

A new adsorbent for Pd (II) ions from aqueous solutions using diphenylphosphine with magnetic properties

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Abstract

The aim of this study was to remove palladium ions from aqueous media in a batch operating system. A newly synthesized magnetic Fe₃O₄/SiO₂/OPPh₂ (diphenylphosphinite) nanocomposite was used as the adsorbent. This nanocomposite was examined by Fourier transform infrared, thermogravimetric analysis and X-ray spectroscopy methods. The factors that influence the adsorption equilibrium were examined, such as pH value, adsorbent dosage, metal concentration, adsorption time, temperature, influence of desorption solutions, concentration of the desorption solution and the influence of the ions present at the same time, namely Cd²⁺, Ni²⁺, Ca²⁺, Co²⁺, Fe³⁺, Ba²⁺ and Pt⁴⁺ were determined based on the adsorbent used (Fe₃O₄ / SiO₂ / OPPh₂). Under optimal conditions and at the same concentrations, the interfering ions have only a very slight influence on the Pd (II) uptake. It was found that the fit isotherm is the Fritz-Schlunder model. The best possible model was determined in advance on the basis of seven error functions. Thermodynamic parameters indicate the endothermic, irreversible and non-spontaneous nature of the adsorption.

1. Introduction

Palladium (Pd) has important and various applications in many industries due to its mechanical and electromagnetic properties and excellent electrical and thermal conductivity. Pd is widely used in electrical communication equipment, electrical relays, the gold industry and the aircraft industry. Pd is a suitable choice to remove chlorinated compounds from environmental pollutants [1, 2]. There are different methods for the removal of palladium from the aqueous media. Solid-phase extraction has advantages over other methods for separation and extraction of metal ions, including lower cost, greater recoveries, no emulsion problems, lower solvent and reagent consumption, less apparatus, greater safety and accuracy, fewer steps and less exposure to toxic agents [3, 4]. Using a suitable adsorbent is one of the main factors in solid-phase extraction. It is possible to control decomposition parameters such as selectivity and sorption capacity with an appropriate adsorbent. Up to the present, several materials have been used as solid-phase adsorbents. Nanoscale adsorbents offer better kinetics for the adsorption of metal ions because of their superior properties, especially their tiny size and high surface-to-volume ratio. Magnetic nanoparticles (MNPs) are superparamagnetic materials, meaning they are absorbed in the magnetic field but leave no magnetic properties after the field is removed. Therefore, magnetic solid-phase extraction (MSPE) with MNPs as an adsorbent has received a lot of attention in global analysis society in recent years. So, the surface functionalization of MNPs with suitable materials plays a vital role in the pre-concentration and selective separation of analytes [5 – 11]. Iron oxide nanoparticles (IONPs) trapped in silica shells have great importance in the field of catalysts, magneto-optical devices and magnetic resonance imaging. The crucial application of IONPs is their use as catalysts. Magnetite (Fe₃O₄) is one of the most widely used iron oxides, which has better catalytic properties for reducing nitro-aromatic compounds. Fe₃O₄ also has better magnetic properties than other iron oxides. A combination of IONPs, hydroxyapatite and palladium (IONPs / HAP / Pd) is one of the best nanocatalysts with high efficiency in removing dye from effluents. High stability, recyclability and no need for light or any harmful

substances are the advantages of this nanocatalyst [12 – 14]. The use of a possible Si source with tetraethyl orthosilicate (TEOS) is a typical process for the production of SiO₂-coated magnetic nanocomposites (15). In an acidic environment the Fe₃O₄ particles are especially reactive and their magnetic forces would be reduced, to prevent this reduction, SiO₂ was used as a solid layer to cover the Fe₃O₄ particles and thus to build up a core-shell structure (Fe₃O₄ / SiO₂) that enables surface modification. (16-19). In present work the, diphenylchlorophosphine -modified hollow Fe₃O₄ / SiO₂ / magnetic composites (Fe₃O₄ / SiO₂ / Opph₂) was synthesized. The big hollow Fe₃O₄ / SiO₂ / opph₂ was considered as an ideal adsorbent to remove Pd (II) ions from wastewater under different test conditions.

2. Experimental

2.1. Materials and solutions

All the chemicals such as FeCl₂.4H₂O, FeCl₃.6H₂O, Ammonia, isopropanol, tetraethoxysilane (TEOS), diphenylchlorophosphine, ethanol, toluene, hydrochloric acid, nitric acid, ammonium nitrate and Sodium hydroxide were of analytical quality and prepared from Sigma Aldrich, Fluka and Merck Companies. The synthesized adsorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) Bruker (Germany, X-ray powder diffractometry (X'pert, Philips, Holland) and thermogravimetric analysis (TGA) (Rheometric Scientific STA 1500H analyzer). The pH values and the metallic ions were measured by Metrohm model 744 pH meter (Zofingen, Switzerland) and the Varian Turbo 150AX ICP-OES instruments, respectively.

