



Nano silica particles loaded with CYANEX-921 for removal of iron(III) from phosphoric acid

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A simple route for preparation of organically modified spherical silica (SiO₂) nanoparticles with CYANEX 921 has been discussed. These modified particles has been used to remove Fe³⁺-SCN complex from 9M phosphoric acid. SEM, XRD, IR and EDS have been used to Characterized the powder in its several stages. The effect of SiO₂ weight, thiocyanate concentration, initial Fe (III) concentration, H₃PO₄ concentration, stirring time, temperature and loaded SiO₂ weight have been used to study the removal percent. The loaded silica succeeded in removal of 70% of Fe (III). Langmuir isotherm model well fit the experimental data with maximum sorption capacity 45.45 mg/g. The reaction kinetic is found to follow the pseudo second order kinetic model the adsorption reaction shows exothermic behavior.

Keywords: Silica nanoparticles, CYANEX 921, Iron, Phosphoric acid

Nanoparticles show unique properties due to its very small size and high surface area. These properties reflect their potential use in a wide range of applications including catalysts, adsorbents, light weight structural materials, sensors and other fine precision equipment⁷.

Silica is a polymer of silicic acid consisting of interlinked SiO₄ in a tetrahedral fashion, which has the stoichiometry SiO₂. The structure of silica surface terminates in either siloxane group (\equiv Si-O- Si \equiv) with the oxygen atom in the surface, or one of the several forms of silanol group (\equiv Si-OH). Surface modification of Silica nanoparticles (SiO₂NPs) mostly proceeded by organic modifier, which form covalent bond SiO₂NPs.

Different methods for synthesis of silica nanoparticles are reported¹⁻⁶. Therefore, different studies used different modifiers in the modification of SiO₂NPs such as, water-soluble polymer²⁵, aminofunctional²⁶, 4-isocya-nato-4'-(3,3'-dimethyl-2,4-dioxo-azetidino) diphenylmethane²⁷, vinyl and acrylate²⁸, Cationic surfactant³⁰, aminosilane, glycidoxysilane, mercaptosilane and vinylsilane³⁰, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane³² and 3-(triethoxysilyl) propylsuccinic anhydride³³.

Phosphoric acid owned its importance from where it acts as chemical intermediate or reagent in the

production of numerous phosphate fertilizers, agriculture feeds, waxes, polishes, soap, detergent, electropolishing, food, soil stabilization and catalyst in polymer preparation³³.

The phosphoric acid was purified by various methods such as crystallization⁸, liquid-liquid extraction⁹⁻¹¹, using modified activated carbon¹², using activated silica^{13,14}, and electroionization¹⁵. Such methods have many disadvantages such as high cost, long experimental time and/or environmental pollution.

In this work, spherical silica nanoparticles were synthesized by modifying the method used by Abdolraouf Samadi-Maybodi and Amir Vahid⁶. The surface of the prepared silica was then modified by impregnation with CYANEX 921 to be used for removal of iron from phosphoric acid. Purification of phosphoric acid produced by the wet method is important since its quality highly affect its use for different purposes.

Experimental Section Chemicals

Cetyl trimethyl ammonium bromide(CTAB) (99%, from Winlab, U.K.), Sodium silicate solution (28 wt.% SiO₂, 5 wt.% Na₂O, 67 wt.% H₂O, Sigma-

Aldrich), dehydrated ethanol (99.9%, International Co. for Supp. & Med. Industries), CYANEX921 (Cyanamid), Iron(III) chloride (99% Sigma-Aldrich), phosphoric acid (85%, BDH, England) and sodium thiocyanate (98%, Himedia laboratories Pvt Ltd., India). All chemicals were used as purchased and no further purification was performed.

Preparation of silica nanoparticles

CTAB surfactant solution was prepared by adding 2.6 g of CTAB to 69 g of double distilled water with continuous stirring to give a clear solution. To this solution, 8.2 g of ethanol was added with continuous stirring. 9.3 g of an aqueous solution of sodium silicate was added to surfactant solution, stirred for an hour, the solution was left for two hours for phase separation. To the bottom phase ethanol was added to yield white precipitate, which will be washed with ethanol twice and dried at 100°C for 24 h.

Surface modification of silica nanoparticles

The surface of the prepared silica was modified by impregnation of 1 g of the synthesized silica in 50 mL ethanol solution containing 0.2 g CYANEX 921. This mixture was stirred for an hour at room temperature followed by removal of ethanol by evaporation at 100°C down to around 10 mL. The obtained suspension was then dried at 35°C till remove all ethanol before the use in the extraction process.

