



Nano zinc ferrite/polyurethane foam composite materials for Cd²⁺ and Cu²⁺ ions removal from aqueous solution

Fatma Hassan Youssef¹, Mohammad Salah Wahsh², Nagwa Burham Burham¹, Sami Mohammad Abdel-Azeem¹

¹ Chemistry Department, Faculty of Science, Fayoum University, Fayoum, Egypt

² Refractories, Ceramics and Building Materials Department, National Research Centre, 12622, El-buhouth St., Dokki, Cairo, Egypt

ABSTRACT:

Zinc ferrite Polyurethane foam composite materials were formed by adding 0.33wt% ZnFe₂O₄ nanoparticles into polyurethane foam (PUF) during the preparation process. ZnFe₂O₄/PUF composite materials have successfully been utilized as a new solid phase extraction (SPE) sorbent for the separation of cadmium and copper ions in various water samples. The XRD results revealed that only the spinel structure of ZnFe₂O₄ was formed, with an average crystallite size of 24nm. The ferromagnetic behaviour of ZnFe₂O₄ nanoparticles was observed, with magnetization of 4.179emu/g and coercivity of 267.11G. The microstructure of the prepared composite materials observed the spongy structure and higher porosity. The aqueous solution and real water (from Fayoum city, Egypt) were used for studying the effects of pH, sorbent dose, and shaking time of the composite materials on the Cd²⁺ and Cu²⁺ ions removal. The batch procedure shows the maximum extraction percentage of Cd²⁺ and Cu²⁺ ions were 95.8% and 96.5% at the optimal conditions.

Key words: Nanoparticles; Zinc ferrite; Polyurethane foam; Heavy metals removal; Water purification.

INTRODUCTION:

Industrial activity annually generates tons of organic and inorganic pollutants that pollute water all over the world. Sewage treatment is a vital issue as the supply of clean water is in decline at the present time (Awad et al.,2019; Yang et al., 2019). Because of their toxicity and hazard to human life, heavy metals in water are a Also, exposure to it causes flu-like symptoms, serious damage like broken bones, renal tubular dysfunction, cancer and hypertension (Awwal et al., 2018; Xu et al., 2014). Cadmium (II) ions are found in a

major source of worry (Geburu and Das., 2018; Singanan 2011). Among other heavy metals, cadmium and copper have attracted great interest due to their hazardous nature. Cadmium (Cd) is a highly toxic metal ion even in low concentration. It can accumulate in many organs of the human body such as the kidneys, lungs, and liver.

variety of industrial settings, including nickel–cadmium batteries, paint pigments, and electroplating, and they can pollute air, water, and soil. As a result, it is critical that we create effective ways for removing

cadmium metal ions (WHO Guidelines for Drinking-Water Quality, 2003; Shang et al., 2015). While Copper (Cu) is one of the most common heavy metal pollutants found in the environment. Copper compounds in industrial and household waste, refineries, mine washing wastes, and toxic paints can be defined as the sources of copper pollution. Furthermore, being an essential element for humans, copper plays a significant role in lipid metabolism, carbohydrate metabolism, and hemoglobin formation. An adult's daily copper intake ranges between 1.5 and 2 mg. However, copper is hazardous when its concentration exceeds 2mg L^{-1} , which is the copper recommendation limit (Turan et al., 2018). Currently, methods adopted for removing heavy metal ions from aqueous solutions include adsorption (Glatstein and Francisca., 2015), precipitation (Charentanyarak., 1999), bioremediation (Amini et al., 2009), membrane filtration (Qdais and Moussa., 2004), ion-exchange (Alyüz and Sevil., 2009) and solvent extraction (Ahluwalia and Goyal., 2007). Among these technologies, the adsorption was considered superior due to its ease of operation and removal with high efficiency, cost effectiveness and availability of effective sorbents.

Recently, nano materials have received much public attention due to the ability of uniform and stable complexity with functional groups, tunable pores and high sensitivity and selectivity (Laus et al 2010). Magnetic nano materials have been used to remove metal ions and dyes (Afkhami et al., 2010) due to their unique properties such as large surface area, small diffusion resistance (Afkhami et al., 2010) and ease of separating the sorbent from the sample solution after removing heavy metal ions with the help of an external magnetic field. Zinc ferrite belongs to a cubic spinel ferrite