2.2. Procedure

2.2.1. Batch adsorption studies

Influence of various specifications, namely pH, mass of the adsorbent, Beginning concentration, moments of equilibrium, interfering ions, different eluents for desorption solution, different temperatures on the adsorption of palladium ions, Effect of potentially interfering ions and the sorption of Pd²⁺ on real samples were determined in batch experiments. All tests were carried out twice in this work and the average values are shown in the figures and tables. The percentage of palladium uptake was achieved by the deviation of the Beginning concentration and the equilibrium concentration. The portion of the ion q_e (mg g⁻¹) retained in the adsorbent was calculated using the quantity equilibrium equation and distribution ratio (K_d) was calculated using Eqs. (1) and (2), respectively.

$$q_e = (C_0 - C_e) \times \frac{V}{m}$$

$$K_d = \frac{qe}{C_e} = \frac{C_0 - C_e}{C_e} \times \frac{V}{m}$$

2

Where C_0 and C_e are the Beginning and balance concentration, respectively (mg L^{-1}) of ions in solution. V / m is the volume expansion of the ion solution in liters for the amount of $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{OPPh}_2$ adsorbent in grams. In the batch experiments, 25 ml of solution and 0.04 g of $\text{Fe}_3\text{O}_4 @ \text{SiO}_2 @ \text{OPPh}_2$ were chosen throughout in this work unless otherwise stated.

2.2.2. Synthesis of the adsorbent $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{OPPh}_2$ nanocomposite

- A. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (9.94 g, 0.05 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (16.2 g, 0.06 mmol) were added to 200mL of deionized water and ammonia solution (25 wt %). The acidity of obtained solution was adjusted to $\text{pH} = 9$, and stored at 25°C for 12 hours. The deposited nanoparticles were then separated by using a permanent magnet and washed with water several times to reach a neutral acidity. ($\text{pH} = 7$). After all, the produced MNPs were placed in a vacuum oven for 24 hours and completely dried at 80°C .
- B. A mixture of eight grams of magnetic nanoparticles with one liter of isopropanol and 100 ml of H_2O was irradiated by an ultrasonic instrument. 300 ml of NH_3 (25% by weight) was added to the mixture and a composition of thirty milliliters of tetraethoxysilane and 250 ml of isopropanol was added drop by drop to the reaction solution with stirring at 25°C . The suspension was stirred at 25°C for 18 hours. The obtained $\text{Fe}_3\text{O}_4 / \text{SiO}_2$ particles were cleaned with deionized water and ethyl alcohol and then separated with a magnet. Finally, the $\text{Fe}_3\text{O}_4 / \text{SiO}_2$ particles were dried in an oven at 80°C for 24 hours
- C. 8.0 gram of $\text{Fe}_3\text{O}_4/\text{SiO}_2$, 100mL of Et_3N and 400 ml of toluene were placed in a clean flask and irradiated with ultrasound for 15 minutes. Following that, 25 ml of diphenylchlorophosphine was added drop by drop with stirring under nitrogen gas, the sample was stirred for 24 hours and then separated with a magnet and cleaned several times with ethyl alcohol and then dried at 80°C to give $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{OPPh}_2$. Scheme 1 shows the synthesis steps.

3. Results And Discussion

3.1. Adsorbent characterization

3.1.2. Thermogravimetric Analysis

In order to observe the thermal stability of the substances, thermogravimetric analyzes (TGA) of Fe₃O₄, Fe₃O₄ @ SiO₂ and Fe₃O₄ @ SiO₂ @ OPhh₂ were used. The TGA curves of Fe₃O₄ and Fe₃O₄ @ SiO₂ nanoparticles slightly changed and the TGA curves (Fig. 2a) of Fe₃O₄ @ SiO₂ @ OPhh₂ nanoparticles change very suddenly with the increase in temperature. In the case of Fe₃O₄ nanoparticles, the weight loss was Approx. 4% which could be related to the adsorbed water and (/ or) structural water in the course of a temperature section of 50°C to 800°C [20]. The TGA curve of Fe₃O₄ @ SiO₂ showed a weight loss about 2% before the temperature of 200°C due to the desorption of water from the surface layers of the silica, and the weight loss was increase 3% more at a temperature range of 200°C to 800°C % which were associated with structural water [16]. For the TGA curves of Fe₃O₄ @ SiO₂ @ OPhh₂, organic polymers decompose rapidly between the temperatures of 200°C and 330°C and the water loss in the breakdown of the built-in magnet (OPhh₂) are probably the reasons of a weight loss of about 5.80%.