Sorption procedure

The uptake percent of iron from phosphoric acid by silica nanoparticles or CYANEX 921 modified silica nanoparticles was investigated. In this concern, a known weight of the solid sorbent was mixed with 100 mL of certain concentration of phosphoric acid contain a certain amount of sodium thiocyanate and known concentration of iron. It was found that the equilibrium uptake was obtained after 2 min. the concentration of iron before and after sorption was then determined by the thiocyanate method using UV/Visible spectrophotometer (Double beam) (T80+, PG instruments Ltd., UK.). The % removal of iron was calculated using the following expression;

$$R\% = \frac{C_o - C_t}{C_o} \times 100 \quad \dots (1)$$

where, C_o and C_t are the initial concentration and the concentration of Fe^{3+} ion at time t , respectively.

Characterization

The characterization of the prepared silica nanoparticles was carried out by Scanning Electron Microscope (SEM) (JSM-636 OLA, Jeol, Japan.), Fourier Transmission Infra Red Spectroscopy (FT-IR) (8400s, Shimadzu, Japan) covered the range from 400-4000 cm^{-1} . IR spectra of solid samples were detected using KBr disc method. X-Ray Diffraction (XRD) (XRD-7000 Shimadzu, Japan) was utilized to estimate crystalline structure of the prepared nanoparticles. Energy dispersive spectroscopy (EDS) SEM with EDS analysis was used to measure the elemental analysis of samples.

Results and Discussion

prepared nano silica

The particles size of prepared nano silica was measured by SEM. In Fig. 1a, the SEM micrograph shows the high homogeneity in the size of the obtained silica nanoparticles with average range of particle size 0.022-0.044 μm and the particles were uniformly distributed without agglomeration. Figure 1b revealed to the XRD pattern of synthesized silica particles. Typical silica characteristic is observed at broad peak centered at $2\theta = 20^\circ$, indicating that the sample is amorphous^{7,16}.

The FTIR spectra of the obtained silica is shown in Fig. 1c. The figure demonstrates common bands assigned to various vibrations in the solid. The analysis of these spectra revealed the broad band centered at around 3445.59 cm^{-1} to correspond to the overlapping of the O-H stretching bands of hydrogen-bonded water molecules (H-O-H...H) and SiO-H stretching of surface silanols hydrogen-bonded to molecular water (SiO-H...H₂O)¹⁷. The absorption bands corresponding to the adsorbed water molecules deformation vibrations appear at 1656.67 cm^{-1} (Ref 18). The adsorption of water molecules on the surface of the aerogels is due to the existence of the surface silanol groups and therefore to the hydrophilic nature of these sol-gel materials. The very intense and broad band appearing at 1054.03 cm^{-1} (Ref 19) and the shoulder at around 1208.32 cm^{-1} (Ref 20) are assigned, respectively, to the transversal optical (TO) and longitudinal optical (LO) modes of the Si-O-Si asymmetric stretching vibrations. On the other hand, the symmetric stretching vibrations of Si-O-Si appear at 798.47 cm^{-1} and its bending mode appears at 441.67 cm^{-1} (Ref 21). The low energy band at around 595.93 cm^{-1} is assigned to Si-O stretching of the SiO₂ network defects. The peak corresponding to C-H vibration

medium intense peak appearing at 1475.44 cm^{-1} (Ref 22). This peak was easily assigned to the C-H symmetric deformation of $-\text{CH}_2$ groups. Strong sharp intense band at 2927.74 cm^{-1} revealed to symmetric stretching of C-H group²².

EDX measurement show that the whole area of prepared silica powder was around stoichiometric composition with high amount of carbons which may

be come from surfactant or contamination from previous sample as demonstrated in Fig. 1d.

