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Separation/Preconcentration of Al(III) from Water Samples via Sorptive-Flotation Technique Using Silica Nanoparticles Modified with Folic Acid

HANY M. YOUSSEF[1, 2]*
[1]Department of Chemistry, College of Science and Humanities in Al-Kharj, Prince Sattam bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia
[2]Department of Chemistry, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

***Abstract**: In the present work, silica nanoparticles functionalized with folic acid (Nano-SiO_2-FA) were synthesized and characterized thru elemental analysis, infrared spectroscopy (FT-IR), Brunauer-Emmett-Teller (BET) surface area determination, and scanning electron microscope (SEM). Nano-SiO_2-FA was examined as a sustainable and promising sorbent for preconcentration of Al(III) from natural water samples by sorptive-flotation (SF) separation technique before its determination by flame atomic absorption spectrometry (FAAS). A several trials were made in lab, to determine the feasibility of using Nano-SiO_2-FA as a sorbent and oleic acid as a surfactant. The influence of: solution pH, temperature, shaking time, surfactant, sorbent and Al(III) concentration and the presence of foreign ions that affect the sorptive-flotation process were investigated. Good results attained under optimum circumstances, at pH 3.5 and ~25°C, according to which nearly 100% of aluminum was separated. The procedure was successfully applied to recover aluminum spiked to some natural water samples. Moreover, a sorption and flotation mechanism is suggested.*

***Keywords:** preconcentration, silica nanoparticles, sorptive-flotation, folic acid*

1. Introduction

Al and Al-salts are being widely used in various industries such as drugs, beverages, packing materials, and dye industry [1]. Al high level in wastewaters prevents the growth of microorganisms which help organic materials stabilization in water. High levels of Al^{3+} ions in water are unpleasant and found to be neurotoxic [2, 3]. Also, it is concerned with several diseases as Parkinson and Alzheimer's [4, 5], bone softening, renal failure and anaemia [6]. Al presents in soils naturally in the form of minerals as, alumino-silicates (kaolin, feldspars and micas), hydroxides and oxides [7]. Foods and water are the most important sources for Al exposure. Al levels in waters with neutral pH ranged (0.001-0.05 $mg \cdot L^{-1}$) [8]. According to Environmental Protection Agency (EPA), Al in drinking water has a level of (0.05-0.2 $mg \cdot L^{-1}$) [9]. The high detection limit (D_L) of flame atomic absorption spectrometry (FAAS) and presence of matrix effects make it impossible for direct analysis of these low levels of metal ions without using a preconcentration procedure. Consequently, separation/preconcentration of analytes is required [10]. Several of separation/preconcentration techniques for metal ions in trace amount including adsorption on dissimilar adsorbents, solvent extraction [11], cloud point extraction, solid-phase extraction, co-precipitation, liquid–liquid micro-extraction have been discussed [12-15]. Recently, separation/preconcentration method namely flotation has received significant attention because it's simple and rapid method, and has good separation yield more than 95% and a wide possibility of usages for recovery purpose [16, 17].

Nowadays, more interest focused on the using of chelating fibers for separation and removing metal ions from aqueous media. Chelating fibers have several advantages as large sorption capacity, ease of regeneration and high selectivity which may be attributed to high sorption kinetics, low cost, large surface areas and presence of active sites [18-20]. Silica one of the most commonly used sorbent in chemical analysis owing to its numerus advantages as thermal, chemical, and mechanical stability, comparing to other sorbents [21].

**email: hanyyoussef178@gmail.com, hany_moustafa@mans.edu.eg*

The silanol groups present on the silica surface is considered being weak ion exchangers and have low interaction and binding force with the target analyte [22]. Hence, certain functional groups must be immobilized on silica surface to give selectivity behavior for surface of silica. Folic acid (Fig. 1), known commercially as vitamin B9 is a water-soluble substance and exhibits versatile ligation behaviors via the carboxylate group which can act as a mono, bi or bridging ligand bind to metal ions [23-25]. Many studies have been reported on the binding between folic acid and metals such as Cd(II), Pb(II), Cu(II), Zn(II), Fe(III), and Hg(II) [24, 26]. So, folic acid is considered being a green and ecofriendly sorbent for binding with metal ions. Owing to the above facts, this work aim to surface modification of chlorinated nanosilica with folic acid to produce Nano-SiO_2-FA nanocomposite. The produced sorbent was used for the preconcentration of Al^{3+} from different water samples by batch mode using sorptive-flotation (SF) technique

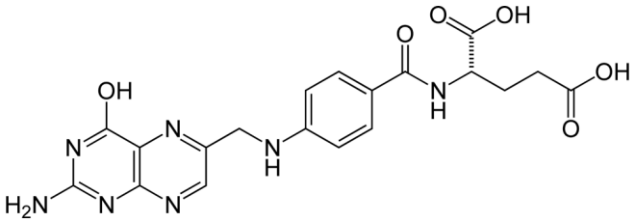

Figure 1. Structure of folic acid

2. Materials and methods

2.1. Materials and reagents

Powder of sodium silicate ($Na_2SiO_3.9H_2O$) which act as Si source was obtained from (Sigma-Aldrich, St. Louis, MO, USA), cetyltrimethylammonium bromide (CTAB) which act as structure directing agent was purchased from (Merck, Darmstadt, Germany), (3-chloropropyl)trimethoxysilane (3-CPTMS) which act as silylating agent was supplied by (Sigma-Aldrich, St. Louis, MO, USA), folic acid (97%) [Pteroylglutamic acid, PGA] from (TITAN BIOTECH LIMITED, India). Doubly distilled water was used during all investigates. The glassware was kept overnight in (10% HNO_3) then, washed by doubly distilled water and air dried. 1000 ppm Al^{3+} ion was prepared by dissolving suitable quantity of $AlCl_3.6H_2O$ (Merck, Darmstadt, Germany) in doubly distilled water. Oleic acid (HOL), 6.36×10^{-2} mol . L^{-1}, was prepared by mixing 20 mL with 1.0 L kerosene. HCl and NaOH were used for adjustment of *p*H.