3.1.3. XRD pattern

Figure 2b shows the XRD types of Fe₃O₄, Fe₃O₄ @ SiO₂ and Fe₃O₄ @ SiO₂ @ OPhh₂ nanoparticles. Eight diffraction peaks (111, 220, 311, 400, 422, 511, 440 and 533) were examined, which suggests a spinel cube made exclusively from magnetite. The similar typical peaks were noted for Fe₃O₄ @ SiO₂ and Fe₃O₄ @ SiO₂ @ OPhh₂ nanoparticles, suggesting that a crystalline structure of Fe₃O₄ was stable during silica coating and ultimately led to surface modification.

3.1.4. FT-IR spectroscopy

The peaks at 588 and 1635 cm⁻¹ became the Fe-O vibration of Fe₃O₄. Attributed [21]. The Fe-O peak in Fe₃O₄ @ SiO₂ was thus fully confirmed. The presence of the peak at 3431 cm⁻¹ is due to the stretching vibrations of OH band. The peak at 1081 cm⁻¹ can be related to the asymmetric and symmetric stretching vibration of SiO₂ bands and the Si-OH band is produced another peak at 798 cm⁻¹ (Fig. 2c).

3.2. Adsorption investigations

3.2.1. Determination of the optimal pH value

In aqueous solution, the pH value is an essential factor parameter for the adsorption performance [16]. In order to obtain the optimum pH, 0.01 g of adsorbent with 25 ml of palladium solution (2 mg L⁻¹) were added to 15 containers. Each of the containers was then adjusted to the desired pH in the range of 1 to 9. The adsorption time were 3.5 hours and the shaking speed was 150 rpm. After the adsorption process the resulting solution was separated using a magnet and analyzed with ICP method. The result of the analysis showed (Fig. 3a) that the optimum pH for maximum adsorption of Pd ions (94.35%) was pH = 6. Therefore, for the next steps this pH value was used as the optimum pH.

3.2.2. Effect of the adsorbent dosage

The optimal amount of the adsorbent has an effect on the process costs of the adsorption. The influence of the amount of adsorbent on the Pd (II) removal ranged from 0.01 to 0.1 g. examined. The adsorbent

was added to each container with 25 ml of palladium ions at a concentration of 3 mg L^{-1} and with the optimal pH (PH = 6) at room temperature. The adsorption has been proceeded in 3.5 hours with 150 rpm shaking speed. The test results are shown in Fig. 3b. The percentage of adsorbent dosage increased from 0.01 to 0.04 g, and a further increase in the adsorbent dosage from 0.04 to 1 g had no effect on the percentage of Pd (II) adsorption. The reason is an overdose of the adsorbent, while the number of active centers of the adsorbent remains constant [22, 23]. The result of the analysis shows that the best amount of adsorbent is 0.04 g at an adsorption percentage of 86.7. The recovery percentage (R %) of Pd(II) ions by Fe₃O₄/SiO₂/OPPh₂ was calculated using the concentration balance equation (3).

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

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3.2.3. Determination of optimum metal concentration:

A range of Pd(II) concentrations including 0.5, 1, 1.5, 2, 2.5 and 3 mg L^{-1} have been tested to reach the maximum removal percent of it from a metal aqueous solution with a volume of 25 ml, PH = 6 and the optimal adsorbent content of 0.04 g. The adsorption time was 3.5 hours and the shaker speed was 150 rpm. The obtained results from analysis of separated solutions are shown in Fig. 3c. As the Fig. 3c shows, the highest percentage of metal removal has reached for 2 mg L^{-1} of Pd(II) which is 89.85.

3.2.4. Desorption solutions and their concentration

3.2.5. Influence of the adsorption time:

After adsorption, three different desorption solution have examined to separate the Pd(II) ions from the adsorbent. The desorption solutions were 1M chloric acid, 1M ammonium nitrate, 1M nitric acid and 1M HNO₃ + HCl mixture. Four sample solution of Pd (II) ions (2mg/l) have been provided and added 0.1 g of adsorbent to them and placed in a shaker for 3.5 hours at room temperature. After the adsorption process the samples were filtered and the adsorbent of the Pd (II) ions remained on filter paper. A volume of 10 ml of each desorption solutions were used to wash the adsorbent and separate the Pd(II) ions. Each desorbent solution analyzed to determine the percentage of desorption. The obtained results are shown in Fig. 3d. 1 M HCl + HNO₃ was the best desorption solution for Pd metal. A range of various concentrations of this mixture have examined (from 0.5 to 5 M) to improve the desorption percentage. 10 ml of different concentrations of mixed HCl + HNO₃ were used to wash the same adsorbents which were prepared by the same way as before (0.04 g of adsorbent with 2 mg / l Pd ions in a volume of 25 ml and a pH of 6 stored in the shaker for 3.5 hours). The obtained desorption percentages are shown in Fig. 3e. The mixed HCl + HNO₃ with a concentration of 0.5 M with 97.95% recovery were the best desorption solution for Pd (II) ions. The contact time of metal ions with adsorbent has an important effect on removal percentage of Pd(II) from the solution. 25 ml of Pd(II) solution with a concentration of 2 mg L^{-1} mixed with 0.04 g adsorbent at pH = 6 and placed in a shaker at three different temperatures of 20, 30

and 40°C. In each cases the samples from the shaker were taken at different times (5, 8, 10, 15, 30, 45, 60, 75, 90, 120min) and analyzed to investigate the influence of contact time. The obtained results are shown in Fig. 3F.