family, where Zn^{2+} and Fe^{3+} ions are situated at tetrahedral and octahedral positions respectively (Das et al., 2019). In addition, ZnFe_2O_4 has good crystallinity and magnetic properties, which are useful for the recovery of adsorbent from a treated solution using an external magnetic field (Alaqarbeh et al., 2020; Das et al., 2020). The spinel ferrite is also found to be a cost-effective adsorbent. But the surface area of metal ferrite (ZnFe_2O_4) is found to be low which may be a limiting factor towards the adsorption process. To increase the adsorption process, the adsorbent should have more surface area. The porous material contains more pores and surface area in comparison to the non-porous ones and is known to have more adsorption capacity (Das et al., 2019; Das et al., 2020). Unfortunately, most of the current inorganic sorbents rarely contain both at the same time, for example, the magnetic nanomaterials have a high surface area, but no adsorbing functional group. On the contrary, the organic polymer contains a large amount of multi-functional groups that can effectively adsorb heavy metal ions, while its small specific area and low adsorption rate limits its application. An effective sorbent with high capacity and rapid adsorption should have the following two main characteristics: functional groups and large surface area (Huang et al., 2011). Therefore, new adsorbents with multi-functional groups and high surface area are still to be expected (Pan et al., 2009; Zhao et al., 2011). In this work, the synthesis and efficiency of $\text{ZnFe}_2\text{O}_4/\text{PUF}$ nanocomposites on removing Cd^{2+} and Cu^{2+} ions from aqueous solution and real water (tap water, Lake Qarun water and Bahr Youssef water from Fayoum, Egypt) was studied. The effects of the pH, sorbent dose and shaking time of the nanocomposites on removal of cadmium and copper ions were also measured.

MATERIALS AND METHODS

The chemicals used for the preparation of the magnetic nanoparticles (ZnFe_2O_4) were ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Mw = 404.00 g/mol], zinc nitrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Mw = 297.47 g/mol], citric acid mono hydrate gritty [$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Mw 210.14 g/mol] and ammonia solution. The magnetic nano powder (ZnFe_2O_4) was synthesized by using modified citrate sol-gel method. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (0.25M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution (0.25M) were prepared by dissolving the metal nitrates in distilled water. The prepared solutions were mixed in molar ratio of $\text{Zn}^{2+}/\text{Fe}^{3+} = 0.5$ under constant stirring to get homogeneous solution with the heating rate of $5^\circ\text{C}/\text{min}$ up to 80°C for 1 h. This mixture solution was added to the citric acid solution (0.25M) and stirred for 2 hours, maintaining a 1:1 molar ratio between metal nitrates solution and citric acid solution. The pH of the solution was adjusted to around 7.5 by adding ammonia solution. A viscous gel formed as the temperature is raised during the stirring process. At proper temperature ignition process started and the formed gel burned itself propagating combustion manner until all the gel was burnt out completely to form fine powder. The prepared powder were fired at 400°C for 1h to form ZnFe_2O_4 nano powder.

Preparation of nanocomposite materials ($\text{ZnFe}_2\text{O}_4/\text{PUF}$)

The grafted PU foam was prepared by mixing 20g of the polyol (polyether) with 0.1g nano powder (ZnFe_2O_4). Then, the mixture was stirred well till complete homogeneity, after that 0.04g stannous octoate is added and stirring is continued, followed by addition 13.5 g toluene diisocyanate (TDI) gradually during vigorous

Preparation of nano sorbent (ZnFe_2O_4)

stirring, then 3 drop of silicon oil was added with good stirring, while this the foaming liquid polymer begin to form, after this 2ml of distilled H_2O was added lead to expanding of foaming mixture. Then, the nano composite foaming mixture is poured into a box with fitted cover to allow homogenous dispersion of carbon dioxide "blowing agent". The foam is left to solidify at room temperature. Then, the foam material is cut into a small cubes washed by 0.1M HCl to remove inorganic impurities followed by doubly distilled water and dried at room temperature.

Experimental methods

The phase composition and average crystallite size of the magnetic nanoparticles were studied using an x-ray diffractometer (Model Bruker D8 Advance, $\text{Cu-K}\alpha 1$, $\lambda = 1.54058 \text{ \AA}$, radiation with a secondary monochromator at a scanning speed of $1^\circ/\text{min}$). Debye– Scherrer's equation was used to calculate the average crystallite size of ZnFe_2O_4 nanoparticles; $D = 0.9\lambda / (\text{FWHM} \times \cos \theta)$, where D is the crystallite size; FWHM is the observed full width at half maximum; θ is the Bragg angle, and λ is the wavelength of the X- ray radiation ($\lambda = 1.54058 \text{ \AA}$). Vibrating samples magnetometer (Lakeshore VSM 7410 model equipped with 3 T magnets) was used to measure the magnetic properties of the prepared ferrite nanoparticles. Transmission electron microscopy was used to investigate the morphology and particle size of the composite materials (HR-TEM, JEOL, JEM-2100 Electron Microscope). The microstructure of the prepared composite materials was examined using a scanning electron microscope (SEM, Quanta FEG 250). Flame atomic absorption spectrometer

(model AA-55, Agilent, Germany) equipped with single element hollow cathode lamps and air-acetylene burner was used for the determination of the metals. Air-acetylene flame and 0.7 mm slit width were used. The

Chemicals and reagents

All reagents used were of analytical reagent grade.

