

# Modification and Improvement of $\text{Fe}_3\text{O}_4$ -Embedded Poly(thiophene) Core/Shell Nanoparticles for Cadmium Removal by Cloud Point Extraction

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## Abstract

Cloud Point Extraction (CPE) as an effective method for pre-concentration and separation of cadmium from aqueous solution is widely utilized. This study involves a surfactant mediated CPE procedure in order to remove cadmium from waste water using Polythiophene nanoparticle and Triton X- 100 as a non – ionic surfactant. Polythiophene – coated iron nanoparticles was successfully synthesized with novel method and as a super magnetic nano-particles (MNPs) for cadmium removal from aqueous solution was evaluated. Polythiophene nano-particles emulsifying method have been synthesized and fabricated. Fabricated nano-particle was characterized by Fourier-transform infrared spectroscopy (FTIR), and analysed transmission electron microscopy (SEM). Effects of pH, buffer volume, extraction time, temperature, amount of nano-particle were essentially investigated. To reach in optimum conditions, related experiments were replicated and accomplished as well. For removal of cadmium by CPE approach the optimization conditions were gained at pH = 7 , volume of buffer acid 1.5 millilitre , electrolyte concentration (NaCl) of 10 -3 mole L<sup>-1</sup> , Triton concentration 5 %, cloud point temperature 80 0 C , extraction time 40 minutes, and 5 mg of modified polythiophene nano-particle. The calibration graph was liner with a correlation coefficient of 0. 9984 and represents appropriate liner correlation with an amount and concentration. The results revealed that 5 gram of modified nanoparticle can significantly increase the efficiency of cadmium removal.

**Keywords:** Polythiophene, Iron nanoparticles, Cadmium removal, Cloud Point Extraction

## 1 Introduction

Heavy metals are released into the environment due to various industrial activities such as mining, plating plants, metal finishing, welding and ably manufacturing. Cadmium as one of the most toxic metals is interred to human body via food chain and air pollution. Cadmium has high –life time from 10 up to 33 years and can be readily accumulated in body organisms like liver and kindness [1-5]. Heavy metals are not biodegradable and with accumulation in living organisms, and having high toxicity leading to serious health problems. Several techniques involving reverse osmoses, membrane process, bio sorption, adsorption, ion-exchange, solvent extraction, Chemical precipitation, Nano filtration, Reveres osmoses have been widely used for waste water treatment. Separation and preconcentration procedure using a – non anionic surfactant can form a micelle solution that in metal removal are easily used. Liquid- Liquid extraction (LLE), Solid Phase Extraction (SPE), co precipitation , cloud point extraction (CPE), dispersive liquid liquid micro extraction (DLLME) and ionic liquid – based single step micro extraction have commonly been considered and utilized for separation of heavy metals. Polythiophene as a conjugated polymer with high

thermal stability and electrical properties at various industries such as chemical and electrical is widely used [6, 7]. Polymerization of thiophene is formed with electro polymerization, metal – catalyzed coupling reactions and chemical oxidative polymerization. Cloud point extraction as a separation approach has complied with “Green Chemistry “ and because of its simplified , highly efficient , low cost , has attracted. Basic principles of CPE is related to phase change behaviour of non- ionic surfactants in aqueous solutions. Cadmium ions are thoroughly transferred to the surfactant – rich phase and measured by electro thermal atomic absorption spectrometry and the surfactant – rich phase is separated by centrifugation [1, 7]. It has been proven that this approach has high efficiency both for organic and inorganic components. Kemplova et al (2013) explored the utilization of the iron nanoparticles for heavy metals removal Cadmium, Lead, and Copper for environment. Cadmium, Lead, and Copper. Their study showed after 24 hours of interaction, the surface of the nanoparticles adsorbed 100 % applied concentration of all the heavy metal. They used of  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$ , standard, residues nanoparticles were removed by membrane filtration. George Z and et al (2014) explored graghene oxide and its application as an adsorbent for waste water treatment. Usually graphene oxide as magnetic particle is used, and has recently been used to waste water treatment. Their Study showed that graghene oxide nanocomposites for the enrichment and

