infra red (NFTIR) using Jasco FT/IR 460 plus spectrometer in the 400–4000 cm⁻¹ of FTIR and 4000–7500 cm⁻¹ of NFTIR wave number ranges.

Sodium silicate based on RHA was chosen as a precursor for the preparation of poly silicic acid (PSi) solution, by dilution of sodium silicate containing 15% SiO₂ with distilled water to a concentration of 0.25 M SiO₂. The diluted solution was reacted with 0.25 M HCl under magnetic stirring; the pH of the final solution reaches about 2 and SiO₂ concentration reaches 0.125 M. A new poly inorganic coagulant was prepared; this is poly aluminum ferric chloride silicate (PAIFeCISi). The preparation was done by the slight neutralization of 0.25 M AlCl₃ and 0.25 M FeCl₃ with 0.25 M sodium carbonate at 60 °C with rapid mixing to obtain poly inorganic coagulants with molar [OH]/[Al] ratio of 2 and basicity 67% and molar Al or Fe/Si ratio of 0.2.

The main factors affecting the adsorption process, e.g. agitation time, sorbent mass and pH of solution, were studied. In all cases, 1 L of aqueous water was contacted with 0.07, 0.028, 0.028 and

0.014 g of PAIFeCISi for lead, iron, manganese and arsenic, respectively. The conditions of each experiment for the removal were adjusted (Table 1); then, the mixture was filtered and the filtrate samples were analyzed for lead, iron, manganese and arsenic concentrations using atomic absorption spectrometer (AAS). Isotherm experiments were carried out. Each sample was mixed with various quantities of PAIFeCISi copolymer ranging from 0.002 to 0.07 g and agitated for 5 min (flocculation step) in all cases at room temperature (27 ± 3 °C). The concentration was measured in the filtrate using AAS (model: ZL8100 Schmitzu).

In all cases, the difference between the initial concentration (C_o) and the equilibrium concentration (C_e) was calculated and used to determine the adsorptive capacity (q_e) as follows: $q_e = V(C_o - C_e)/M$. Where V is the total volume of solute solution (L), M the mass of adsorbent used (g), C_o the initial concentration of the solute (g L⁻¹) and C_e is the residual concentration of the solute (g L⁻¹).

3. Results and discussion

3.1. Characterization of the prepared samples

The data listed in (Table 2) represent the results of chemical analysis of the prepared rice husk ash (RHA) sample and its comparison with a previous study [1]. (Table 2) shows that the ash produced from the rice husk burning contains a larger amount of silica and small amounts of other elements which are considered as impurities. The most common trace elements in RHA are sodium, potassium, calcium, magnesium, iron, titanium and manganese [15]. Differences in composition may occur due to geographic factors, type of soil, period of harvest, sample preparation and analysis method, in RHA preparation the sample was burnt at 650 °C with no acid treatment and no water washing (the content of silica reach to 87.5% and metal oxide reach to 8%).

Fig. 1a shows the FTIR spectrum of RHA. The spectrum displayed the characteristic bands for Si–O and Si–O–Si at 1098 and 800 cm⁻¹, respectively [16]. The X-ray diffractogram of RHA shows the amorphous character of silica produced from calcination of rice husk at 650 °C. The chemical analysis of sodium silicate as obtained by ion chromatography is shown in Table 3.

The FTIR spectrum shown in Fig. 1b displayed the characteristic bands of sodium silicate for silanol OH groups and adsorbed water, Si–O–Si and Al–O–Si as broad bands at (2923–3390), (994–1443) and (464–877) cm⁻¹, respectively [16,17]. NFTIR spectrum shown in Fig. 2a displayed characteristic bands of sodium silicate for the overtones OH-stretch Si–OH, OH-stretching, (OH-stretching (2) crystal water, H₂O combination) and H₂O bending at 7327, (6971–6611), (5338–5204) and 4451 cm⁻¹, respectively [18]. The X-ray diffraction pattern of sodium silicate powder, obtained by grinding after drying at 105 °C for 2 h, shows a sharp peak characteristic of sodium silicate (*d* spacing 3.24 Å) [19].