Preparation of standard solutions

Standard cadmium (II) solution: (1000 µg/ml) Cd (II) standard solution was prepared by dissolving 2.7543 g of cadmium nitrate [Cd(NO₃)₂.4H₂O], (Panreac, Spain) in DDW containing 2 mL of conc HNO₃ and accurately dilute to one-liter standard flask. Working solution of Cd (II) of concentration (10µg/mL) was prepared daily before experimental processes by dilution of 1mL from the stock solution with DDW up to 100 ml standard flask.

Standard Copper (II) solution: (1000µg/ml) Cu (II) standard solution was prepared by dissolving 3.9291 g of cupric sulphate pentahydrate [CuSO₄.5H₂O], (Aldrich, USA) in DDW containing 2 ml of concentrated H₂SO₄ and accurately dilute the solution up to one-liter standard flask. Working solution of Cu (II) of concentration (10µg/mL) was prepared daily before experimental processes by dilution of 1mL from the stock solution with DDW up to 100 ml standard flask.

Sodium hydroxide: 1 mol/l (Adwic, Egypt) was prepared by dissolving the reagent in DDW and used in the determination method. NaOH (0.1 mol/l) and HCl (0.1 mol/l) were used to adjust the pH

HCl solution: HCl (Adwic, Egypt) of different concentrations was prepared by appropriate dilutions from the concentrated acid

Methods of determination of the studied metal ions.

pH was measured using a microprocessor pH meter BT 500 BOECO, Germany. A mechanical shaker with up to 200rpm (SL 350, Nuve, Akyurt, Ankara, Turkey) with speed control was used.

Determination of cadmium (II) by FAAS (Flame Atomic Absorption Spectrometry)

Operational conditions for measurement of Cd (II) with FAAS are lamp current (mA) ~ 12.0, slit width (nm) ~ 0.7, wave length (nm)~ 228.8 and burner height (cm) 10

Determination of Copper (II) by FAAS

Operational conditions for measurement of Cu (II) with FAAS are lamp current (mA)~ 15, slit width (nm)~ 0.7, wave length (nm)~ 324.8 and burner height (cm)~ 10

Batch procedure

In the batch method a quantity of the chromatographic stationary phase or sorbent is added to the sample and the mixture is shaken for a specified time. Then the sorbent was separated from the sample solution by filtration. Finally, the resultant solution is analyzed by an appropriate method.

Effect of pH:

In order to investigate the effect of pH on the extraction of Cd (II), or Cu (II) onto nano powder and composite nano powder, 25mL solution containing 20µg of individual metal ion was adjusted to a pH range of 2-8 using NaOH or HCl solution, and the mixture was shaken for 1h by a mechanical shaker, the amount of the metal ion remained in the solution was measured using the recommended method after separation of the sorbent by filtration. The percentage sorption of metal ion by the sorbent was calculated from the relation:

$$\%uptake = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C₀ and C are the initial and remaining concentrations of the metal ion, respectively

Effect of sorbent dose:

In order to determine the optimum sorbent dose for the extraction of Cd (II) or Cu (II) ions by ZnFe₂O₄/PUF composite, 25mL of the solution containing varying amounts of (ZnFe₂O₄/PUF) in the range from 0.05 to 0.3 g and 20µg of individual metal ions was adjusted to the optimum pH and shaken for 1h by a mechanical shaker, the amount of the metal ion remained in the solution was measured using the recommended method after separation of the nanocomposite by filtration.

Effect of shaking time:

For this purpose, the effect of shaking time on the extraction of Cd (II) and Cu (II) by composite nano powder was studied, where 0.1g of composite nano powder was added to 25mL of the tested metal ion solution containing 20µg of Cd (II) or Cu (II) at the optimum pH and automatically shaking for different time intervals by a mechanical shaker. From the equation: % E = [(C₀-C) / C₀] × 100, where C₀ and C are the initial and final concentrations, respectively, of metal ions in solution, the percent extraction was determined

Extraction isotherm and determination of capacity

Batch adsorption studies with different initial concentrations of Cd (II) and Cu (II) were performed in order to determine the extraction isotherm for Cd (II) and Cu (II)

$$\% R = \frac{C}{C_0} \times 100 \quad (3)$$

Where C₀ and C are the initial and final concentrations of metal ion in solution (µg/l), respectively