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removal of inorganic and organic pollutants from large volumes of aqueous solution can be used [8-11]. Xiang zhao et al (2012) investigated the removal of heavy metal ions Cd, Zn, Pb, Cu, from aqueous solution by polymer- modified magnetic nanoparticles. They proposed several nanoparticles such as, Fe304 magnetic nanoparticles (MNPs) modified with 3- amino propyltriethoxysilane (Aps) and copolymer of acrylic acid (AA) and crotonic acid (CA). Their study showed that MNPs could be more effective for removal of such heavy metal and maximum adsorption capacity was seen at pH= 5.5. Abbas Afkhami et al (2010) investigated simultaneous removal of heavy- metal ions in waste water using nano- alumina modified with 2, 4- dinitrophenyl hydrazine (DNPH). The results displayed that adsorbent has the highest adsorption capacity for removal of Pb ( ii), Cr (iii) and Cd (II) [5, 12]. Xiupei Yang and et al (2017) investigated cloud point extraction – flame atomic adsorption spectrometry for pre-concentration and determination of trace amounts of silver ions in water samples. PH of the aqueous solution as effective factor was presented and highest adsorption was seen at pH 5.0 [13]. Shahrm nekouei and Farzin nekouei (2015) investigated the application of cloud point extraction for manganese (II) determination in water samples. They studied various parameters such as pH, concentration of CHAPSO as chelating agent, Ion pairing reagent concentration, nonionic surfactant concentration, and Ionic salt concentration. Their study showed that the quantities of manganese in the water samples from the rivers located in much more than the non- industrial area [14]. Cloud point extraction based on ion association system (CPE) has much higher sensitivity compared to CPE located one simple metal- chelate complex. Wael et al (2014) evaluated cloud point extraction of some precious metals using Triton X- 114 and a thiomide derivative with salting – out effect. The main factor such as pH, Concentration of the ligand, amount of Triton as non- ionic surfactant were investigated. They reported the enrichment factors 52, 46, and 56 for palladium, silver, and gold respectively [15]. Dilek et al (2017) studied pre concentration and determination of Cd, Zn and Ni using microorganism streptomycess [16]. The optimum pH values, amount of adsorption, elution solution and flow rate were studied. They reported recovery of Cd, Zn, and Ni by this microorganism 77.83, 93.80, and 98.73 respectively. Cennet Karadaş (2017) evaluated a novel cloud point extraction method for separation and pre concentration of cadmium and copper from natural waters. Various parameters such as sample pH, ligand amount, concentration of surfactant, incubation temperature and time were investigated and optimized. Their results showed good agreement with certified values and was applied to tap water, river water and seawater samples with satisfactory results [17]. This work presents the improved nano-particle in order to separate cadmium as heavy metal from aqueous solution. Such nano-particle has been prepared with two different approach and polythiophene nano-particle as super magnetite was synthesized with emulsion method. In fact we have improved and increased the efficiency of iron nano-particle for better extraction.

## 2 Materials and Methods

### 2.1 Materials

All chemicals and reagents were analytical grade. SDS, thiophene, hexadecane, FeCl2.4H2O (99.9% w/w), FeCl3.6 H2O (96% w/w), diphenylamine sulfonic acid, KCl salt, citrate, hydrochloric acid (37% w/w) and ammonia solution (25% w/w), were purchased from Merck (Darmstadt, Germany) and used without further purification. Cadmium (II) was purchased from Sigma-Aldrich, Germany. The spectrophotometric measurements were carried out with a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia) at a wavelength of 420 nm. A

transmission electron microscope (906E, LEO, Germany), pH- meter (632Metrohm, Herisau, Switzerland) and a super magnet (1.2 T, 10cmx5cmx2 cm) were used. In order to determine the particle size and morphology of the prepared nano-particles a scanning electron microscopy (SEM) model Jsm 6400 jeol company (Tokyo, Japan) was used. To observation of the formed surface modification both nano-particle Fe and Fe3O4 @ PTE nano-particle, Fourire – transform in frared (FT- IR) was employed.