2.2. Apparatus

2.2.1. Flame atomic absorption spectrometry

The remaining concentration of Al^{3+} ion in the filtrate was determined by Flame Atomic Absorption Spectrometry (FAAS) (GBC, SensAA Series) with air-acetylene flame under the optimal instrumental conditions shown in Table 1.

Table 1. Optimum instrumental conditions for Al^{3+} determination by FAAS:

Wave length, nm	309.3
Working calibrating range, ppm	0.02-0.12
Sensitivity, µg/ml	0.03

2.2.2. Infrared spectra

FT-IR spectra were performed via (Nicolet *i10* FT-IR, ThermoFisher Scientific, USA) spectrometer in the range of (4000-400 cm^{-1}).

2.2.3. Scanning electron microscope

Scanning electron microscope (SEM, Quanta FEG 250 (Field Emission Gun), ThermoFisher Scientific, USA) at an accelerating voltage of 30 kV, magnification 14×up to 1000000, was used for the assessment of surface morphology.

2.2.4. Surface area

The surface area investigation of prepared sorbent was carried out with nitrogen adsorption at -196°C using surface area analyzer (QUANTACHROME-NOVA@2000e series).

2.2.5. Flotation cell

The flotation process was occurred in a cylindrical test tube with 1.5 cm inner diameter and 29 cm length.

2.3. Methodology

2.3.1. Preparation of sorbent

2.3.1.1. Synthesis of nanosized silica

Synthesis of nanosized silica was carried out using cetyltrimethylammonium bromide (CTAB) as template, sodium silicate powder ($Na_2SiO_3.9H_2O$) as Si source and HCl as *p*H controlling agent. 12 g CTAB was placed in 460 mL of doubly distilled water, followed by stirring for 15 min then 80.377 g of Na_2SiO_3. $9H_2O$ was added to the mixture followed by stirring for 30 min. Concentrated HCl added to the mixture for *p*H adjustment at 9. The stirring non-stop for 4. The resulting bulky white gelatinous precipitate was transferred to a vessel of Teflon and left for 24 h at 25ºC. After that, the final product was filtered and washed with doubly distilled water after that dried at 50ºC for 6 h finally, the sample was calcined at 550ºC for 6 h [27].

2.3.1.2. Immobilization of silylating reagent

2.0 g of prepared nano-SiO_2 were mixed with 50 mL of dry toluene in a 250 mL flask. Then, 4.0 mL of (3-chloropropyl)trimethoxysilane was added and the product refluxed at 110°C with non-stop stirring for 6 hrs. The final product of nano-SiO_2-Cl separated and washed by diethylether and ethanol many times then dried at 50°C.

2.3.1.3. Functionalization of chlorinated nanosilica with folic acid

2.0 g of prepared nano-SiO_2-Cl was added to 50 mL of dry toluene in a 250 mL flask, then 2.0 g of folic acid was added and the mixture refluxed at 110°C and non-stop stirring for 6 hrs. The final product of nano-SiO_2-FA separated by filtration and washed by diethylether and ethanol many times and finally dried at 50°C.

2.3.2. Batch method for metal ion uptake via sorptive-flotation (SF) technique

10 mL aqueous solution containing defined amounts of Al^{3+} ion, sorbent and (HNO_3 or NaOH for *p*H-controlling) was placed in a flotation tube followed by shaking for the optimum time, after that 3 mL of HOL (with optimum concentration) was added, finally the tube was inverted 20 times upside down by hand then kept 5 min standing for complete flotation.

The removal % of Al^{3+} ions calculated as following:

$$\mathbf{Re\ \% = [(C_i - C_r)/C_i] \times 100} \qquad \mathbf{(1)}$$

where, C_r and C_i indicated the residual and initial Al^{3+} concentrations, respectively.

2.3.3. Effect of foreign ions

To study the applicability of the proposed procedure, the effect of interfering ions which could interfere with Al^{3+} ions removal using Nano-SiO_2-FA was tested under the optimum conditions.

2.3.4. Desorption study

To test sorbent desorption, 25 mg Nano-SiO_2-FA was added to 25 mL solution containing 10 ppm Al^{3+} at *p*H 3.5 and 25ºC and shacked for 30 min. The sorbent was filtered and washed with doubly distilled water, to remove the unloaded Al^{3+}. Then, 5 mL of HNO_3 of different concentrations was added to Nano-SiO_2-FA-Al^{3+} complex followed by shaking for 15 min finally, mixture was filtrated and Al^{3+} concentration was measured in the filtrate. The desorption ratio (D%) was determined by equation (2):

$$\mathbf{D\% = [C_d V_d / (C_o - C_e)\, V] \times 100} \qquad \mathbf{(2)}$$

where C_d is the concentration of Al^{3+} in desorption solution (ppm); V_d is the volume of the desorption solution (L); and V is the volume of solution (L), C_o (ppm) and C_e (ppm) initial and equilibrated Al^{3+} ion concentrations, respectively.