Regeneration and reusability studies

The regeneration experiments were conducted to estimate the reusability of the two composites (ZnFe₂O₄/PUF). This test was drawn with respect to Cd (II). For this purpose, 0.2 g from the composite materials was mixed together with 20 µg Cd (II) solutions at pH 6. final volume was 25ml, and the shaking time for 1 hr. After that, the loaded composite was washed with DDW

and sorbent capacity using the two composites, where the optimized weight of the two composite nano powder were added to 25mL of the tested metal ion solution containing varying concentration of Cd (II) or Cu (II) from 10-100 µg at the optimum conditions. The sorption capacity was calculated from the relation; $Q = [(C_0 - C) \times V] / m \dots (2)$

where V is the sample volume in liter and m is the weight of composite in gram, C₀ and C are the initial and final concentrations in mg/L.

Pre-concentration of metal ions:

For this purpose, 25-1500 ml solution containing 20µg from each metal ion was adjusted to the optimum pH, addition of 0.2gm of the composite (ZnFe₂O₄/PUF) and the mixture was shaken for 1h by a mechanical shaker. Using 10 ml of 0.5 mol.L⁻¹ HCl solution as eluting agent, the amount of each metal ion in the eluate was measured by the recommended method. The concentration factor (CF) could be calculated from the ratio of the initial volume of the sample to the final volume after concentration. The recovery % was calculated from the initial concentration of the metal ion in solution and its concentration in the eluate according to equation (3).

and air-dried. Secondly, the composite was treated with 10 ml of 0.5 mol. L⁻¹ HCl solution as the eluting agent. After each desorption experiment, the adsorbent samples were washed several times with DDW till free from acid, air-dried, and used for the next run. The reusability of the two composites (ZnFe₂O₄/PUF) for Cd (II) adsorption was assessed by repeating 7

cycles of successive adsorption and desorption

Analysis of real samples

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ion; the method was applied to the determination of Cd (II) and Cu (II) ions from different matrices such as tap water, Qaroun lake water and Bahr Youssef water, from Fayoum Governate.

Real water analysis

100 ml of tap water sample was collected from our research laboratory in the Faculty of Science at Fayoum Governate., Qaroun lake water, underground water or Bahr Youssef water, at Fayoum City were spiked with 20 μ g of the standard solution of the tested metal ions, and the mixture was shaken for 1h by a mechanical shaker, The metal ions were eluted by 10 ml of 0.5 mol. L⁻¹ HCl solution. The concentration of each metal ion in the eluate was measured by the recommended method.

RESULTS AND DISCUSSION:

X-ray diffraction (XRD)

Figure (1) shows the XRD patterns of ZnFe₂O₄ nanoparticles. The main diffraction peaks appeared at $2\theta = 29.919^\circ$, 35.264° , 42.844° , 53.11° , 56.629° , 62.212° , and 73.513° , which were attributed to the crystal plane of ZnFe₂O₄ structure (220), (311), (400), (422), (511), (440) and (533) planes, respectively (XRD JCPDS data file No.22-1012). The prepared ZnFe₂O₄ nanoparticles have high crystallinity and a single cubic phase with spinel structure, as shown by these XRD peaks. The average crystallite size of ZnFe₂O₄ nanoparticles is 25.6 nm.

Magnetic Properties of ZnFe₂O₄ Nanoparticles

Figure (2) shows the hysteresis loops and the magnetic parameters (saturation magnetization (M_s) and coercivity (H_c)) of the prepared ferrite nanoparticles fired at 400°C for 1h by using a vibrating samples magnetometer at room temperature. It was observed that the saturation magnetization (M_s) and remanent magnetization (M_r) of the fired sample are 4.175emu/g and 1.141emu/g. Also, ZnFe₂O₄ nanoparticles observed the ferromagnetic behavior and have 267.11G coercivity.

Transmission electron microscopy (TEM) analysis:

High-resolution transmission electron microscopy (HR-TEM) analysis was carried out to provide evidence for the morphology of the ZnFe₂O₄/PUF composite as shown in Figure (3). It was observed that the ferrite nanoparticles are scattered in the PUF and/or agglomerated together inside the PUF. This is due to the magnetic nature of the ferrite nanoparticles leading to the form of agglomerations inside the PUF. The estimated average particle sizes of the samples were found to vary between 5.37 nm and 25.45 nm for the ZnFe₂O₄ sample as shown in Figure (3).