3.2.6. Adsorption isotherms modeling and Thermodynamic properties

The adsorption of Pd (II) ions was investigated at different temperatures of 20, 30 and 40°C. The containers with a volume of 25 ml were used and the 0.04 g of adsorbent, a certain amount of metal solution (from 0.5 mg L⁻¹ to 10 mg L⁻¹) with pH = 6 were added to them. The mixtures were shaking in water bath with 300 rpm for 3.5 h and everything were the same at different temperatures. After removing the samples from the shaker, they were filtered with an external magnetic field and the filtered solutions were separated for analysis. The obtained data were examined with the adsorption isotherm models Jessons, Fritz Schlunder, Weber-Van Viet, generalized and the non-linear isotherm fit curves (Fig. 4). The results of the model parameters obtained are shown in Tables 1 and 2. Thermodynamic parameters indicate the endothermic, irreversible and non-spontaneous nature of the adsorption (Table 1 and 4). The concentration of the Pd (II) ions rose from 0.5 to 10 mg L⁻¹ with an increase in temperature and the influence of the sorption capacities was shown by Pd (II) in equilibrium is shown in Fig. 3F and illustrates the importance of adsorption kinetics as an important factor between contact time and adsorption capacity[24]. To display the experimental kinetic data, the diffusion types pseudo-first and pseudo-second order were analyzed at different temperatures and the associated parameters were calculated; the results are shown in Tables 1 and 3 and in Fig. 4. The influence of temperature on the rate constant of adsorption was investigated using the Arrhenius equation. (Table 1). The k_0 of activation energy (E_a) is 8.06×10^8 g. mg. min⁻¹ with a C_0 of 2.0 mg L⁻¹. The magnitude of E_a indicates the adsorption mechanism, for the chemical adsorption E_a should be in the range of 40-800 kJ mol⁻¹ and for physical adsorption it should be between 5 to 40 kJ mol⁻¹ [25]. The evaluated activation energy in this work was 59.96 kJ mol⁻¹, which verifies the chemisorption as the dominant adsorption mechanism.

3.2.7. Effect of co-existing ions

The presence of foreign ions even in low concentrations through the matrix affect the spectrometric analysis of the ions in the trace range. Therefore, under optimal conditions for the adsorption of Pd (II) ions (5 mg L⁻¹), the presence of interfering ions (5 mg L⁻¹) such as Cd²⁺, Ni²⁺, Ca²⁺, Co²⁺, Fe³⁺, Ba²⁺ and Pt⁴⁺ were determined by means of the adsorbent used (Fe₃O₄ / SiO₂ / OPPh₂). The interfering ions have very little influence on the Pd (II) uptake, as shown in Fig. 3g.

3.2.8. Prepare real samples

The sensible application of the presented method was investigated on the basis of the adsorption of palladium from the two different water samples. 25 ml of the tap water and spring water samples at optimized conditions were exposed to the addition of 0.2, 0.4 and 0.6 mg / L Pd (II) ions. The obtained results for the two samples (with and without addition of the Pd (II) ions) are shown in Table 5.

4. Conclusions

Various methods including XRD, FT-IR and TG were used to study the synthesis of a new adsorbent for the removal of Pd ions from aqueous medium. In order to obtain optimal conditions for the adsorption of Pd ions, we have optimized the effective parameters for the adsorption. The optimal pH value with the adsorption percentage of 94.35 at pH = 6 was obtained. The 0.04 g of adsorbent was reached to an adsorption percentage of 86.7. The best concentration for Pd(II) ion was 2 mg / L with an adsorption percentage of 89.85. A mixture of HNO₃ + HCl solution with concentration of 0.5M was the best extracting agent for Pd(II) ions with 95.5 extraction percent. According to the obtained dG data, the reaction occurs spontaneously with negative data (0.5, 1 and 2 mg L⁻¹) and with positive data (4.6.8 and 10 mg L⁻¹) is not a spontaneous reaction. The entropy (dS) calculation shows that the irregularity is less when the positive data is the most irregular and when the data is negative. Enthalpy calculation (dH) shows that the energy level is lower than the energy level of the starting materials and the released heat is displayed with negative enthalpy. Finally, the first and second pseudo diagrams at temperatures of 20, 30 and 40°C drew and the related value of R² was calculated. As a result, we follow the second pseudo-diagram at 20°C, the first pseudo-diagram at 30°C and the second pseudo-diagram at 40°C. The best fits at temperatures of 20, 30 and 40°C were Generalized, Jossens, Fritz-Schlunder, and Weber-van Viel isotherm models respectively.