2.3.5. Analytical application

Natural water samples were collected from different locations in Egypt (Mansoura, Gamasa, Ras El-Barr, El-Manzalah and Alexandria), at a depth of 50 cm from the upper level, then all these samples were filtered then total dissolved salts (TDS) and *p*H were determined and finally all samples acidified with HNO_3 and preserved in a dark polyethylene bottle in a refrigerator at 5ºC for future use. The applicability of Nano-SiO_2-FA for uptake of the Al^{3+} ion from different natural water samples was studied for spiked concentration. The investigates were performed using 25 mL of filtered sample at *p*H 3.5 containing 25 mg sorbent and 1×10^{-3} mol/L HOL, finally the mixture shacked for 30 min. The removal % was determined by equation (1).

3. Results and discussions

3.1. Sorbent characterization

3.1.1. Elemental analysis (C, H and N)

The obtained results from elemental analysis of Nano-SiO_2-FA sorbent have been shown in Table 2. It's obvious that, after the chlorination step and modification of chlorinated nanosilica, the presence of nitrogen content considered as a good indication for insertion of the folic acid moieties onto the chlorinated nanosilica.

Table 2. Elemental analysis (C, H and N) for prepared sorbent:

% C	% H	% N
26.66	3.39	10.16

3.1.2. FT-IR analysis

The FT-IR spectra of different steps for prepared sorbent are illustrated in Figure 2. Before calcination, FT-IR spectrum exhibited bands at 3422 cm^{-1} (O-H stretching from H_2O and Si-OH), 2926/2855 cm^{-1} (C-H stretching of CTAB), 1650 cm^{-1} (Si-OH and H-OH bending for Si-OH and H_2O), 1481 cm^{-1} (CH_2 bending of CTAB), 1226/1068 cm^{-1} (asymmetric Si-O-Si stretching), 962 cm^{-1} (Si-O stretching of Si-OH), 795 cm^{-1} (symmetric stretching of Si-O-Si), 455 cm^{-1} (Si-O-Si bending) [28]. After calcination and functionalization, bands due to CTAB is absent from spectra and 3 distinctive peaks at 454, 845 and 1084 cm^{-1} are present which refer to Si-O-Si stretching, Si-O stretching and Si-O bending vibrations, respectively. Nano-SiO_2-FA was found to give many other peaks at 3530, 3419, 2967, 1695, 1608, 1485, 1412 and 1340 cm^{-1} that are assigned for N-H stretching, O-H stretching, C-H stretching, C=O stretching, C=N stretching, C=C stretching, C-C bending and C-N stretching vibrations,

respectively. The obtained results of FT-IR confirmed the successful surface loading of Nano-SiO_2 with folic acid to form Nano-SiO_2-FA [29-31].

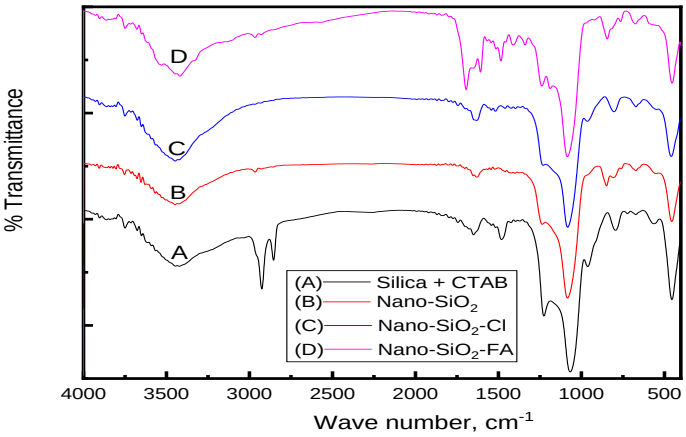

Figure 2. IR spectra of prepared nanosized silica and different modified forms

3.1.3. Scanning electron microscope

SEM was used to evaluate surface morphology and existence of Nano-SiO_2-FA nanocomposite in the form of nanoparticles. Figures (3a, 3b) represent the SEM graphs for Nano-SiO_2 and Nano-SiO_2-FA, respectively. From Figures (3a, 3b) it was notice that, the Nano-SiO_2 is consists of homogenous, uniform and almost spherical nanoparticles. But the immobilized FA on Nano-SiO_2 surface was found to be in aggregate forms, which refers to the covering of sorbent surface with folic acid.

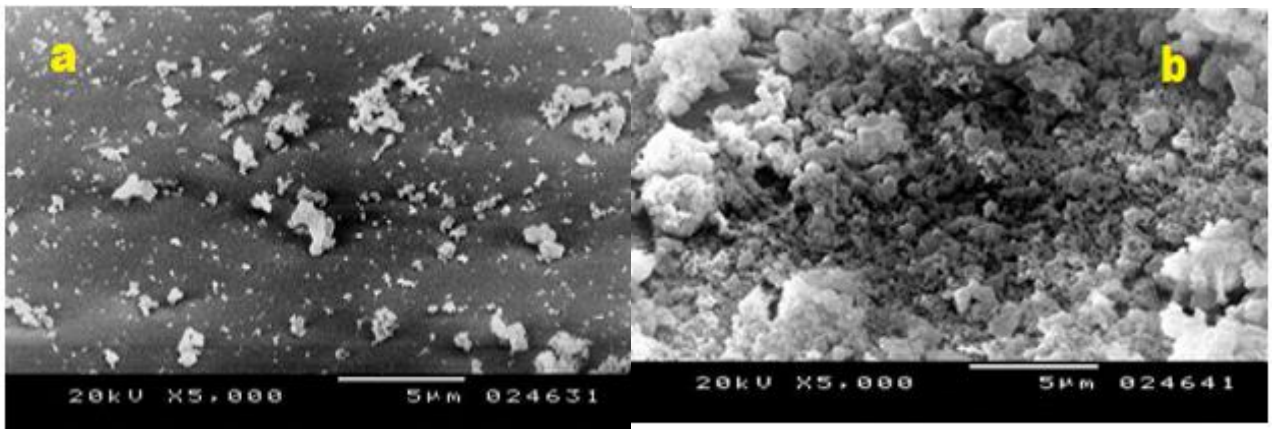

Figure 3. SEM images of (a) Nano-SiO_2, (b) Nano-SiO_2-FA

3.1.4. Surface area

The surface area found to be 455.438 m^2/g.