Scanning electron microscope (SEM)

Figure (4) shows the microstructure of the prepared composite (ZnFe₂O₄/PUF). It was observed that the microstructure of the prepared composites has a spongy structure (spherical shaped) and the nanoparticles (white spots) disperse inhomogeneity inside the PUF structure. In addition, it was detected that the composite PUF/ZnFe₂O₄ containing three types of pores: coarse, medium and fine with different pore sizes 1.117mm – 655.8 μ m, 613.1 μ m – 286.2 μ m and 9.624 μ m – 1.529 μ m, respectively.

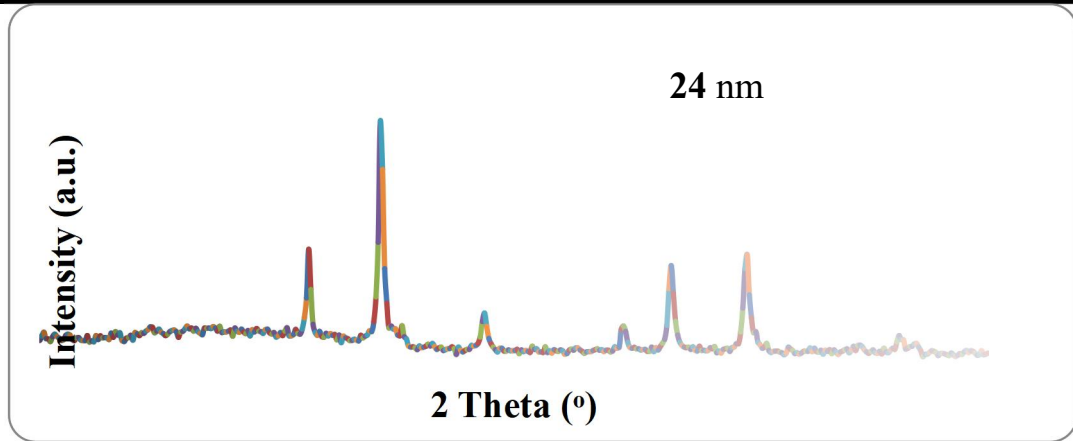


Fig. 1: XRD of the ZnFe₂O₄ nanoparticles

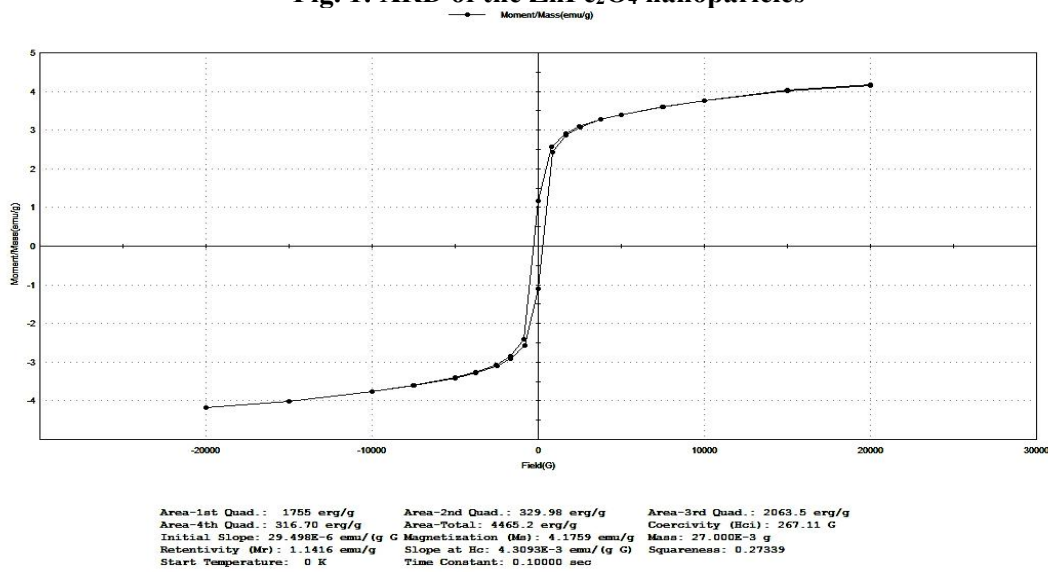


Fig. 2. The hysteresis loops and the magnetic parameters of the ZnFe₂O₄ nanoparticles