Declarations

COMPETING INTERESTS

The authors declare that they have no competing interests.

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Tables

Table 1 is available in the Supplemental Files section.

Table 2. Generalized, Jossense, Fritz Schlunder and Weber Van Vliet isotherm constants for the adsorption of Pd(II) ions onto Fe₃O₄/SiO₂/ OPPh₂.

Isotherm	Parameter	T(C)		
		20	30	40
Generalized	qm	4.35	2.871	2.3012
	km	2.940	3.356	1.521
	nm	0.917	0.752	0.753
	R ²	0.9209	0.9777	0.9745
	χ^2	0.4674	0.0365	0.0481
Jossense	kj	15.50	6.218	22.503
	nj	2.780	2.666	3.326
	mj	0.208	0.467	0.555
	R ²	0.9529	0.9664	0.9328
	χ^2	2.6319	0.4118	0.6611
Weber-van.	kw	0.700	2.610	1.225
	lw	-1.000	0.420	-0.831
	mw	0.650	0.022	0.755
	nw	3.925	1.750	4.524
	R ²	0.9831	0.9756	0.9636
χ^2	1.1119	0.4040	0.6851	
Fritz-schl.	Kf1	3680	2.940	10.464
	Kf2	2925	3.359	10.098
	mf	4.440	1.237	1.629
	nf	4.000	0.907	1.363
	R ²	0.9380	0.9807	0.9811
χ^2	0.2923	0.0322	0.0350	

Table 3. Parameters for kinetic models of Pd (II) sorption onto Fe₃O₄/SiO₂/ OPPh₂. (Solution volume=25mL; initial Pd (II) concentrations=2 mg L⁻¹; sorbent dosage=0.04g; pH=6.0)

Isotherm	Parameter	T(k)		
		293	303	313
Pseudo 1st order	q _e	1.3514	0.8493	0.8990
	k ₁	0.0116	0.0378	0.0727
	R ²	0.9848	0.8658	0.8338
	χ ²	0.0339	0.2323	0.2639
Pseudo 2nd order order	q _e	2.1345	1.0300	1.0372
	k ₂	0.0036	0.0415	0.0856
	R ²	0.9841	0.8996	0.8986
	χ ²	0.0351	0.1401	0.1550

Table 4 Thermodynamic results of Pd(II) ions adsorption by Fe₃O₄/SiO₂/ OPPh₂ in temperatures of 293, 303 and 313.

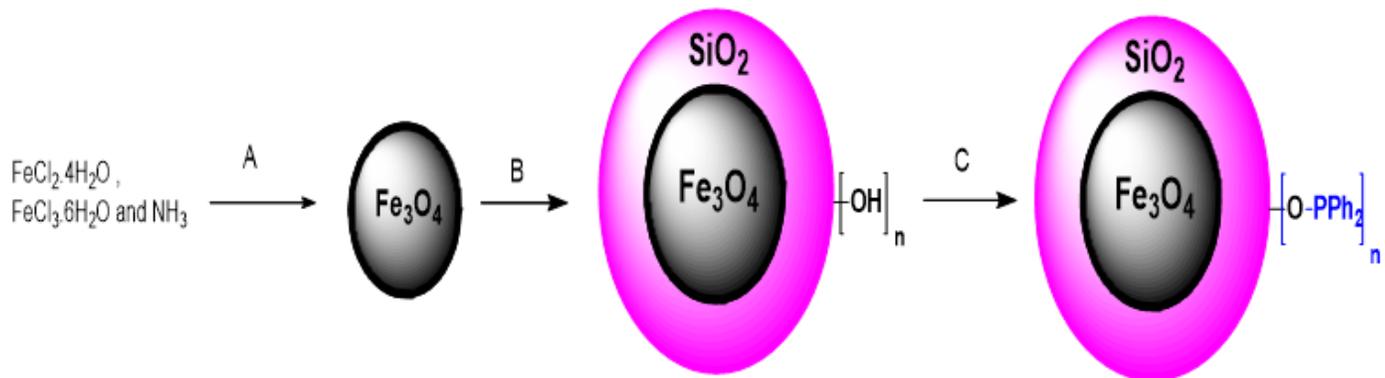
C_0 (mg L ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS° (J mol K ⁻¹)	ΔG° (kJ mol ⁻¹)			Kc		
			293	303	313	293	303	313
0.5	-2.0953	1.3968	-2.5048	-2.5187	-2.5327	2.7946	2.7165	2.6453
1	-27.4220	-82.6294	-3.1988	-2.3725	-1.5463	3.7153	2.5634	1.8110
2	-25.3780	-77.7600	-2.5838	-1.8062	-1.0287	2.8867	2.0476	1.4845
4	-16.2300	-53.8700	-0.4427	0.0960	0.6348	1.1992	0.9626	0.7836
6	-15.3000	-54.1300	0.5164	1.0578	1.5991	0.8091	0.6573	0.5411
8	-15.7000	-57.4500	1.1123	1.6868	2.2613	0.6336	0.5121	0.4196
10	-14.1000	-53.8200	1.6291	2.1673	2.7056	0.5125	0.4232	0.3537

Table. 5 Results obtained for Pd(II) ion determination in real samples.