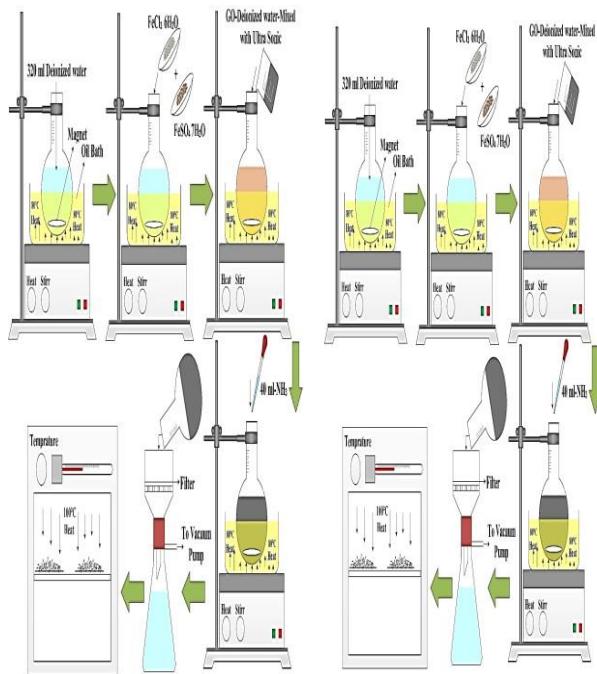
### 2.2 Experimental Section

Polythiophene – coated iron nano-particles was successfully synthesized with novel method and as super magnetic nanoparticles (MNPs) for removal of cadmium from aqueous solution was evaluated. Fabricated nanocomposites were characterized by Fourier transform infer- red (FTIR), and analyzed transmission electron microscopy. In order to sustain the pH of sample solutions and at the determined optimum pH a suitable buffer should be selected and used, therefore different buffers with pH = 7 were investigated. For this purpose, a number of volumetric balloons of 50 millilitres were prepared and 0.005 grams of polythiophene / iron nanoparticles, 10 millilitres of triton (X- 100), 0.5 millilitres of sodium chloride solution and 0.5 millilitres from cadmium (II) solutions with concentrations of mg 10 milligram per litters and 1.5 millilitres of phosphate buffers, folic acid, potassium hydrogen phthalate and citrate, with pH = 7 were added into them, with water were volume. After shaking the balloons, the contents of the balloon were transferred to a centrifuge tube of 50 millilitres. In order to carry out the extraction process, the cloud points of the tubes were placed in a hot bath at 80 ° C for 40 minutes and then were placed in an ice bath for 30 minutes. The control solutions were prepared in the same way in the absence of analyte. Then the upper blue phase was discarded and the bottom phase, which was a pre-condensed fermentation-rich phase, was centrifuged for 2 minutes and the nanoparticles were discarded, then 3 millilitres of nitric acid 3 molar units were added to the nanoparticles and were centrifuged for 3 minutes. Subsequently, the nanoparticles were transferred to a test tube and the concentration of metal ions in the final solution was measured by a flame atomic absorption device. Based on the results, it can be seen that in the range of 0.1-0.5 millilitres of the physicochemical buffer, there is an increasing trend in the recovery rate of cadmium, therefore, the amount of 1.5 millilitres of the financial buffer solution acid is considered as an optimal buffer volume. The citrate buffer solution with pH 4.5 was prepared using citric acid (0.1 M), NaOH and HCL (0.1 M).

### 2.3 Preparation of Fe3O4 Nanoparticles Modified by Polythiophene Nanoparticles

The reaction was performed in a 250mL flask equipped with a mechanical stirrer at 50 °C. 0.1 g SDS and 2 g thiophene was added into 60mL deionized water and the mixture was stirred at 300 rpm for 20 min. Magnetic polythiophene nanoparticles were prepared by co-precipitation method. Fe3O4 nanoparticles were synthesized by the co-precipitation of ferric and ferrous salts. The amount 4.55 g of FeCl3•6H2O, 3.89 g of FeSO4•7H2O and 1 g polythiophene nanoparticles were dissolved in 320 ml of deoxygenated distilled water. After stirring for 1 h, chemical precipitation was achieved at 80°C under vigorous stirring by adding 40 ml of NH3 solution (25%, v/v). During the reaction process, the pH was maintained approximately at 10. After adding ammonia solution, it was stirred for 1 h. afterwards, the precipitate was washed with distilled water to remove all existing in the effluents. Next, using a magnet, magnetic adsorbent prepared into the balloon bottom was collected and the above solution was discarded. Then the adsorbent was washed 5 times

with distilled water and again by using a magnet the above solution was discarded till non-magneted particles and also additional non-reacted ammonia with chlorides and iron sulfates were removed within the adsorbent particles. The discontinuous extraction method is used in this research.



**Figure 1.** Schematic of PT-  $\text{Fe}_3\text{O}_4$  preparation.

#### 2.4 Adsorption Experiments

The adsorption experiments were done by means of batch method. 0.03 g of Polythiophene-coated iron nano particles were equilibrated with 50 ml of solution containing various amounts of nickel in the presence of 0.03 g of diphenylamine sulfonic acid. The pH value of the samples was adjusted by using diluted solutions of NaOH and HCl (0.1 M). After addition of Polythiophene-coated iron nano particles, the resulting solution was stirred for a defined time 5 min. Then, the suspension was allowed to settle by a magnet and the supernatant was analyzed for measuring the remaining Cadmium (II) by atomic absorption apparatus. In all experiments adsorption percentage of the Cadmium (II) (R %) was calculated with equation (1):

$$R (\%) = \left( \frac{C_o - C_f}{C_o} \right) * 100 \quad (1)$$

Where  $C_o$  and  $C_f$  represent the initial and final ion concentrations, respectively. All experiments were done duplicate. Samples of the Cadmium (II) solution were analyzed using a UV-Vis spectrophotometer at  $\lambda_{\text{max}}=420$  nm. All measurements were conducted triplicate.

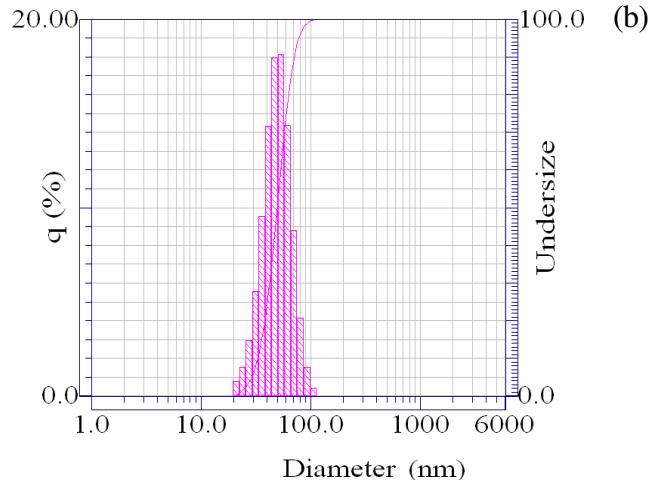
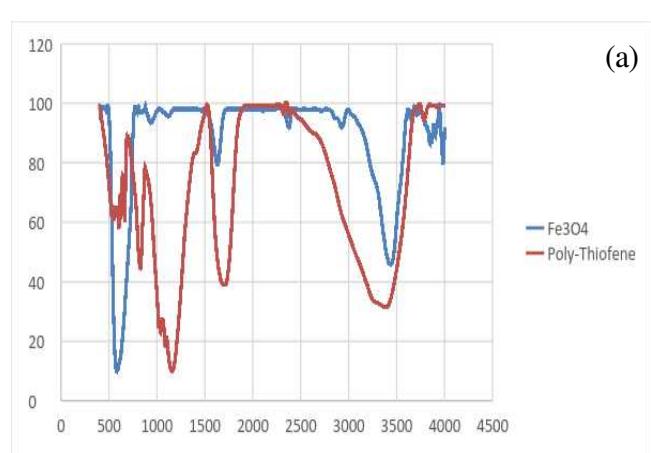
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### 3 Results and Discussion