Fig. 1c shows the FTIR spectrum of poly aluminum ferric chloride silicate PAIFeCLSi. The spectrum displayed the characteristic bands for OH-stretch, H₂O–OH stretch, H₂O bend Al–OH₂ bend, Si–O stretching SiO(OH)₃, Al–O symmetric and/or Al–O–Si and antisymmetrical AlO₄⁻¹ (FeO₄⁻¹) located at 3413, 1629, 1121, 898, 702 and 480 cm⁻¹, respectively [18].

Fig. 2b shows NFTIR spectrum of poly aluminum ferric chloride silicate (PAIFeCSi). The spectrum displayed the characteristic bands of OH-stretch Si–OH, OH-stretch, (1) FeOH/AIOH combi-

Chemical composition of RHA sample prepared as compared with a reference [rice husk market, 2003].

Parameter (%)	SiO ₂	Fe ₂ O ₃	MnO	Al ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Residue
RHA	87.5	2.0	0.043	1.0	0.7	0.65	1.45	2.1	0.057	≈4.5
Reference	62.5–97.6	0.01–2.78	0.01-1.96	0.01–1.01	0.01–1.96	0.1-1.31	0.01-1.58	0.1–2.54	0.01–2.69	-

Table 2



Fig. 1. FTIR spectra of (a) RHA, (b) sodium silicate and (c) PAIFeCISi copolymer.

Table 5			
Chemical analysis of sodium	silicate sample	prepared in	n this study.

SiO ₂	Na ₂ O	MnO	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	K ₂ O	P ₂ O ₅	Residue
64.4%	29.94%	0.028%	0.65%	0.45%	0.42%	1.3%	1.35%	0.036%	≈1.0

nation of (OH-stretching (1+2) FeOH or AlOH + crystalline water, H_2O combination (bend 1+stretch 1) Al_{13} combination (bend 2+stretch 1) crystal H_2O + Al_{13}) at (7368, 7326), 7040, (6802–6743), (6446–6366) and 5199 cm⁻¹, respectively [18].

X-ray diffractogram of poly ferric aluminum chloride silicate (PAIFeCISi), indicates the same characteristic broad band of amorphous silica [17] and two sharp peaks in the ranges of 2θ at 32° and 44° .

3.2. Factors affecting adsorption and removal of the heavy metals under investigation

3.2.1. Effect of agitation time

The time-profile of adsorption of Pb, Fe, Mn and As ions onto PAIFeCISi copolymer [the optimum condition of eight poly inorganic co-agulants (PIC)] at room temperature $(27 \pm 3 \circ C)$ is presented in Fig. 3. As agitation time (slow mix) increases, cation removal initially increases and then gradually approaches a more or less constant value, denoting attainment of an equilibrium. Obvi-



Fig. 2. NFTIR spectra of (a) sodium silicate and (b) PAIFeCISi copolymer.

ously, the equilibrium was attained after shaking for about 5 min in case of Fe, Mn, Pb and As ions, beyond which there is no further increase in the adsorption which ensure that adsorption equilibrium was reached in each case.

3.2.2. Effect of sorbent mass

Fig. 4 shows that the increase of PAIFeCISi polymer concentration increases the percent removal (R%) to reach 100% from separate 1 L solution containing 10, 4, 3 and 1.5 mg/L of Pb, Fe, Mn and As ions, respectively. Constant removal is attained after a particular PAIFe-CISi copolymer concentration (optimum dosage) and varying from 1 to 100 ppm while keeping the other parameters as given in Table 1. The results obtained show that the removal efficiency of copolymer for lead is higher than other pollutants due to higher ionic radius and easier ionic bond formation (Pb \gg Fe > Mn > AS) which facilitate co-precipitation.

3.2.3. Effect of pH of sorbate solution

The effect of pH on the adsorption of Pb, Fe, Mn and As was studied at room temperature by varying pH of metal solution-



Fig. 3. The sorbent phase concentration of PAIFeCISi copolymer as a function of time for Fe, Pb, Mn and As ions removals.



Fig. 4. Effect of PAIFeCISi copolymer dose on the adsorption of Fe, Pb, Mn and As ions.

copolymer from 6 to 9. Increasing the solution pH increases the percent removal (R %) to reach 100% from separate 1 L solution containing 10, 4, 3 and 1.5 mg/L of Pb, Fe, Mn and As ions at different PAIFeCISi polymer concentrations of 70, 28, 28 and 14 mg/L, respectively. The minimum pH required for the complete removal of previous concentration of ions is about 8.5. It can be shown that the removal of each metal exhibits similar trend, i.e. it increases with increasing pH. The greatest increase in the adsorption rate of metals ions on copolymer were observed in a range of pH from 7.0 to 8.5 which may be due to either ion exchange or co-precipitation with metal hydroxide.