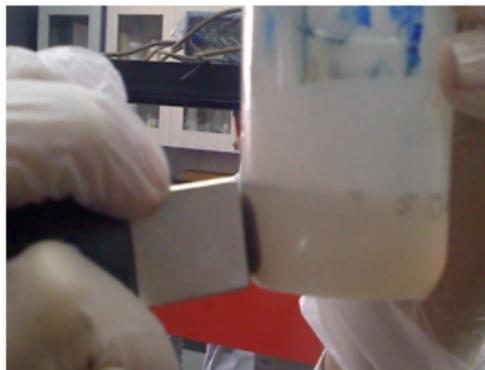
Water samples	Found Pd(II) (without spiking) (mg L ⁻¹)	Added Pd(II) (mg L ⁻¹)	Found Pd(II) average (After spiking) (mg L ⁻¹)	Pre-concentration factor	Recovery (%)	Standard deviation	Relative standard deviation (%) ^a
Tap water	ND	0.2	0.188	10	96.00	0.0197	10.25
		0.4	0.403	10	100.8	0.0208	5.16
		0.6	0.580	10	97.00	0.0400	6.90
spring water	0.136	0.2	0.336	10	100.1	0.0158	4.70
		0.4	0.543	10	101.4	0.0306	5.62
		0.6	0.756	10	102.8	0.0153	2.02

a: For three determinations , ND: Not Detected

Figures



Before



After

Figure 1

The synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{OPPh}_2$ nanoparticles and Adsorbent appearance before and after separation with magnet