#### 3.1 Characterization of Nanocomposites:

To characterize the functional groups in adsorbent, FTIR was applied. The FT-IR spectra of  $\text{Fe}_3\text{O}_4$  nanoparticles in the range of

400-4000  $\text{cm}^{-1}$  are represented in Fig. 2 (a). An adsorption band at 593  $\text{cm}^{-1}$  is belonged to the vibrations of the Fe-O functional group. The bands appearing at 3447  $\text{cm}^{-1}$  can be attributed to O-H group that cover iron oxide surfaces in an aqueous environment. Modification of Polythiophene onto the  $\text{Fe}_3\text{O}_4$  was also ascertained by FTIR. As shown in Fig 2 (b), the sharp peak at 612  $\text{cm}^{-1}$  corresponds to Fe-O vibration in magnetite. The peak at 3412  $\text{cm}^{-1}$  belongs to the C-H bond of polythiophene that indicates the presence of Polythiophene-coated iron nano-particles. Also, several peaks have been viewed in this Figure which can be related to the groups of C=C, N-H and etc. Furthermore, SEM images provide information about size and morphology of Polythiophene-coated iron nano-particles. Figs (15) and (16) are shown SEM images, respectively. It can be observed that the magnetic nano-particles with the mean size of 70 nm have a high surface area and abundant pore for adsorption of ions. Also, particle size distribution of adsorbent is displayed in Fig 2 (b). As shown the average size of particles is about 70 nm.



**Figure 2.** (a): FT-IR spectra of  $\text{Fe}_3\text{O}_4$  nano-particles, (b): Particle size distribution of adsorbent.

#### 3.2 Effect of Solution pH and Buffer Volume

Initial solution pH is one of the effective parameters in adsorption of metal ions, because hydrogen ion competes with metal ions to relocate active sites of the adsorbent (Rafatullah et al., 2009). As is shown from Fig (3), effect of solution pH on recovery of cadmium at range 4 to 10 has been studied.

Maximum of recovery is seen at pH = 7, therefore pH= 7 as optimum pH was selected and optimization of other effective factors to measure metal ions was accomplished at this pH. In optimization step was observed that pre- concentration process at pH lower than 7 was not formed as well. As well as the results showed that at pH high than 7.0 amount of adsorption decreases. Showed decreased amount of adsorption at high than 7.0 .The effect of pH was conducted by mixing 0.03 g (0.6 g/L) of adsorbent in 50 ml Cadmium solution with the concentration of 20 mg/L. HCl and NaOH was utilized for the purpose of keeping pH in the range of 4-10 throughout the experiments. It can be observed that the removal of Cadmium increased with increase in pH and reached a maximum at pH (7). At lower pH values, Cadmium removal was inhibited, because at low pHs the medium contains a high concentration of hydrogen ions, therefore competition between H<sup>+</sup> and Cadmium for the available adsorption sites could be possible. The percentage removal of Cadmium was observed to be sharp between pH values of 7. At pH values greater than (7), the adsorption of Cadmium decreases because of the precipitation of resulting from Cadmium reacting with Polythiophene /Fe<sub>3</sub>O<sub>4</sub> nanoparticles. In further works, the pH of the solutions was adjusted by using Phosphate buffer volume. The effect of buffer volume on the removal efficiency is displayed in Fig. (4)

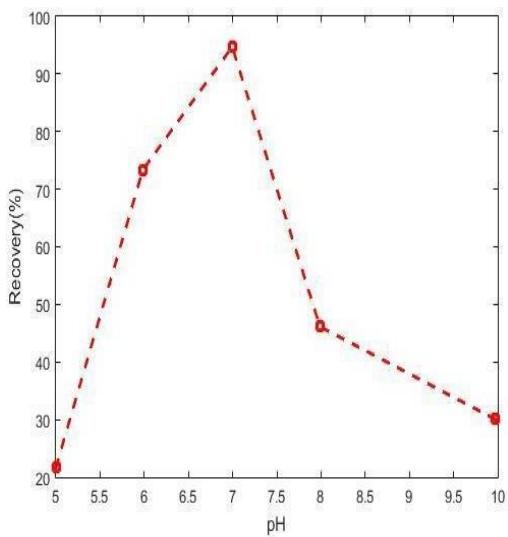


Figure 3. Effect of solution pH.