3.2. Batch process using sorptive-flotation (SF)

3.2.1. Influence of *p*H

The removal % of Al^{3+} ions over *p*H range (2-6) was studied to get optimum *p*H. Figure 4 shows the effect of the *p*H on the removal % of 20 ppm of Al^{3+} ions using 30 mg of Nano-SiO_2-FA and 1×10^{-3} $mol.L^{-1}$ of HOL. At *p*H< 3, functional groups of Nano-SiO_2-FA are protonated with H_3O^+ ions and the overall surface charge on the sorbent becomes positive. Thus, at *p*H below 3, the removal efficiency of Al^{3+} is low which can be attributed to the competition between Al^{3+} ions and protons for the active sites of sorbent surface. At *p*H range (3–6), there are lower competition between H_3O^+ and Al^{3+} ions for the

active sites of sorbent surface therefore more sites are easily available for metal ion binding, so the removal % of metal ions is increased and the optimal *p*H value found to be 3.5.

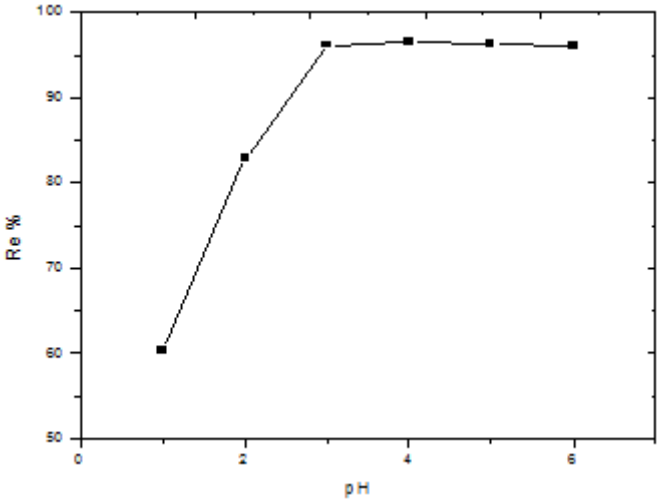

Figure 4. Effect of *p*H on the flotation of the Al^{3+} [Experimental conditions: 10 mL aqueous solution containing: 20 ppm Al^{3+} ion, 30 mg of Nano-SiO_2-FA, [HOL]=1×10^{-3} mol.L^{-1}, at 5 min shaking time and 25ºC]

3.2.2. Influence of sorbent and sorbate concentrations

Two runs of trials were done to test the influence of Nano-SiO_2-FA dosage (Figure 5) and Al^{3+} concentration (Figure 6) on the removal % of Al^{3+}ions from aqueous medium at *p*H 3.5 using 1×10^{-3} mol.L^{-1} of HOL. Figure 5 shows that, the removal % of Al^{3+} improved with raising Nano-SiO_2-FA dose, while it reduced with increasing Al^{3+} concentration (Figure 6). Achieving the maximum separation of Al^{3+} ions at a higher Nano-SiO_2-FA dose may be owing to increasing number of active sites present on the sorbent surface and available to Al^{3+}. Therefore, 30 mg of Nano-SiO_2-FA can be appropriate amount for the removal of $Al^{3+}$with a concentration ≤ 20 ppm.

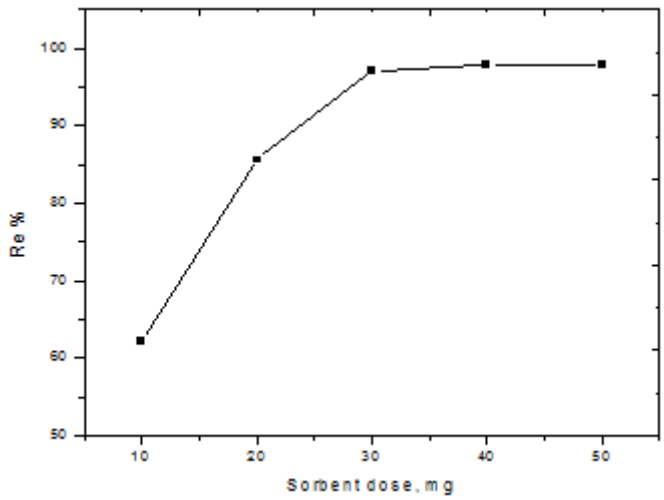

Figure 5. Effect of sorbent dose on the flotation of the Al^{3+} [Experimental conditions: 10 mL aqueous solution containing: 20 ppm Al^{3+} ion, [HOL]=1×10^{-3} mol.L^{-1}, at *p*H 3.5, 5 min shaking time and 25ºC]