Modified silica nanoparticles

By loading CYANEX921 on SiO_2 nanoparticles, the FTIR spectra shows characteristic peaks for SiO_2 at 449.38 , 1053.06 and 1479.3 cm^{-1} , are shifted to 454.20 , 1078.13 and 1456.16 cm^{-1} with some decrease

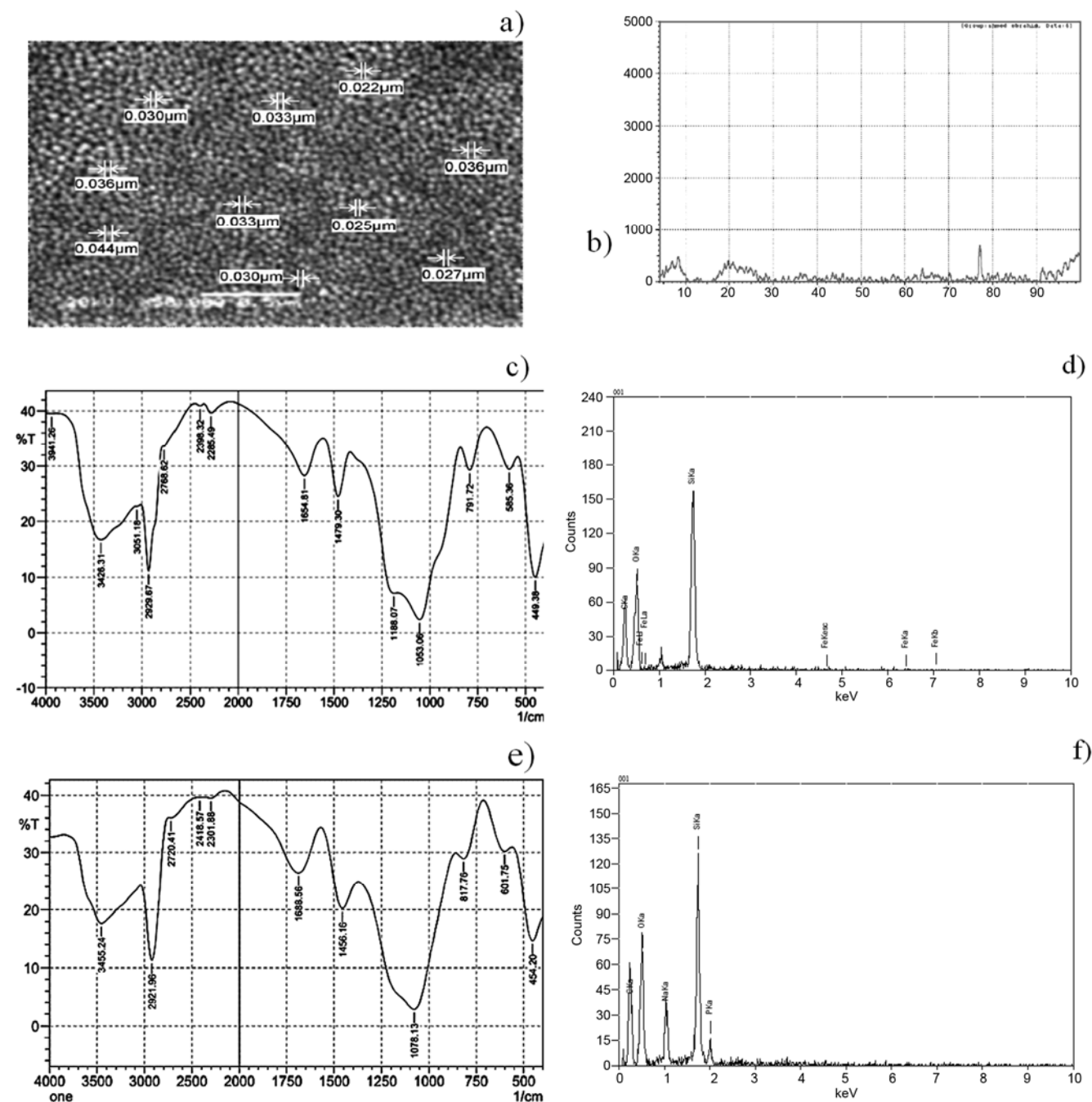


Fig. 1 — a) SEM micrographs of the obtained silica, b) XRD pattern of the obtained silica, c) FT-IR spectra of the obtained silica, d) The EDS analysis of the obtained silica, e) FT-IR spectra of SiO_2 NPs + CYANEX921 and f) The EDS analysis of SiO_2 NPs+ CYANEX 921

in the intensities and the peak at 1188.07 cm^{-1} disappears as shown in Fig. 1e, this is due to the formation of covalent bond between O-atom present in nano SiO_2 and CYANEX921. Moreover, the phosphorus was detected by EDS measurement as showed in Fig. 1f.