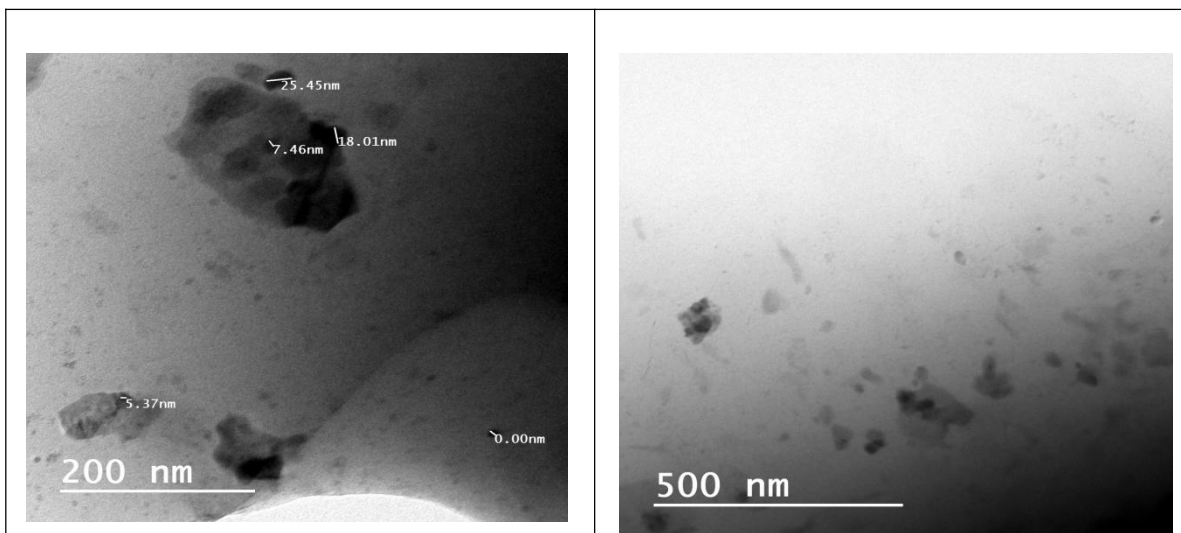


Fig. 3: HR-TEM of the ZnFe₂O₄/PUF composite

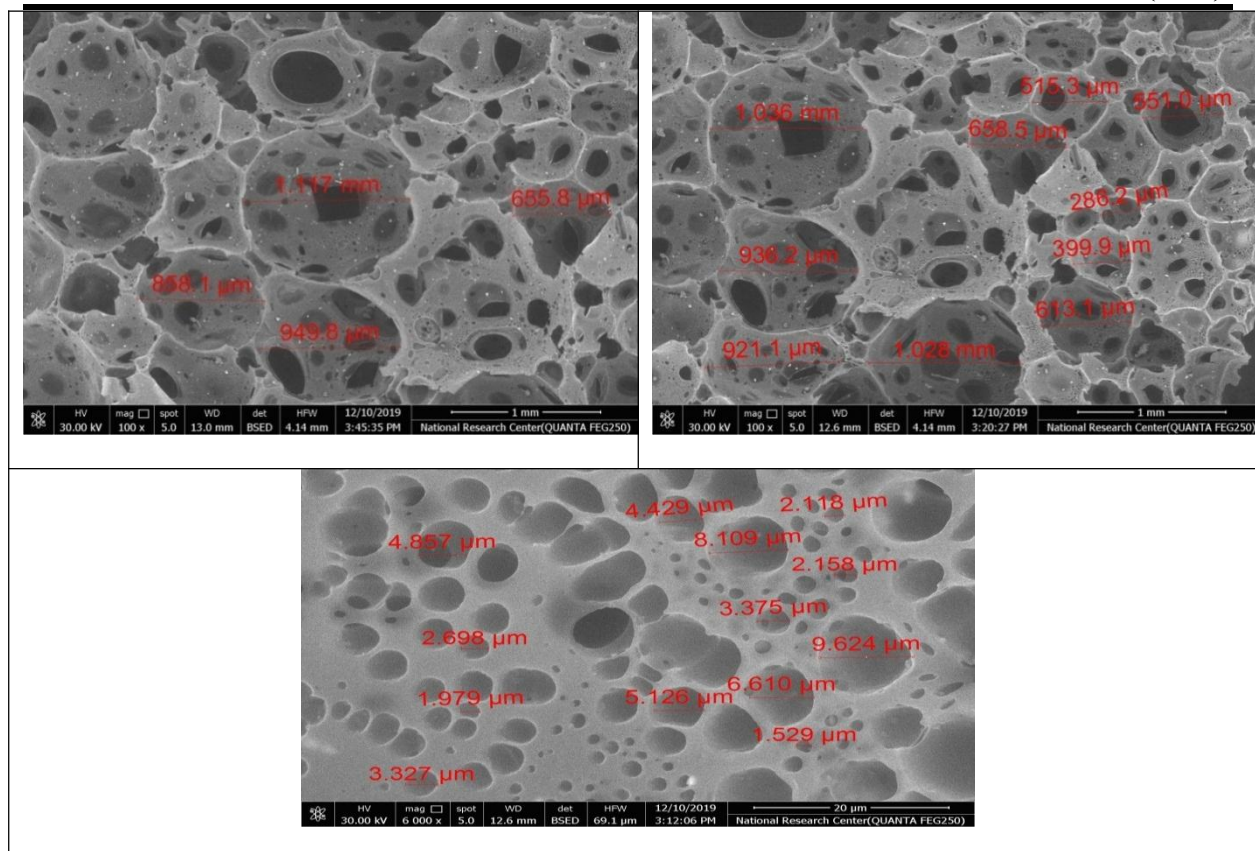


Fig. 4. Microphotography of the $\text{ZnFe}_2\text{O}_4/\text{PUF}$ composite.

Batch Procedure

Effect of pH:

The pH of the aqueous solution was clearly an important parameter that controlled the uptake process. As it influences not only the metal ion speciation but also the charges on the active adsorption sites. So, the effect of solution pH on the removal of Cd (II) and Cu (II) from aqueous solution onto nano ZnFe_2O_4 and $\text{ZnFe}_2\text{O}_4/\text{PUF}$ composite adsorbents was studied over the pH range 2-8 and the results were plotted in the Figures 5 and 6. It is clear that the uptake percentage increase with increasing in the solution pH from 2 to 4 and from 2 to 5, then it becomes steady up to pH 8, this trend was observed for Cd^{2+} and Cu^{2+} ions, respectively, **Fig. 5**. This could be attributed to the degree of speciation and the ionization of the adsorbate which are mainly affected by the solution pH (Bidabadi et al., 2009). The extraction of the nano sorbent for the studied analyte ions are

93 % and 95 % for Cd^{2+} and Cu^{2+} ions on ZnFe_2O_4 nano sorbent. While the maximum uptake for the composite materials is 96% and 97 % onto $\text{ZnFe}_2\text{O}_4/\text{PUF}$ at the pH 6 and pH 5 for Cd^{2+} and Cu^{2+} respectively, as shown in Fig. 6. At lower pH values, there is a decrease in the removal capacity of all sorbents due to the electrostatic repulsion of the protonated active sites on the sorbent surfaces with the positively