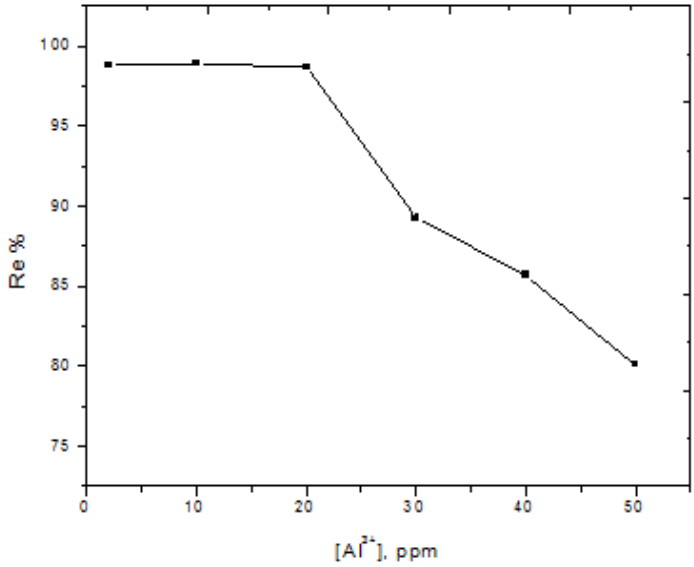

Figure 6. Effect metal ion concentration on the flotation of the Al^{3+} [Experimental conditions: 10 mL aqueous solution containing: 30 mg of Nano-SiO_2-FA, [HOL]=1×10^{-3} mol.L^{-1}, at *p*H 3.5, 5 min shaking time and 25ºC]

3.2.3. Influence of surfactant concentration

A run of trials were performed to remove 20 ppm of Al^{3+}ions from aqueous solutions at *p*H 3.5, using 30 mg of Nano-SiO_2-FA and different concentrations of HOL [1×10^{-3}-8×10^{-3}] mol . L^{-1}. The data obtained in Figure 7 confirmed that, a quantitative separation of Al^{3+} ions was achieved at HOL concentration of (1×10^{-3}-4×10^{-3} mol . L^{-1}). The removal of Al^{3+} ions reduced at higher concentrations, a phenomenon that can be attributed to the formation of a stable hydrated envelop of surfactant on the surface of air bubble, or due to the formation of hydrated micellar layer on the sorbent surface. In both cases, the hydrophobicity of the sorbent surface decrease the flotation efficiency [32, 33].

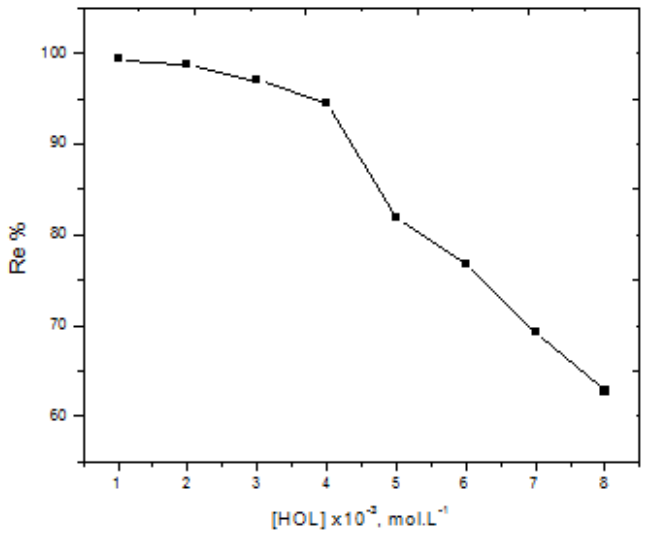

Figure 7. Effect of surfactant concentration on the flotation of the Al^{3+} [Experimental conditions: 10 mL aqueous solution containing: 20 ppm Al^{3+}ion, 30 mg of Nano-SiO_2-FA, at *p*H 3.5, 5 min shaking time and 25ºC]

3.2.4. Influence of shaking time

The effect of shaking time was also examined utilizing 20 ppm of Al^{3+} ions, 30 mg of Nano-SiO_2-FA and 1×10^{-3} M of HOL at *p*H 3.5. The range of shaking time was (1-10) min. The attained results in Figure 8 exposed that, the removing % enhanced to its maximum value after shaking time of 5 min. Subsequently, 5 min of shaking was believed to be sufficiently for the quantitative removal of Al^{3+} ions.

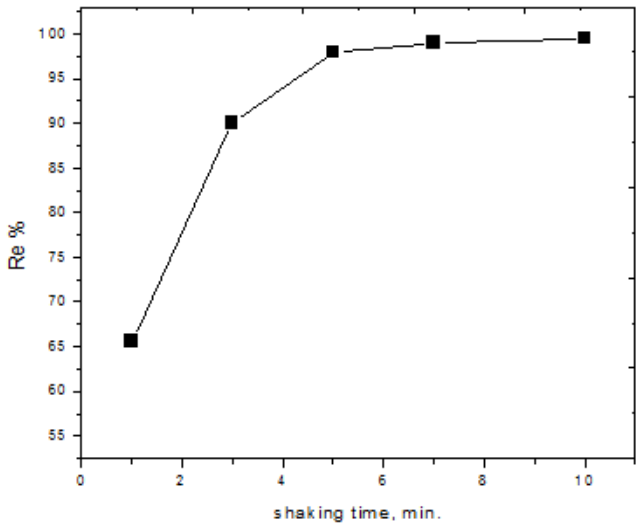

Figure 8. Effect of shaking time on the flotation of the Al^{3+}
[Experimental conditions: 10 mL aqueous solution containing:
20 ppm Al^{3+} ion, 30 mg of Nano-SiO_2-FA,
[HOL]=1×10^{-3} mol.L^{-1}, at *p*H 3.5 and 25°C]

3.2.5. Influence of temperature

For such study, one solution containing 20 ppm of Al^{3+} ions and 30 mg of Nano-SiO_2-FA and a second solution containing 1×10^{-3} mol.L^{-1} of HOL were heated up or cooled to the same temperature utilizing a water bath. Surfactant was rapidly poured onto the Al^{3+} solution, after which the mixture was floated. The found results in Figure 9 confirmed that, the removal % of Al^{3+} ions decreased with temperature increasing.