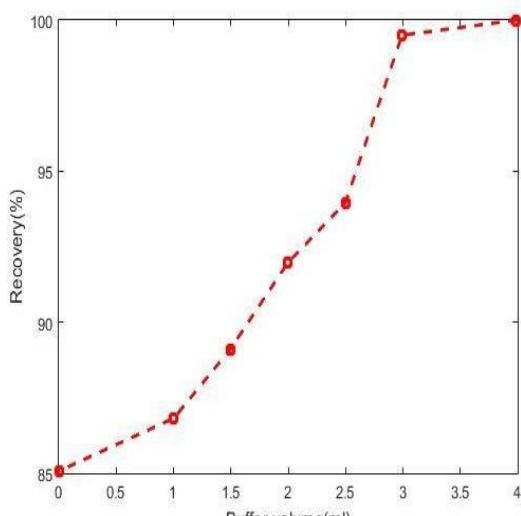


Figure 4. Effect of buffer volume (ml).

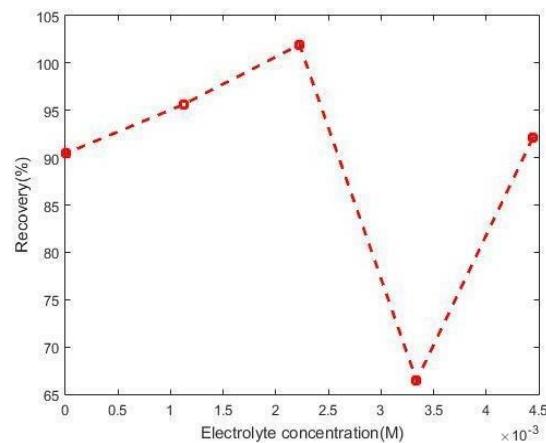


Figure 5. Effect of electrolyte concentration.

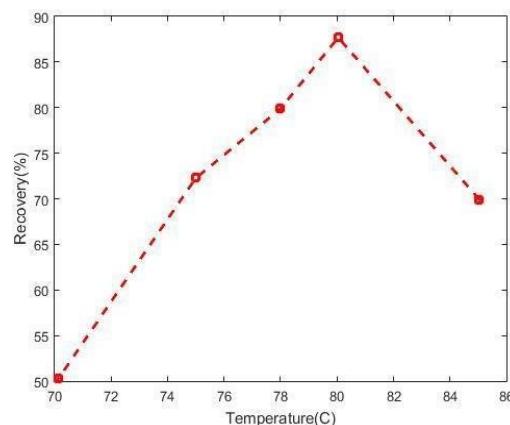


Figure 6. Effect of temperature.

### 3.3 Select of the Buffer Type

The results show that the adsorption rate in the presence of a fiscal acid buffer is in good agreement with the results obtained from the pH optimization step. While phosphate buffers, citrate and potassium hydrogen phthalate interfere with this measurement method.

### 3.4 Effect of Electrolyte Concentration

The effect of different concentrations some multi-electrolytes such as, (adjusted by KCl), on the cloud extraction point of iron-modified poly-thiophene nanoparticles in the presence of ions of cadmium (II) were investigated. According to the gained results, it was observed that the presence of low electrolyte concentrations up to a concentration of 3 to 10 molar pre- concentration of the nanoparticles was carried out well in the surfactant-rich phase and significant increase in concentration greater than 10 <sup>-3</sup> was not observed.

### 3.5 Effect of Cloud Extraction Temperature

In order to investigate the cloud extraction process in the range of 85-70 ° C, As it is clear from figure (6) adsorption recovery increased with increase of temperature and after 80 adsorption capacity decreased considerably. Accordingly this temperature as optimum temperature is considered.

### 3.6 Effect of Contact Time

Contact time is one of the important parameters in adsorption process. The effect of stirring time on the performance of nanoparticles in adsorbing cadmium (II) was investigated. The solution pH and Fe<sub>3</sub>O<sub>4</sub> nanoparticles modified by polythiophene

dosage were fixed at their obtained optimum values. Fig. (7) Shows removal efficiencies for cadmium (II) as a function of stirring times (20- 50 min). These data elucidate that adsorption started immediately upon adding the  $\text{Fe}_3\text{O}_4$  nanoparticles modified by polythiophene to cadmium (II) solution. The removal efficiency of cadmium (II) was rapidly increased from as the stirring time was increased from 20 to 40 min. The results showed that the adsorption efficiency with increasing contact time and reached adsorption equilibrium within 40 min. After this time, the increase in adsorption capacity for cadmium (II) is not significant. Therefore, 40 minutes is selected as the optimal time. The kinetics adsorption of cadmium (II) consists of two stages: the initial rapid stage is related to the instantaneous adsorption stage or external surface adsorption due to the availability of more numbers of free adsorption sites and lower mass transfer resistance on the surface during adsorption. The second stage is slower, it refers to the gradual adsorption stage where intraparticle diffusion controls the adsorption rate when the total metal adsorption sites are saturated as long as the metal adsorption reaches the equilibrium.