3.3. Adsorption isotherms

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherm such as Langmuir or Freundlich isotherm, which related adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase C_e . The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq^0} + \frac{C_e}{q^0} \tag{3.1}$$

$$\frac{1}{a_e} = \frac{1}{a^0} + \frac{1}{ba^0} \frac{1}{C_e}$$
(3.2)

where C_e is the equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium time (mg/g) and q^o and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively, which can be calculated from the $1/q_e$ vs. $1/C_e$ plot. The linear Langmuir plot is shown in Fig. 5. The Langmuir parameter q^o were found to be (416, 222, 158 and 146 mg/g for Fe, Pb and Mn and As, respectively. This is due to the variation of ionic radius of 119, 78, 67, 58 pm of Pb, Fe, Mn and As ions, respectively.

Comparison of the adsorption values of Fe, Pb, Mn and As onto PAIFeClSi copolymer with literature data indicated that the adsorption capacity of PAIFeClSi copolymer is much greater than the other adsorbents (the adsorption capacity of Fe⁺² and Mn⁺² were 3.6 and 2.54 mg/g, respectively, with granular activated carbon [19], the adsorption capacity of Pb⁺² is 3.19 mg/g with Sawdust [20] and other researchers [12,13]. The Freundlich adsorption isotherm was also applied for the adsorption of Fe, Pb and Mn and As ions onto PAIFeClSi copolymer. The favorable nature of adsorption can be expressed in terms of a dimensionless separation factor of equilibrium parameter namely (R_L) to reveal the essential characteristics



Fig. 5. Langmuir plot of Fe, Pb, Mn and As ions removal by PAIFeCISi copolymer.

of Langmuir isotherm relating *R* with the Langmuir constant *b* and the initial concentration of the adsorbate solution C_0 , i.e., $R_L = 1/(1 + bC_0)$; the values of R_L where determined and were 0.999 showing favorable isotherms for all metals studied.

The Freundlich equation is presented as:

$$q_{\rm e} = k_{\rm f} C_{\rm e}^{1/n} \tag{3.3}$$

Rearranging Eq. (3.3) gives

$$\log q_{\rm e} = \log k_{\rm f} + \frac{1}{n \log C_{\rm e}} \tag{3.4}$$

Hence, a plot of $\log q_e$ vs. $\log C_e$, Fig. 6, enables the constants k_f and exponent n to be determined. The constants are listed in Table 4. Freundlich equation produced correlation coefficients of 0.998, 0.999 for all metals indicating the validity of using the Freundlich equation to model the adsorption isotherm over the studied concentration range.



Fig. 6. Freundlich plot of Fe, Pb, Mn and As ions by PAIFeCISi copolymer.

Table 4

Langmuir and Freundlich constants of Pb, Fe, Mn and As ions sorption by PAIFeCISi copolymer.

Adsorption system	1 Langmuir constants			Freundli	Freundlich constants		
-	qº (mg/g)	b (L/mg)	RL	k_{f}	п	RL	
Pb	416	0.000166	0.99	0.021	0.994	0.99	
Fe	222	0.000125	0.99	0.028	0.996	0.99	
Mn	158	0.000176	0.99	0.028	0.997	0.99	
As	146	0.000095	0.99	0.014	0.993	0.99	



Fig. 7. FTIR spectra of (a) (PAIFeCISi), (b) (Pb + PAIFeCISi), (c) (Fe + PAIFeCISi), (d) (Mn + PAIFeCISi) and (e) (As + PAIFeCISi).

3.4. The proposed mechanisms

Coagulants destabilize colloids and dissolved constituents by a combination of the following mechanisms: compression of the double layer, counter ion adsorption, charge neutralization, enmeshment in a precipitate, heterocoagulation, the ion-exchange reaction and covalent bonding [21–23].