charged metal species. The H^+ ions concentration also plays an important role in the removal of the analyte ions by the solid phase, because H^+ ions can undergo exchange with the surface of composite materials. The percentage of removal obtained indicated that this composite material has a greater affinity towards Cu^{2+} ions but less affinity towards Cd^{2+} ions in the range of pH 2 and 3. Adequate removal for the effective extraction of the studied metal ions has become a paramount issue. Thus, many nanomaterials

have been developed as economical; have a high surface area and good sorption capacity. ZnFe₂O₄/PUF composite materials have been investigated because the white foam is widely known to have great surface area. As was observed in Fig. (6), the removal percent increases with increasing the pH value, then it decreases at pH 7 and 8, this decrease in the uptake may be attributed to the possible precipitation of metal hydroxides. The proposed procedure recommends the

extraction solution at pH 6 for Cd (II) and Cu (II) ions on ZnFe₂O₄/PUF composite materials where the removal percent was recorded at 96% and 97% for Cd (II) and Cu (II) ions respectively. While the extraction percent on ZnFe₂O₄ sorbent at pH 5 for Cd (II) and Cu (II) are 91% and 96% respectively. The pH value of the aqueous solution is an important factor for the quantitative removal of the analyte ions.

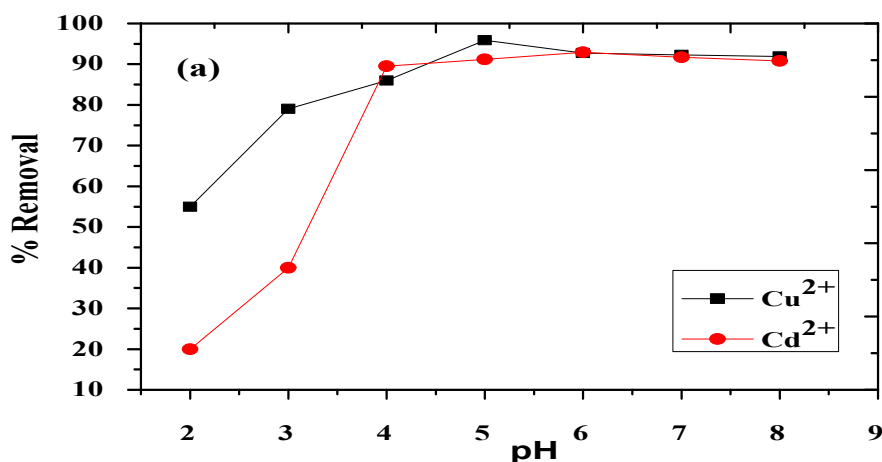


Fig. 5. The effect of pH on the removal percent of Cd²⁺ and Cu²⁺ ions on to ZnFe₂O₄ nano adsorbents at C₀=0.8 ppm, m/v = 0.1 /25 mL and shaking time 60 minutes.