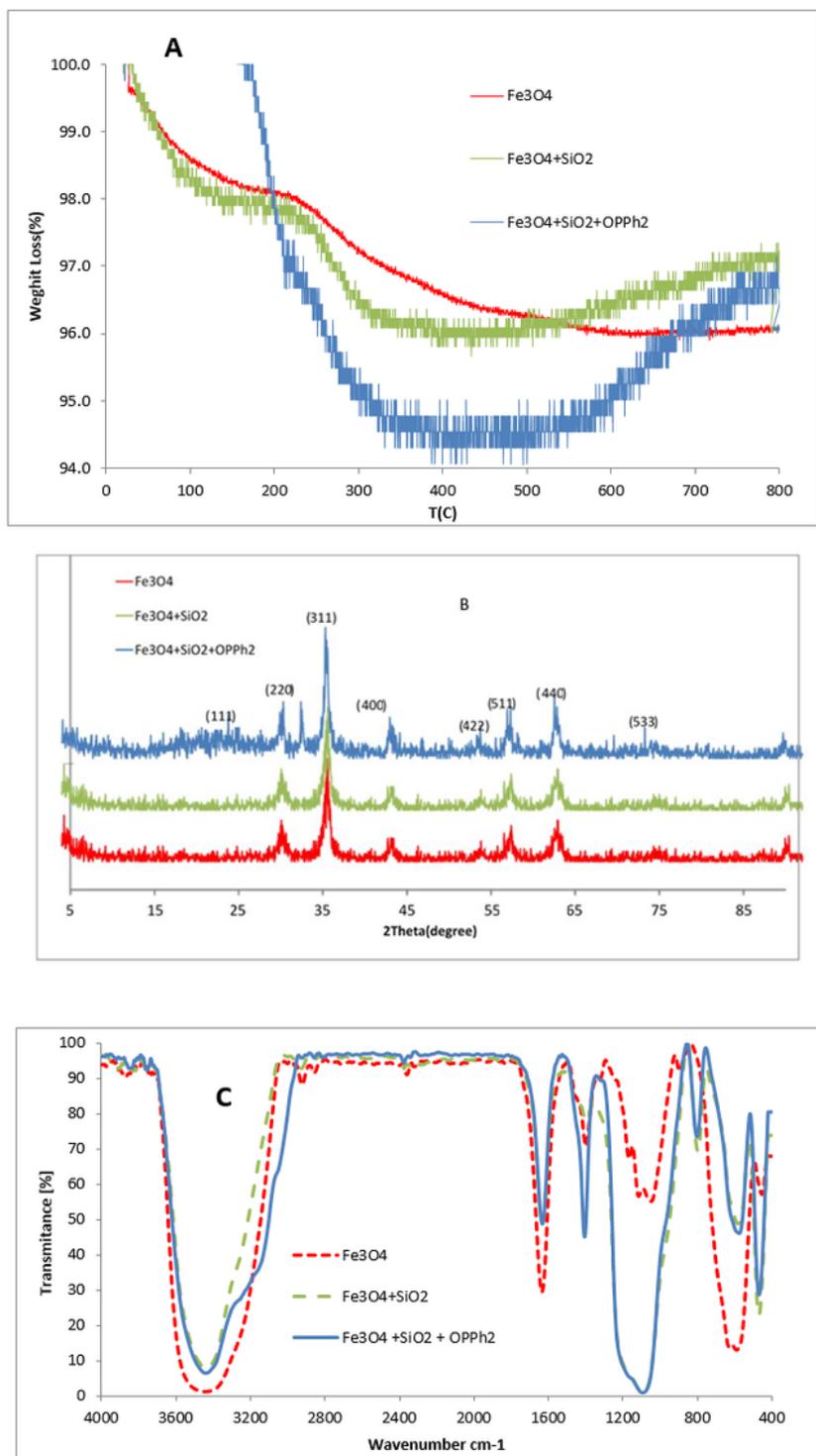


Figure 2

(a) Thermogravimetric analysis ,(b) XRD analysis and (c) FT-IR analysis of Fe₃O₄, Fe₃O₄ @ SiO₂, Fe₃O₄ @ SiO₂ @ OPPh₂ particles.

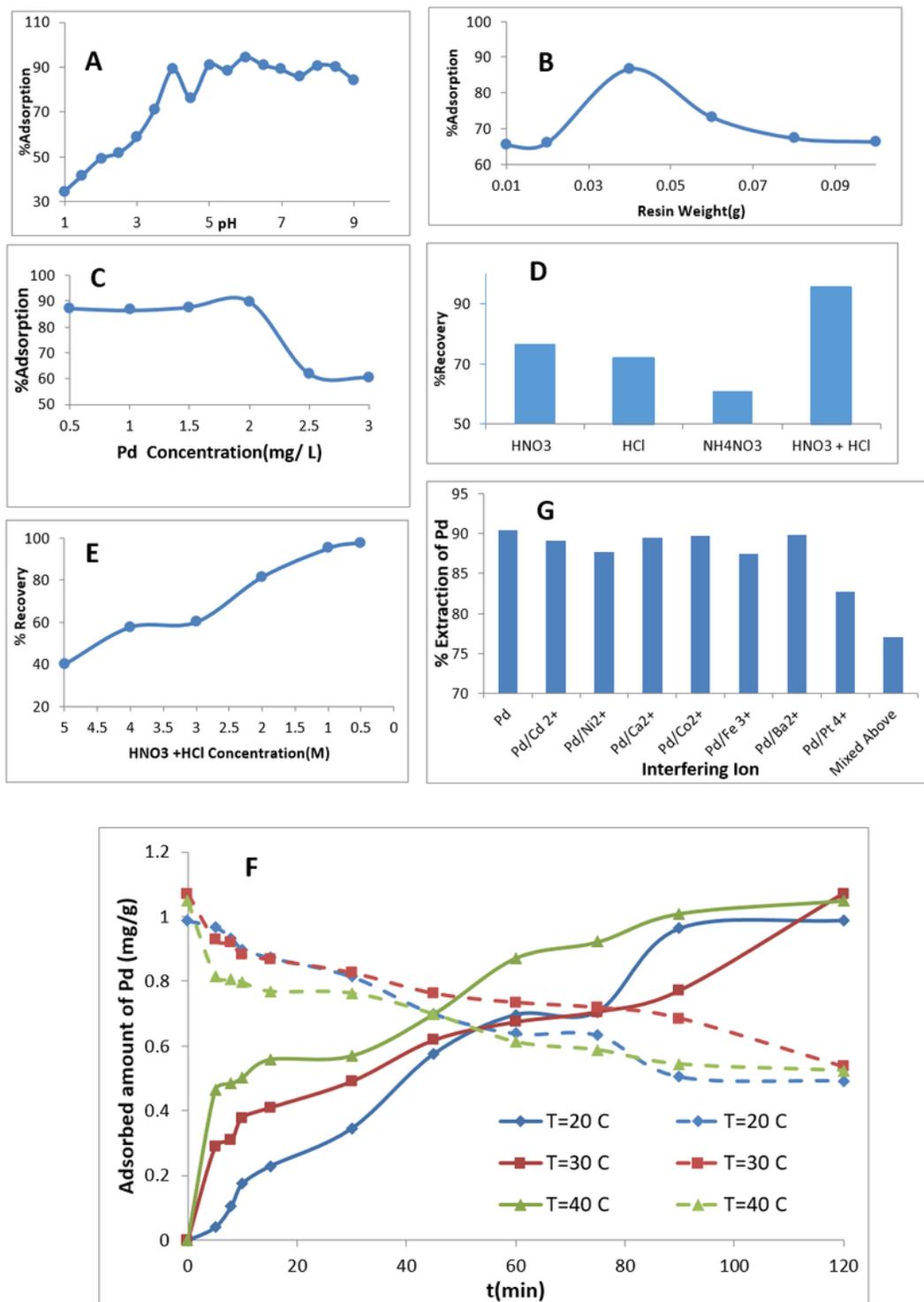


Figure 3

Effect of (a) pH, (b) sorbent dosage, (c) initial concentration of Pd(II) on the sorption of Pd (II) ions by adsorbent, (d) Desorption results of Pd(II) from adsorbent surface at different solvents, (e) Desorption results in different concentrations, (f) contact time at different temperatures on the adsorption and desorption processes, (g) interfering ions on sorption