In the case of enmeshment in a precipitate: the iron and aluminum co-precipitation/adsorption process, ferric and aluminum a salt (e.g., PAIFeClSi copolymer) is added to water and forms an amorphous precipitate of iron oxyhydroxide ($Fe_2O_3 \cdot H_2O$) and $Al_2O_3 \cdot H_2O$. The trace elements (both dissolved and suspended) are adsorbed onto and trapped within the precipitate. The settled precipitate is then separated from the water leaving a purified effluent. Depending upon the solution pH, the oxide surface can act as a weak acid or base and gain or lose a proton (i.e., it can undergo protonation or depronation). The following reacted to occur at the surface

$$\overline{SO}^{-} + H^{+} = \overline{SOH}$$

 $\overline{\text{SOH}} + \text{H}^+ = \overline{\text{SOH}_2^+}(\overline{\text{SOH}} \text{ represents a singly protonated oxide site})$

Cation adsorption reaction:

$$\overline{\text{SOH}} + \text{M}^{n+} + m\text{H}_2\text{O} = \overline{\text{SO.M(OH)}_m^{n-m-1}} + (m+1)\text{H}^+$$

Anion adsorption reaction:

$$\overline{\text{SOH}} + \text{A}^{n-} + m\text{H}^+ = \overline{\text{SOH}_{m+1}\text{A}^{m-n}}$$

M and *A* represent cationic and anionic adsorbate, respectively

In the case of ion-exchange mechanism: the reaction on the silica surface is accomplished through the substitution of protons of the surface silanol groups by the metal ions from solution, as follows:

$$M^{n+} + x (\equiv = SiOH) \leftrightarrow M (\equiv = SiO)_{x}^{(n-x)+} + xH^{+}$$
(3.9)

where the symbol ((()) distinguishes surface complexes from soluble complexes, M^{n+} = metal ion with n + charge, (((SiOH) = silanol group on the SiO₂ surface and xH^+ = number of protons released.

Besides, the previous mechanisms that can be responsible for the adsorption of the four metal ions onto the PAIFeCISi copolymer, the FTIR was used to evaluate the mechanisms involved. Fig. 7 Shows FTIR spectra of PAIFeClSi copolymer (original), with Pb, Fe and Mn and As ions. Fig. 7 also shows broad bands around 3700, 3400 and 1100 cm^{-1} which may be due to Si–OH which hydrogen bonded –OH and Si–O group, respectively, the peak at 450 cm^{-1} is due to the presence of free SiO₂. The peak at 1100 cm^{-1} is due to the presence asymmetric Si–O stretching bond. The peak at 800 cm⁻¹ is considered to be the bonding between C and Si or the overlapping of the Si and Si-OH vibrations [9,10]. Also, the intensity of the peak near 3700 cm⁻¹, due to the Si–OH stretching which decreased after the uptake due to the interaction between the metal ion and the surface groups. The band in the region of 1628 cm^{-1} has been observed for PAIFeClSi copolymer due to OH bending and shifted to higher wave numbers after metal removal. The bands at 1799, 1799. 1799 and 1805 cm^{-1} are due to the uptake of Pb. Fe and Mn and As ions, respectively. The new peaks observed at 1420, 1414, 1425 and 1423 cm⁻¹ in the spectrum of PAIFeCISi copolymer impregnated with Pb, Fe, Mn and As ions, respectively, correspond to the metal oxide stretching mode. The peaks at 872, 1149, 1016 and 1023 cm⁻¹ appears after uptake of Pb, Fe, Mn and As ions, respectively. The peaks at 709, 709, 708, 707 cm^{-1} are due to SiO-Fe or SiO-Al in the presence or absence of Pb, Fe, Mn and As ions, respectively. The peak of Al–OH or Fe–OH located at 2363 cm⁻¹ is shifted to higher wave number 2517, 2517, 2519 and 2519 due to the adsorption of Pb, Fe, Mn and As ions, onto iron and aluminum hydroxide precipitate, respectively.

4. Conclusion

Within limits of the present study it was found that sodium silicate (activated silica) was regarded as one of coagulant modifiers which has many features like very fast hydrolysis, promote rapid settling rates, extremely efficient in cold water, give low soluble residual aluminum, consume less alkalinity, very little effect on pH, increase the stability of coagulant and leads to a denser compacted sludge. Poly inorganic coagulants based on silica or iron are more favorable in removal of pollutants from waste waters. The maximum adsorption capacity of iron and aluminum copolymer impregnated with silica (PAIFeCISi) for lead, iron, manganese and arsenic are found to be 416, 222, 158, 146 mg/g, respectively. The residual aluminum level does not exceed the permissible limits (0.2 mg/L).

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