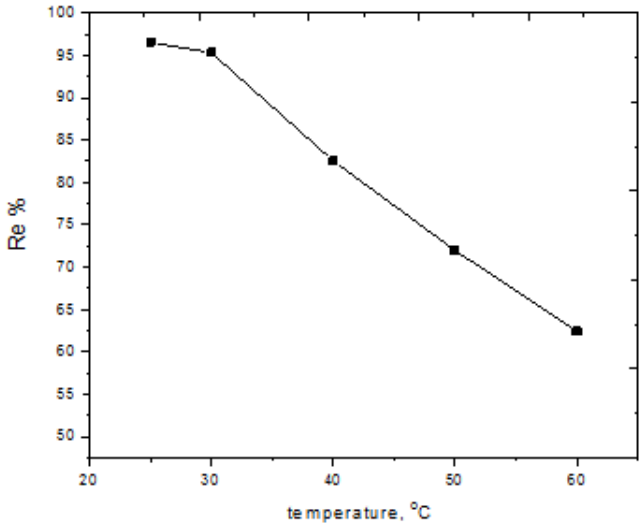

Figure 9. Effect of temperature on the flotation of the Al^{3+}
[Experimental conditions: 10 mL aqueous solution containing:
20 ppm Al^{3+} ion, 30 mg of Nano-SiO_2-FA, [HOL]=1×10^{-3} mol.L^{-1},
at *p*H 3.5 and 5 min shaking time]

3.3. Effect of foreign ions

To check the selectivity of the suggested methods and in order to investigate the relevance of Nano-SiO_2-FA for separation of Al^{3+} ions, the interference of several foreign ions on the removal of Al^{3+} ions was examined with pre-optimized experimental procedures. All cations were used as chlorides salt while the anions were applied as sodium salts. The data showed maximum tolerable concentration of foreign ions, with relative error ≤ 5%. The results attained in Table 3 indicated that, all the studied foreign ions with relatively high concentrations (compared to that of Al^{3+} ions) have no adverse effect on the analysis of Al^{3+} by the mentioned techniques. Although Mg^{2+} and Ca^{2+} ions may form magnesium and calcium oleats, the expected harmful effect on the recovery of Al^{3+} ions was not observed. Consequently, the suggested sorptive-flotation procedure could find its own applications for the recovery of Al^{3+} ions from different water matrices.

Table 3. Effects of foreign ions (in binary mixtures) on recovery of Al^{3+}:

Interfering ions		Added salt	Tolerable limit ($\mu g\ mL^{-1}$)	Re %
Anions	CH_3COO^-	CH_3COONa	180	95.5
	Cl^-	NaCl	1000	99.0
	NO_3^-	$NaNO_3$	900	97.8
	HCO_3^-	$NaHCO_3$	1000	97.9
	$C_2O_4^{2-}$	$Na_2C_2O_4$	190	95.4
	SO_4^{2-}	Na_2SO_4	800	97.1
	PO_4^{3-}	Na_3PO_4	150	97.3
	$C_6H_5O_7^{3-}$	$Na_3C_6H_5O_7$	190	97.0
Cations	NH_4^+	NH_4Cl	250	98.9
	K^+	KCl	1000	97.9
	Na^+	NaCl	1000	99.3
	Mg^{2+}	$MgCl_2$	100	97.8
	Ca^{2+}	$CaCl_2$	100	96.0
	Ba^{2+}	$BaCl_2$	120	96.4
	Cd^{2+}	$CdCl_2$	100	95.7
	Cu^{2+}	$CuCl_2$	100	96.2
	Hg^{2+}	$HgCl_2$	100	98.0
	Fe^{2+}	$FeCl_2$	100	97.1
	Zn^{2+}	$ZnSO_4$	90	97.7
	Ni^{2+}	$NiSO_4$	50	98.3

Experimental conditions: 10 mL aqueous solution containing: 20 ppm Al^{3+}, 30 mg of Nano-SiO_2-FA, at *p*H 3.5 using 1×10^{-3} mol.L^{-1} of HOL, shaking time 5 min and 25ºC.

3.4. Desorption study

Desorption tests contribute to regenerate the sorbent, also to recover Al^{3+} ions from the used sorbent moreover protecting the environment from solid waste disposal difficulties. Tries were made to desorb Al^{3+} ions from the metal laden sorbent using different concentrations of HNO_3. The effect of HNO_3 concentration (0.1, 0.5, 1.0 and 1.5 M) on the elution yield was assessed and the results offered in Table 4 display that quantitative extraction was achieved at concentrations of 1.5 M of nitric acid and quantitative yield (>96%) was obtained when 5 mL of 1.5 M HNO_3 was taken.

Table 4. Desorption study of Al^{3+} by HNO_3:

[HNO_3], mol.L^{-1}	Desorption %
0.1	52.61
0.5	63.37
1.0	85.12
1.5	96.87

3.5. Analytical applications

To examine the application of flotation procedures, a run of trials were conducted to recover spiked concentration of Al^{3+} ions added to some natural water samples. The results present in Table 5 show that

the recovery was quantitative and satisfactory (~ 100%) with a relative standard deviation (RSD) does not exceed 1.15 %.