Sorption of iron(III)

At studying the effect of shaking time on the extraction of Fe (III) thiocyanate, it is indicating that 5 seconds-mixing time is enough to reach extraction equilibrium, as illustrated in Fig. 2a. Therefore, by study the effect of initial Fe (III) ions concentration on the removal percent (%R) of Fe (III) thiocyanate from pure 9 M phosphoric acid solution, the results obtained are given as a relation between the Fe (III) ions concentration in aqueous phase (ppm), and removal percent (%R), as in Fig. 2b. It was found that the increase in Fe (III) ions concentration leads to the decrease in removal percent (%R) of Fe (III) from phosphoric acid solution. The values of the removal percent (%R) were traced against the respective SiO_2 weight in rang (0.005-0.1g) as given in Fig. 2c. This Figure showed that the values of (%R) increases as SiO_2 weight increase in the used range.

The removal percent (%R) was plotted vs. the corresponding thiocyanate ions concentration (M) in range (0.00 – 1.58M) as a relation in Fig. 2d. It is clear that the removal percent (%R) increased with increase thiocyanate ions concentration. Furthermore, the effect of H_3PO_4 concentrations on the removal percent (%R) of Fe (III) thiocyanate was studied at acid concentration range (1-9M), the results obtained

are given as a relation between molar phosphoric acid concentration and removal percent of iron (%R), Fig. 2e. It is clear that the %R is decrease by increasing the concentration of phosphoric acid.

The removal of Fe (III) thiocyanate was influenced by the varying in the temperature, this investigated in the range from 10 to 50°C . The results obtained were plotted as a relation between the iron %R and temperature, as in Fig. 2f. The relation was obviously clear that the extraction of Fe (III) increased with lowering the temperature.

The extraction of Fe (III) thiocyanate complex by loaded silica nanoparticles was confirmed by FTIR where SCN^- band appear at 2051 cm^{-1} as in Fig. 3a and EDS analysis where the phosphorus, iron and sulfur were detected as in Fig. 3b. From the figure we observed that the percent of the phosphorus increase this may be referred to adsorption of phosphoric acid.

Adsorption isotherms

Adsorption data for a wide range of adsorbate concentrations are most conveniently described by adsorption isotherm, which relate adsorption density q_e to equilibrium adsorbate concentration in the bulk fluid phase, C_e . The Langmuir Isotherm²⁴ was tested by plotting C_e/q_e vs. C_e according to the relation;

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad \dots (2)$$

where, C_e (mg/L) is the equilibrium concentration of the investigated metal ion, q_e (mg/g) is the metal ion concentration in the loaded solid phase and Q_o is the

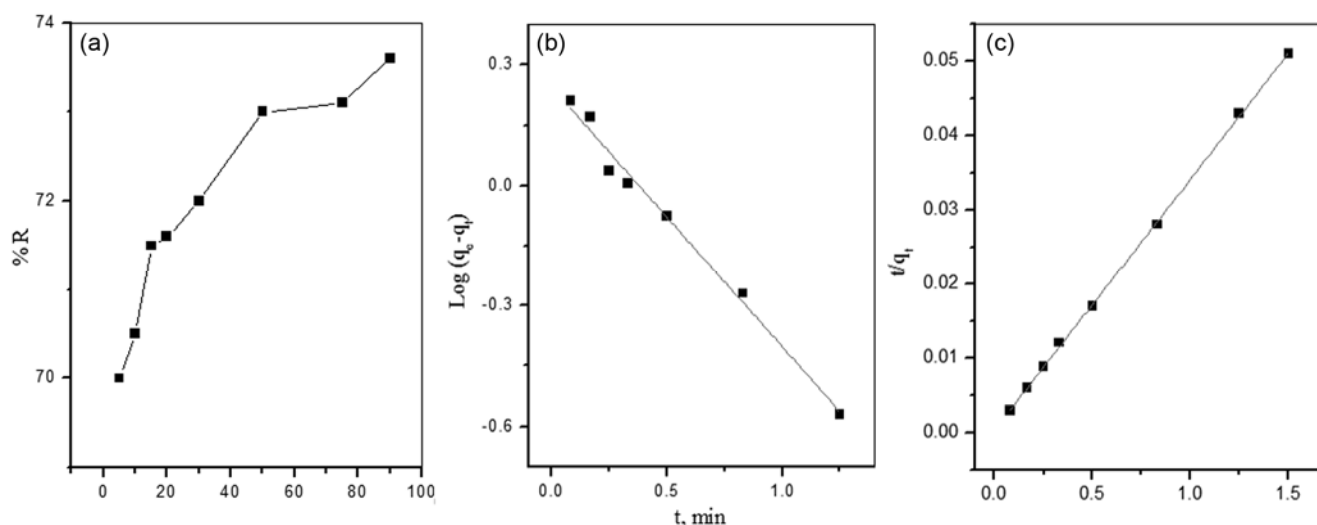


Fig. 2 — Effect of a) contact time, b) pseudo 1st order and c) pseudo 2nd order on the removal of Fe (III) thiocyanate complex from 9 M phosphoric acid. [Fe (III)]: 4000 ppm SiO_2 : 0.05 g $[\text{SCN}^-]$: 1.2 M Temperature: 20°C