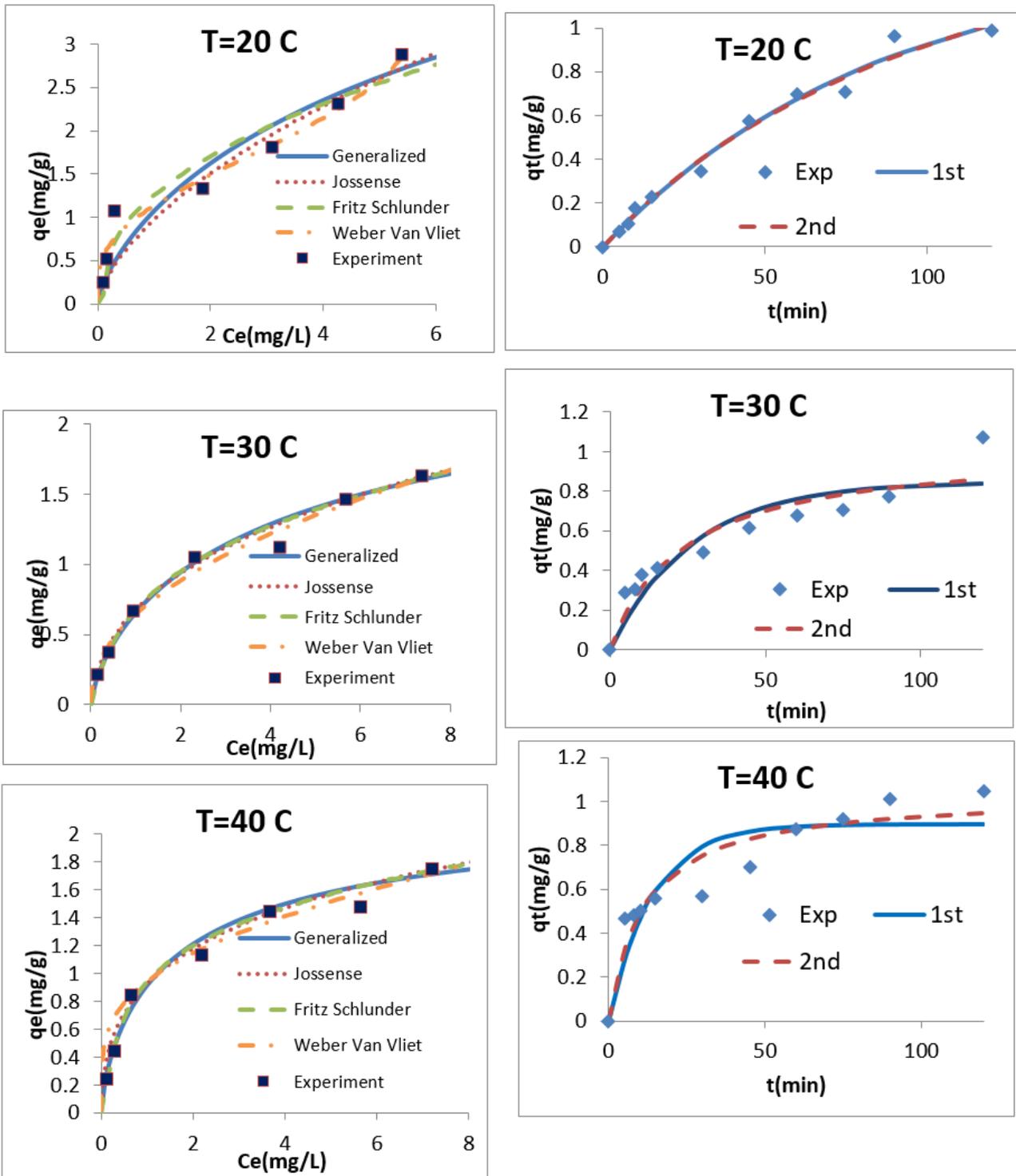


Figure 4

Isotherm curves obtained by the best non-linear modeling and pseudo first, second order at different temperatures for the removal of Pd (II) ions on Fe₃O₄ / SiO₂ / OPhh₂.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Table1.docx](#)