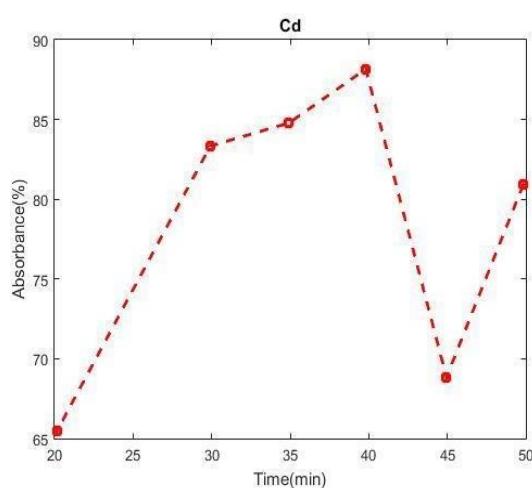


Figure 7. Effect of contact time.

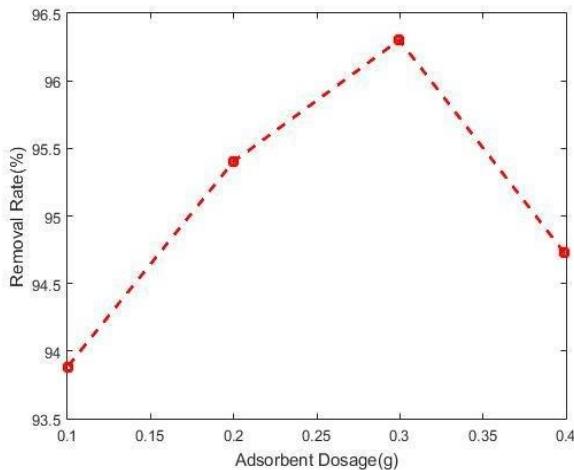


Figure 8. Effect of adsorbent dosage.

The Effect of Polythiophene Modified with Iron Nano Particles  
Regarding the results, it was observed that by adding more than 2 milligrams of polythiophene nanoparticles modified with iron nanoparticles to the studied system, the absorption changes diagram in terms of the amount of polythiophene nanoparticles modified by the iron nanoparticles was added in a maximum

amount, with the slope that is very slight and the chart is almost flat. Therefore, the optimal amount of polythiophene nanoparticles modified with iron nanoparticles added to the system with a final amount of 5 mg was considered.

### 3.7 Effect of Adsorbent Dosage

The effect of adsorbent dose on the removal of cadmium (II) ions is studied by changes the adsorbent dosage and without any changes in other parameters. The Figure (8) has shown with increasing adsorbent dose, removal efficiency increased. This phenomenon is due to an increase in the available binding sites on the surface of the adsorbent to adsorption of cadmium (II) ions. The removal efficiency of cadmium (II) increases dramatically from 93.88% to 96.3% and from 94.82% to 98.65% when the PT- $\text{Fe}_3\text{O}_4$  dosage increases from 0.1 to 0.3 g increases, then the efficiency decreases with further increase of the adsorbents dosage.

### 3.8 Calibration Curve

According to determined optimum condition in the previous section the calibration curve using sample volume 50 milliliters for different concentrations of cadmium (II) was plotted. This curve as is shown in fig (8) in the concentration region (3-250 mg L<sup>-1</sup>) was linear for cadmium (II). The liner equation and correlation coefficient for these results are obtained as follows  
The amount of the correlation coefficient in the linear of this method is equal to .09984 and indicates the appropriate linear relationship between the values of A and concentration.

$$0221/0 + C0043 / 0 = A$$

Where C is the concentration of cadmium in the sample solution and A is the amount of absorption relative to the control. The correlation coefficient for the method in the linear range of this method is equal to 0.9989 and indicates the appropriate linear relationship between the values of A and the concentration.

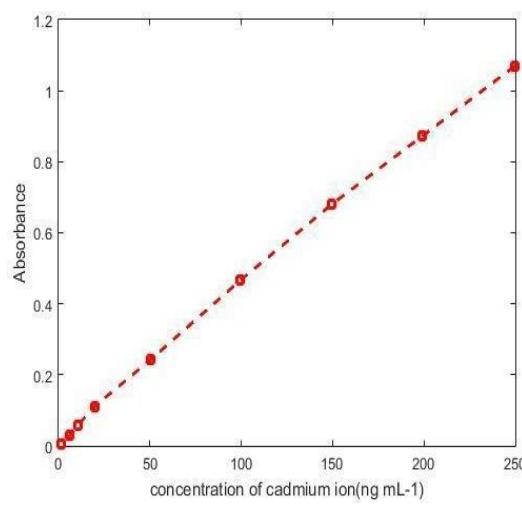


Figure 9. Cadmium (II) calibration curve.

### 3.9 Adsorption Isotherms

Batch adsorption applications were analyzed using Freundlich and Langmuir isotherm models. Freundlich model assumes that the uptake of adsorbate occurs on a heterogeneous surface of the adsorbent (fig11). The Langmuir model describes the monolayer sorption process onto the adsorbent surface with specific binding sites. The linearized forms of the model equation is given as

Freundlich model (Eq. 2) and linear plot of the model of Freundlich is shown in Fig 11 [Freundlich, 1906].