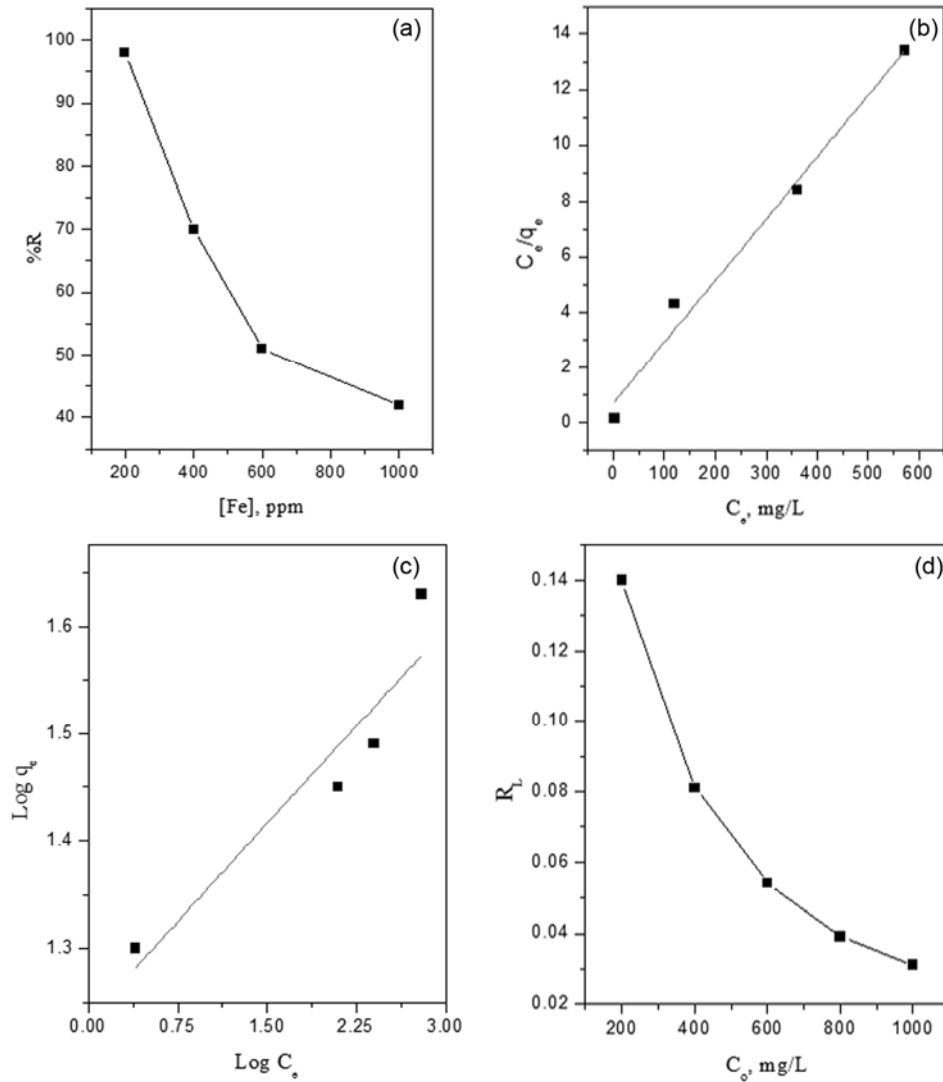


Fig. 3 — a) Effect of Fe (III) concentration on the removal percent (%R) of Fe(III) thiocyanate complex from 9 M phosphoric acid, b) Langmuir adsorption isotherm and c) Freundlich adsorption isotherm of iron by loaded silica and d) variation of dimensionless factor R_L with initial concentrations (C_0). Time: 5 sec SiO_2 : 0.05 g $[(\text{SCN})^-]$: 1.2 M Temperature: 20°C

monolayer adsorption capacity (mg/g) as shown in Fig. 4a.