Table 5. Recovery of 20 ppm of Al (III) ions added to some water samples:

Sample type	Sample location	Al^{3+} found, ppm	Uptake %
Tap water	Mansoura city	19.992	99.96
Nile water	Mansoura city	19.936	99.68
Lake water	El-Manzalah	19.678	98.39
Sea water	Ras El-Barr	19.868	99.34
	Gamasa	19.958	99.79
	Alexandria	19.974	99.87
Underground water	Mansoura city	19.952	99.76

3.6. Suggested mechanism for sorptive-flotation process:

Prior to talk about the probable mechanism, the following points should be taken into account:

1. Utmost metal ions are separated by: (i) adsorption onto sorbent surface by co-precipitation as $M(OH)_{(s)}$; (ii) flocculation by adsorption of hydrolytic forms or (iii) complexation with surface functional groups [34, 35].
2. Aluminum species may present as: $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ $Al(OH)_3^0$ ($Al_n(OH)_m^{(3n-m)+}$) , $Al(OH)_3(s)$ according to the *p*H of the medium [36].
3. The presence of N-H, C=O and O-H groups on sorbent surface was confirmed by the characteristic bands at 3530, 3419 and 1695 cm^{-1}, respectively.
4. Oleic acid begins to dissociate at *p*H ≥ 5.2 [37].

Consequently, the proposed mechanism for sorptive-flotation can be as follows:

1. At *p*H < 3, the charge on sorbent surface becomes positive due to protonation with H_3O^+ ions. Thus, at *p*H below 3, the removal efficiency of Al^{3+} is owing to the adsorption of hydrolytic species of aluminum on sorbent surface.
2. In the *p*H range 3–6, where the maximal removal of Al^{3+} ions occurred, adsorption may be electrostatically in nature and taking place via co-precipitation of the colloidal positive precipitates of aluminum.
3. Then, the adsorbent-adsorbate system is made hydrophobic by combination with un-dissociated surfactant molecules through H-bonds and/or chemically with oleate anions, then the resultant aggregates are floated to solution surface with the support of air bubbles.
4. In alkaline medium, the removal of Al^{3+} ions decreases which may be attributed to the inability of adsorption of the negative species, $Al(OH)_4^-$, or negative oleate ions on the negative surface of sorbent [38].

4. Conclusions

Preparation and using of nanosilica functionalized with folic acid in clean technology has discussed in the present work. Nano-SiO_2-FA was successfully prepared thru loading of folic acid on the surface of chlorinated nanosilica (Nano-SiO_2-Cl) and its structure was proved by several assessments. Nano-SiO_2-FA was used as an effective sorbent for selective separation and preconcentration of Al^{3+} ions from natural water samples using sorptive-flotation separation method before its determination by flame atomic absorption spectrometry (FAAS). The experimental data showed that the Al^{3+} removal by Nano-SiO_2-FA was dependant on *p*H. Also, it was indicated that the prepared sorbent can be regenerated easily using HNO_3 as eluent. Finally, the separation method was applied to the preconcentration of Al^{3+} ions from real samples without matrix interference.

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References

1. G. SPOSITO, The environmental chemistry of aluminum, CRC Press, 1995.
2. L. KOCHIAN, O. HOEKENGA, M. PINEROS, How do crop plants tolerate acid soils: Mechanisms of aluminum tolerance and phosphorous efficiency Annu. Rev, Plant Physiol. Plant Mol. Biol, 46 (1995) 237-260.
3. T.P. FLATEN, A.C. ALFREY, J.D. BIRCHALL, J. SAVORY, R.A. YOKEL, Status and future concerns of clinical and environmental aluminum toxicology, Journal of Toxicology and Environmental Health Part A, 48 (1996) 527-542.
4. A. CAMPBELL, The potential role of aluminium in Alzheimer's disease, Nephrology Dialysis Transplantation, 17 (2002) 17-20.
5. R.A. YOKEL, The toxicology of aluminum in the brain: a review, Neurotoxicology, 21 (2000) 813-828.
6. D. KREWSKI, R.A. YOKEL, E. NIEBOER, D. BORCHELT, J. COHEN, J. HARRY, S. KACEW, J. LINDSAY, A.M. MAHFOUZ, V. RONDEAU, Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide, Journal of Toxicology and Environmental Health, Part B, 10 (2007) 1-269.
7.B.-S. NEGREANU-PIRJOL, T. NEGREANU-PIRJOL, R. SIRBU, D.R. POPOVICIU, Bio-accumulation and Effects of Aluminium on Plant Growth in Three Culture Plants Species, *Rev. Chim.*, **70**(2), 2019, 602-604.
8. A. WHO, W.H. Organization, International Programme on Chemical Safety, Geneva, Environmental Health Criteria, 194 (1997).
9.*** U. EPA, Environmental Protection Agency, Secondary Drinking Water, Guidance for Nuisance Chemicals (2000), in.
10.I. NARIN, M. TUZEN, M. SOYLAK, Aluminium determination in environmental samples by graphite furnace atomic absorption spectrometry after solid phase extraction on Amberlite XAD-1180/pyrocatechol violet chelating resin, Talanta, 63 (2004) 411-418.
11. I.C. POPESCU , L. STOICA, C. CONSTANTIN, A.M. STANESCU, Equilibrium and Kinetics of $U(VI)_{(aq)}$ Adsorption on in situ Generated $Fe_2O_3.nH_2O$, *Rev. Chim.*, **70**(10), 2019, 3482-3485.
12. S. BAYTAK, A.R. TÜRKER, Determination of chromium, cadmium and manganese in water and fish samples after preconcentration using Penicillium digitatum immobilized on pumice stone, Clean–Soil, air, water, 37 (2009) 314-318.
13.A. BAYSAL, M. KAHRAMAN, S. AKMAN, The solid phase extraction of lead using silver nanoparticles-attached to silica gel prior to its determination by FAAS, Current Analytical Chemistry, 5 (2009) 352-357.
14.H. CIFTCI, Solid phase extraction method for the determination of cobalt in water samples on duolite XAD-761 resin using 4-(2-Pyridylazo) resorcinol by FAAS, Current Analytical Chemistry, 6 (2010) 154-160.
15. M. REZAEE, Y. YAMINI, A. KHANCHI, M. FARAJI, A. SALEH, A simple and rapid new dispersive liquid–liquid microextraction based on solidification of floating organic drop combined with inductively coupled plasma-optical emission spectrometry for preconcentration and determination of aluminium in water samples, Journal of hazardous materials, 178 (2010) 766-770.
16. L. STOICA, M. DINCULESCU, C.G. PLAPCIANU, Mn (II) recovery from aqueous systems by flotation, Water Research, 32 (1998) 3021-3030.
17.S.E.-S. GHAZY, S.E.-S. SAMRA, A.E.-F.M. MAHDY, S.M. EL-MORSY, Flotation-separation of aluminum from some water samples using powdered marble waste and oleic acid, Analytical sciences, 19 (2003) 1401-1406.
18.S. DENG, R. BAI, J. CHEN, Behaviors and mechanisms of copper adsorption on hydrolyzed polyacrylonitrile fibers, Journal of colloid and interface science, 260 (2003) 265-272.
19.S. DENG, R. BAI, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, Water research, 38 (2004) 2424-2432.