$$\ln q_e = 1/n \ln C_e + \ln K_f \ln q_e = 1/n \ln C_e + \ln K_f \quad (2)$$

Langmuir model (Langmuir, 1918):

$$C_e / q_e = 1/KL q_m + C_e / q_m \quad (3)$$

In Eq. (2)  $K_f$  (Lg<sup>-1</sup>) and  $n$  (dimensionless) are Freundlich isotherm constants, being indicative of the extent of the adsorbent and the degree of nonlinearity between solution concentration and adsorption, respectively. The plot of  $\ln q_e$  versus  $\ln C_e$  for the adsorption was employed to generate  $K_f$  and  $n$  from the intercept and the slope values, respectively. In Eq. (3)  $q_m$  is the monolayer adsorption capacity of the adsorption (mol g<sup>-1</sup>); and  $KL$  is the Langmuir constant (L mol<sup>-1</sup>), and is related to the free energy of adsorption. A plot of  $1/q_e$  versus  $1/C_e$  for the absorption of Cadmium (II) onto modified biomass shows a straight line of slope,  $1/q_m KL$ , and intercept,  $1/q_m$ . In order to determine the variability of adsorption, a dimensionless constant called as separation parameter 'RL' was used and defined as in the Eq (4):

$$RL = 1/(1 + kl C_o) RL = 1/(1 + kl C_o) \quad (4)$$

Where  $C_o$  is the highest initial Cadmium (II) concentration (mol L<sup>-1</sup>). The value of separation parameter indicates the shape of isotherm to be either favorable ( $0 < RL < 1$ ), unfavorable ( $RL > 1$ ), linear ( $RL = 1$ ) or irreversible ( $RL = 0$ ) (Hall et al., 1966; Weber and Chakravorti, 1974).

### 3.10 Modeling of Isothermal Adsorption

The capacities of magnetic nanoparticles to adsorb Cadmium (II) were examined by measuring the initial and the final concentration of Cadmium (II) at the pH of 4.5 and the temperature of 25 °C in a batch system. Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The correlation of ion adsorption data with the Langmuir isotherm model was higher (with  $r^2$  values of 0.9825) than the Freundlich model ( $r^2 = 0.996$ ). Summarizes the models, constants, and coefficients are listed in Fig (10).and Fig (11). According to this table, the maximum predictable adsorption capacity Cadmium (II) is 454.54 mg ion/g adsorbent.  $KL$  represents the equilibrium adsorption constant, and therefore higher values of  $KL$  were indicative of a favorable adsorption process.

### 3.11 Kinetic Modeling of Adsorption

To describe the adsorption behaviour and rate, the data obtained from adsorption kinetic experiments were evaluated using pseudo first- and pseudo-second-order reaction rate models. Fig (12) gives a summary of these models and constants along with the determination coefficients for the linear regression plot of the testing ion. As shown in Fig.13 higher values of  $r^2$  were obtained for pseudo-second-order adsorption rate models, indicating that the adsorption rate of Cadmium (II) onto the magnetic nanoparticles can be described best by using the pseudo-second order rate rather than the first-order.

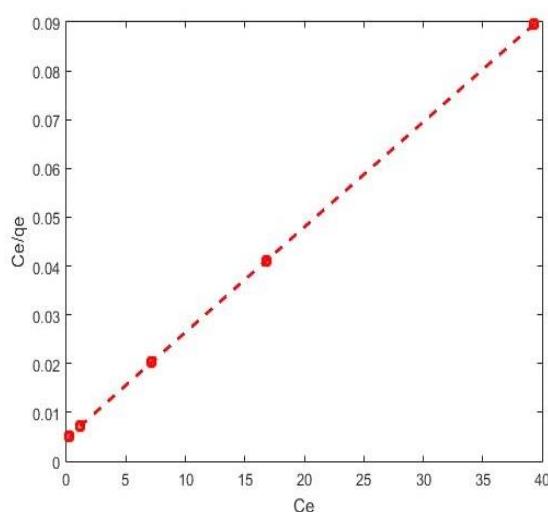


Figure 10. Linear plot of the model of Langmuir.