Freundlich isotherm²⁵ is also tested revealed to;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (3)$$

where K_f and n Freundlich constant which determined from the intercept and slope of the linear of $\log q_e$ vs $\log C_e$, respectively, as shown in Fig. 4b. The fitting of the data to Freundlich isotherm suggests that adsorption is not restricted to one specific class of sites and assumes surface heterogeneity. The calculated constants of isotherm Eqs. and R^2 are summarized in Table 1.

Table 1 — Langmuir and Freundlich constants for adsorption of Fe^{3+} by loaded silica.

Adsorbent	Langmuir isotherm model			Freundlich isotherm model		
	Q_0 (mg/g)	b (L/mg)	R^2	n	K_f (mg/g)	R^2
Fe^{3+}	45.45	0.031	0.980	8.33	16.98	0.830

Analyzing to the Langmuir data in the Table 1. The Langmuir model fitted the experimental data better than Freundlich model. This indicates that the Fe^{3+} adsorbed on the loaded silica as a monolayer.

The separation factor (R_L), is a dimensionless parameter, which can be calculated from Langmuir isotherm according to the equation;

$$R_L = \frac{1}{1 + bC_o} \quad \dots (4) \quad q_e = \frac{(C_o - C_e)v}{1000w} \quad \dots (6)$$

The adsorption reaction can be characterized by R_L where, $R_L > 1$ unfavorable; $0 < R_L < 1$ favorable and $R_L = 0$ irreversible. In this work, the value of R_L calculated from the equation 5 and plotted against the initial metal concentration C_o , as shown in Fig. 11. From the Fig. 4c, the R_L value change from 0.14 to 0.031 for the initial concentration range 200-1000 mg/L. This suggesting a favorable Fe adsorption onto the loaded silica.

Sorption kinetics

The mechanism of the sorption process can be explained by fitting the kinetic data pseudo first order and pseudo second order kinetic models. The two kinetic models can be expressed as below;

pseudo-first-order presented by Lagergren equation³⁴ Eq. (6).

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad \dots (5)$$

where, q_e (mg /g) is the amount of sorption at equilibrium time, q_t (mg /g) is amount of sorption at time and K_1 (min^{-1}) is the rate constant of pseudo first order sorption.

where C_o is the initial concentration (mg/L), C_e is the dye concentration at equilibrium time intervals (mg/L), V is the volume of dye solution (mL) and W is the mass of adsorbent (g.)

$$qt - \frac{(C_o - C_t)v}{1000w} \quad \dots (7)$$

where C_t is the dye concentration at different time intervals (mg/L)

And pseudo-second-order expressed by Ho equation³⁵ the equation developed in a linear form as; Eq. (9).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \dots (8)$$

where, K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo second order reaction .

The kinetic data were explained by both the pseudo first order and pseudo second order kinetic models as shown in Figs. 5a and 5b. The calculated constants of the two kinetics equations and correlation coefficients R^2 are obtained from fitting the experimental data using the linear Eq. (6 and 9) and listed in Table 2.