20. M. YIĞITOĞLU, M. ARSLAN, Selective removal of Cr (VI) ions from aqueous solutions including Cr (VI), Cu (II) and Cd (II) ions by 4-vinly pyridine/2-hydroxyethylmethacrylate monomer mixture grafted poly (ethylene terephthalate) fiber, Journal of hazardous materials, 166 (2009) 435-444.
21. D.L. KAPLAN, Introduction to biopolymers from renewable resources, in: Biopolymers from renewable resources, Springer, 1998, pp. 1-29.
22. F. OKIEIMEN, C. SOGBAIKE, J. EBHOAYE, Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers, Separation and purification Technology, 44 (2005) 85-89.
23. R.C. MEHROTRA, A. SINGH, Recent trends in metal alkoxide chemistry, Progress in Inorganic Chemistry, 46 (1997) 239-454.
24. M.A. EL-WAHED, M. REFAT, S. EL-MEGHARBEL, Synthesis, spectroscopic and thermal characterization of some transition metal complexes of folic acid, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 70 (2008) 916-922.
25.N. NOMBONA, W. CHIDAWANYIKA, T. NYOKONG, Photophysical behaviour of asymmetrically substituted metal free, Mg and Zn phthalocyanines in the presence of folic acid, Polyhedron, 30 (2011) 654-659.
26. E. HAMED, M. ATTIA, K. BASSIOUNY, Synthesis, spectroscopic and thermal characterization of copper (II) and iron (III) complexes of folic acid and their absorption efficiency in the blood, Bioinorganic chemistry and applications, 2009 (2009).
27.F. HAVASI, A. GHORBANI-CHOGHAMARANI, F. NIKPOUR, Pd-Grafted functionalized mesoporous MCM-41: A novel, green and heterogeneous nanocatalyst for the selective synthesis of phenols and anilines from aryl halides in water, New Journal of Chemistry, 39 (2015) 6504-6512.
28.C. HUO, J. OUYANG, H. YANG, CuO nanoparticles encapsulated inside Al-MCM-41 mesoporous materials via direct synthetic route, Scientific reports, 4 (2014) 3682.
29. T.M. ABDEL-FATTAH, M.E. MAHMOUD, Selective extraction of toxic heavy metal oxyanions and cations by a novel silica gel phase functionalized by vitamin B4, Chemical engineering journal, 172 (2011) 177-183.
30. Y. CAI, C. LI, D. WU, W. WANG, F. TAN, X. WANG, P.K. WONG, X. QIAO, HIGHLY active MgO nanoparticles for simultaneous bacterial inactivation and heavy metal removal from aqueous solution, Chemical Engineering Journal, 312 (2017) 158-166.
31. Z. PENG, C. XIONG, W. WANG, F. TAN, Y. XU, X. WANG, X. QIAO, Facile modification of nanoscale zero-valent iron with high stability for Cr (VI) remediation, Science of the Total Environment, 596 (2017) 266-273.
32.V.I. KLASSEN, V.A. MOKROUSOV, An introduction to the theory of flotation, Butterworths, 1963.
33. S. GHAZY, S. SAMRA, S. EL-MORSY, Removal of copper (II) from aqueous solutions by flotation using limestone fines as the sorbent and oleic acid as the surfactant, Adsorption Science & Technology, 19 (2001) 175-185.
34. R. APAK, E. TÜTEM, M. HÜGÜL, J. HIZAL, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water research, 32 (1998) 430-440.
35. A. ZOUBOULIS, K. KYDROS, K. MATIS, flotation of metal-loaded clay Anion Exchangers, water res, 29 (1995) 1755.
36. P.G. CAMPBELL, M. BISSON, R. BOUGIE, A. TESSIER, J.P. VILLENEUVE, Speciation of aluminum in acidic freshwaters, Analytical Chemistry, 55 (1983) 2246-2252.
37. S. GHAZY, S. SAMRA, S. EL-MORSY, Sorptive–Flotation of Copper (II) from Water Using Different Types of Powdered Activated Carbons as Sorbents and Oleic Acid as Surfactant, Adsorption Science & Technology, 19 (2001) 721-736.
38. A. ZOUBOULIS, N. LAZARIDIS, D. ZAMBOULIS, Powdered activated carbon separation from water by foam flotation, Separation science and technology, 29 (1994) 385-400.

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