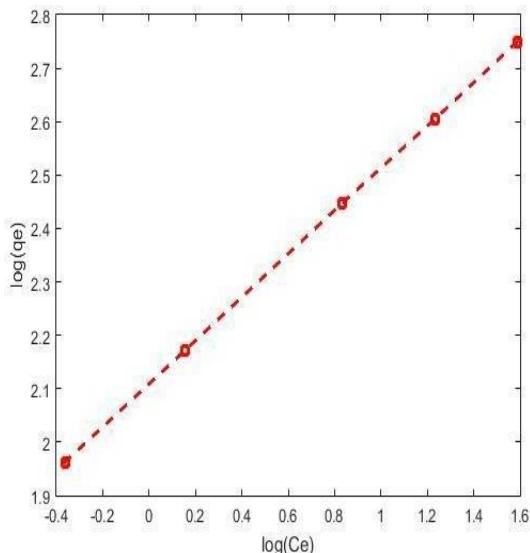


Figure 11. Linear plot of the model of Freundlich

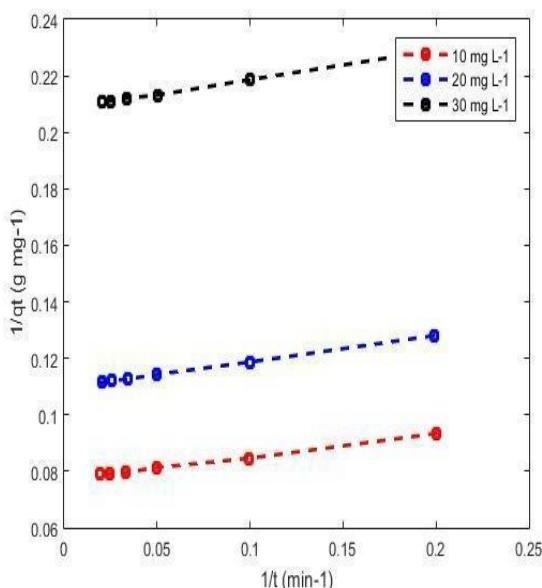


Figure 12. Linearized pseudo-first order plots

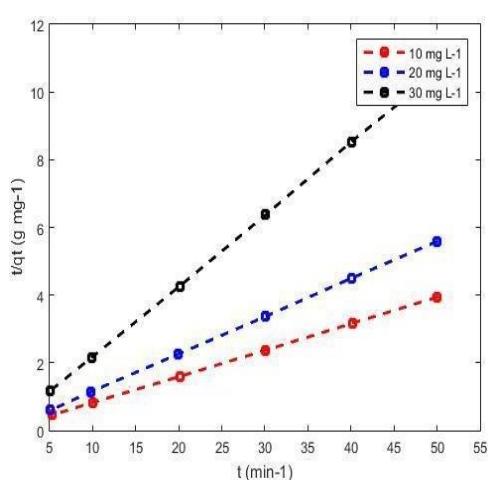


Figure 13. Linearized pseudo-second order plots

### 3.12 Scanning Electron Micrograph (SEM)

Scanning Electron Micrograph (SEM) Figure (15) shows the SEM images for the  $\text{Fe}_3\text{O}_4$ -Embedded Poly(thiophene) Core/Shell Nanoparticles, which confirms that the  $\text{Fe}_3\text{O}_4$  MNPs (PT) are cubic and highly uniform in size. In addition, Figure (14) shows the PSA image spectra for the  $\text{Fe}_3\text{O}_4$  MNPs coated with Poly (thiophene).

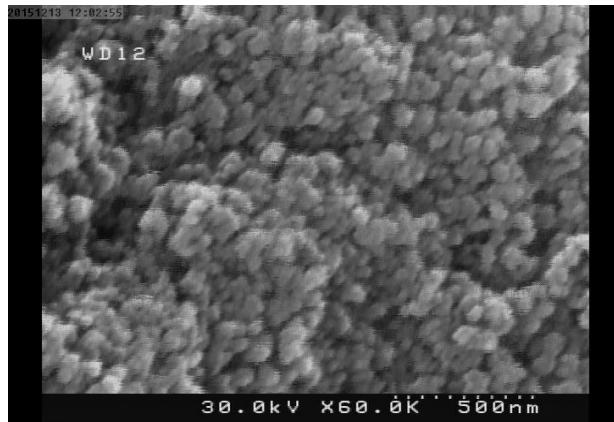


Figure 14. SEM images of  $\text{Fe}_3\text{O}_4$  nano particle

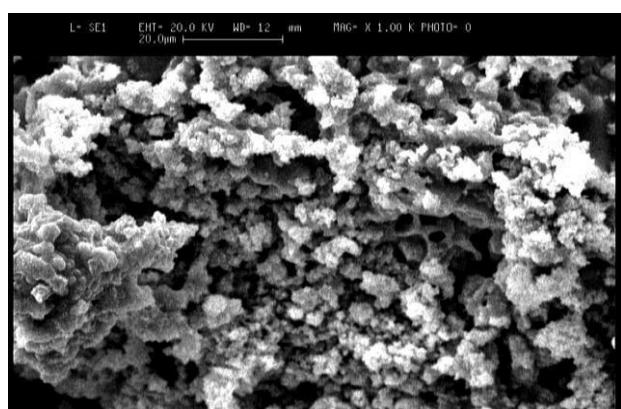


Figure 15. SEM images of Poly thiophene/Fe<sub>2</sub>O<sub>3</sub> particle

## 4 Conclusion

In this study Cloud Point Extraction (CPE) approach in order to removal of cadmium from industrial waste water was used.

For separation and pre-concentration of cadmium ions, nano-Poly(thiophene) particles with novel procedure have been successfully synthesized and calibrated. Different effective parameter such as pH, extraction time, buffer volume, cloud point temperature, and amount of used nanoparticles were investigated. Results show with. Optimum condition and amount 5 mg of applied nano-particles, cadmium can be separated up to 95 %. The adsorption kinetics fit well with the pseudo-second- order model and the equilibrium data fit well with the Langmuir model. The kinetic studies concluded that the adsorption of Modification  $\text{Fe}_3\text{O}_4$ - Poly (thiophene) Core/Shell Nanoparticles followed pseudo-second order rate equation, while the removal with iron oxide nanoparticles followed pseudo-first and pseudo- second order rate equations. Resulting tests on the Cadmium (II) removal from effluent using Modification of  $\text{Fe}_3\text{O}_4$ - Poly (thiophene) Core/Shell Nanoparticles showed the potential applicability of these absorbents in industrial waste water treatment.

## Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

## Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

## Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

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