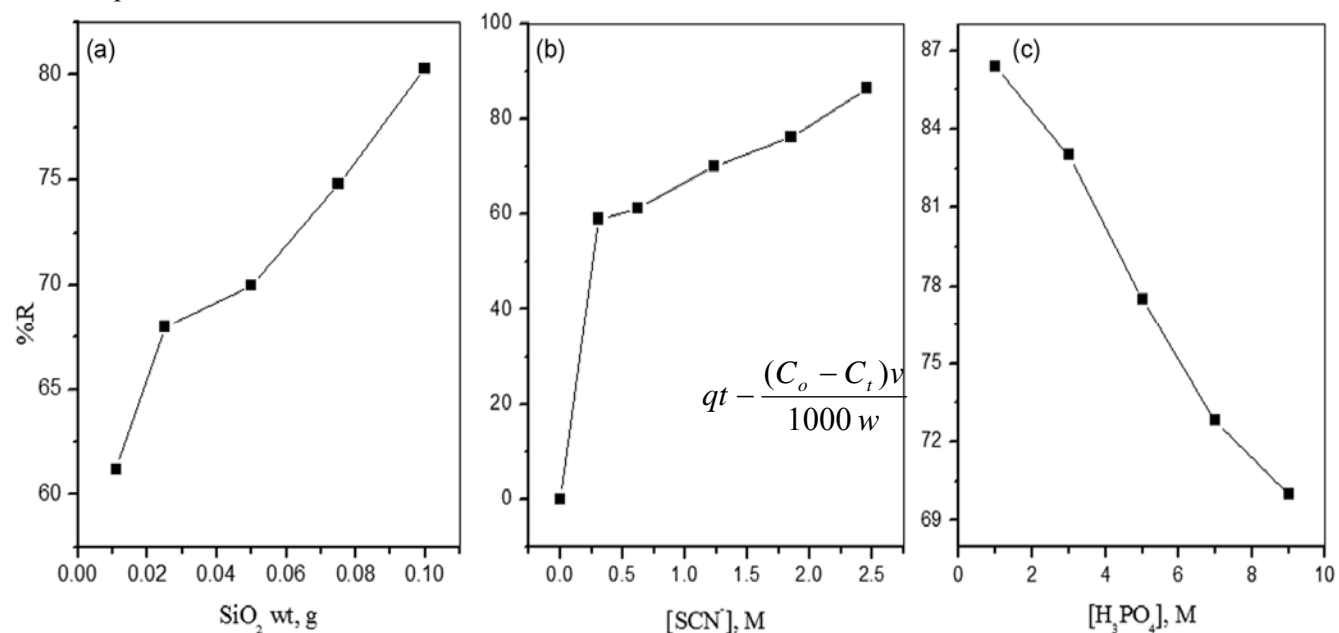


Fig. 4 — a) Effect of SiO_2 weight on the removal percent of Fe(III) thiocyanate complex from 9 M phosphoric acid (Time: 5 sec., $[\text{Fe(III)}]$: 400 ppm, $[\text{SCN}^-]$: 1.2 M, Temperature: 20°C), b) Effect of thiocyanate ion concentration on the removal percent of Fe(III) thiocyanate complex from 9 M phosphoric acid (Time: 5 sec., $[\text{Fe(III)}]$: 400 ppm, SiO_2 : 0.05 g, Temperature: 20°C) and c) Effect of H_3PO_4 concentration on the removal percent (%R) of Fe (III) thiocyanate complex from 9 M phosphoric acid (Time: 5 sec., SiO_2 : 0.05 g, $[\text{SCN}^-]$: 1.2 M, Temperature: 20°C).

The pseudo second order kinetic model was fitted the experimental data better than the pseudo first order kinetic model with correlation coefficient value ($R^2 = 0.999$). moreover, the calculated ($q_e = 29.59$) value much closer to the experimental ($q_{exp} = 29.66$) value.

Thermodynamic studies

The change in standard free energy (ΔG° in kJ mol⁻¹), enthalpy (ΔH° in kJ mol⁻¹) and entropy

(ΔS° in kJ mol⁻¹) of adsorption were calculated using the equations 10 and 11.

$$\Delta G^\circ = -RT \text{Ln}K_o \quad \dots (9)$$

where R is the universal gas constant (8.314 J/mol K) and T is temperature (K).

$$\text{Ln}K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (10)$$

Table 2 — Calculated parameters of the pseudo First-order and pseudo Second-order kinetic models

Adsorbent	$q_{e \text{ exp}}$ (mg /g)	First-order kinetic parameter			Second-order kinetic parameter		
		K_1 (min ⁻¹)	$q_{e \text{ cal}}$ (mg /g)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	$q_{e \text{ cal}}$ (mg /g)	R^2
Fe ³⁺	29.66	-1.50	1.74	0.987	4.05	29.59	0.999

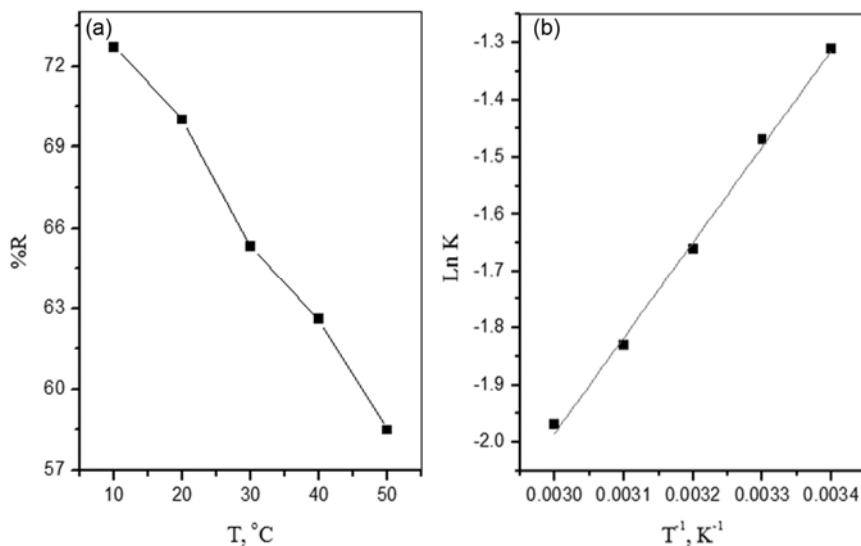


Fig. 5 — a) Effect of temperature on the removal percent (%R) of Fe (III) thiocyanate complex from 9 M phosphoric acid and b) Thermodynamic isotherm of removal of Fe (III) thiocyanate complex from 9 M phosphoric acid. (Time: 5 sec, [Fe (III)]: 150 ppm, SiO₂: 0.05 g,) [(SCN)⁻]: 1.2 M)

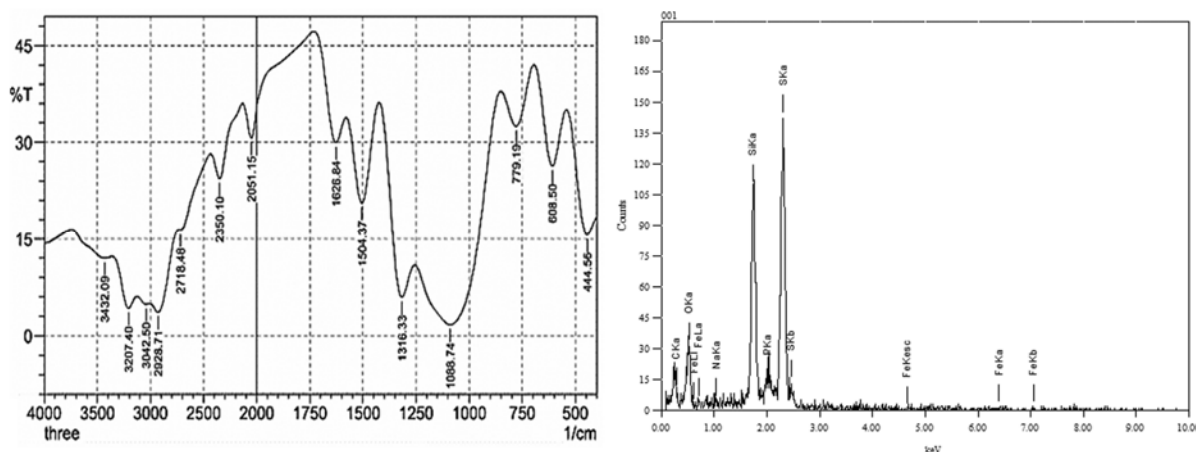


Fig. 6 — a) FT-IR spectra and b) The EDS analysis of SiO₂ NPs + CYANEX 921+ FeSCN

Table 3 — Thermodynamic parameters for Fe³⁺ removal from 9M phosphoric acid.

T (K)	ΔG (kJ/mole)	ΔH(kJ/mole)	ΔS (J/mole/K)
293	-3.19	-14	-58.40
303	-37.03		
313	-43.19		
323	-49.14		
333	-54.54		

By plotting $\ln K$ vs. T^{-1} (Fig. 6), from the slope and intercept, ΔS° and ΔH° parameters can be calculated, respectively. The values of ΔG° , ΔS° and ΔH° are calculated and recorded in Table 3. Referring to the data in the Table 3, the adsorption reaction is spontaneous where the ΔG° has negative values. Furthermore, the negative value of enthalpy change (ΔH°) for the processes further contras the exothermic nature of the process, the negative entropy (ΔS°) reflects the affinity of the adsorbent material toward the metal species.

Conclusion

In this contribution, we present a fast and simple method for removal of Fe (III) from phosphoric acid using modified SiO₂ NPs has been presented. The prepared SiO₂ NPs exhibit diameter between (0.022-0.044 μm) determined by SEM, have amorphous structure estimated by XRD, show all SiO₂ stretching and bending in IR region and EDS analysis shows the chemical composition of SiO₂ NPs near the stiometeric value with high content of carbon. The SiO₂ NPs were modified with CYANEX921 and this loading was confirmed by IR and EDS analysis. The modified SiO₂ NPs were succeeded in removing of FeSCN complex from phosphoric acid. The kinetic of the adsorption processes was found to follow the pseudo-second-order kinetic model. The Fe(III) adsorbed as a monolayer based on the obtained adsorption isotherm data and the adsorption reaction tend to be exothermic.

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