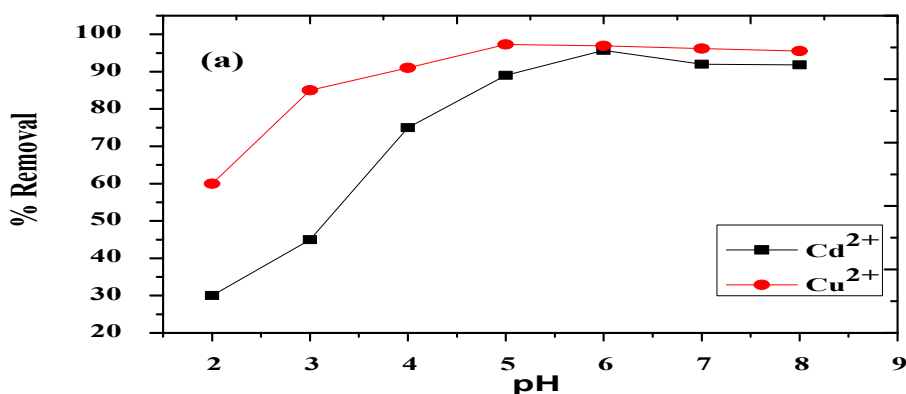


Fig. 6. Effect of pH on the removal of Cd²⁺ and Cu²⁺ onto ZnFe₂O₄/PUF adsorbent at C₀=0.8 ppm, m/v = 0.1gm/ 25 mL and shaking time one hour.

Effect of shaking time

The removal time is another important factor in determining the possibility of the application of the new composite for the removal of Cd (II) and Cu (II) ions. The effect of the shaking time on the uptake of the two analyte ions was studied as shown in **Fig (7)**. The percent of the uptake of two analyte ions by the ZnFe₂O₄/PUF composite depends on the time at which equilibrium attained, which considered as the equilibrium time (Burham et al., 2009). The rate of the removal Cd (II) and Cu (II) ions was studied over a series of varying removal time from 1 to 75 minutes. It is clear that the removals percent increase with increasing the contact time and reach 94.8% and 96% for Cu (II) and Cd (II) onto ZnFe₂O₄/PUF. Also, the time required to reach maximum removal is around 60 minutes. This is considered a short period, which confirms the accessibility of the ZnFe₂O₄/PUF composite materials for the rapid removal of Cd (II) and Cu (II) ions from aqueous solution, also the binding constant between the analyte ions and the removal composite materials is possibly high. The results also indicate that, the ZnFe₂O₄/PUF composite materials are suitable for the application in flow systems which are faster removal. In addition, this composite used in the pre-concentration of trace ions after 60 minutes.

Effect of sorbent dosage:

Many researchers showed that adsorbent dosage has a significant effect on the removal of metal ions from aqueous solutions (Setshedi et al ., 2013 ; Prasad et al ., 2006) .The effect of ZnFe₂O₄/PUF composite weight on the removal of Cd²⁺ and Cu²⁺ from aqueous solutions was tested as which 20 µg of each element were placed in 25 ml sample at the optimum pH and optimum shaken time with varying amount of the composite from 0.025 to 0.3 g /25 mL and the results were presented in **Fig(8)**, it shows that the extraction percent of Cd (II) and Cu (II) increases with increasing of the composite weight from 0.025 to 0.2 g. The uptake efficiency enhances with the adsorbent content which reaches 95.8% at 0.2 g /25 mL for Cd (II) and 96.5% at the same dose for Cu (II) onto ZnFe₂O₄/PUF. This could be attributed to increasing adsorbent content, increasing the number of active sites available for adsorption and hence efficient removal was achieved (Burham and Sayed., 2016). When the composite dose increased more than 0.2g, there is no significant increase in the uptake percentage of the studied ions by the composite. This behavior suggests that after a certain dose of the composite, the maximum uptake is attained and hence the amount of the ions remains constant even with further increasing of extractor dose. The increase of the extractor weight prevents the analyte ions from reaching the various sites of the composite.

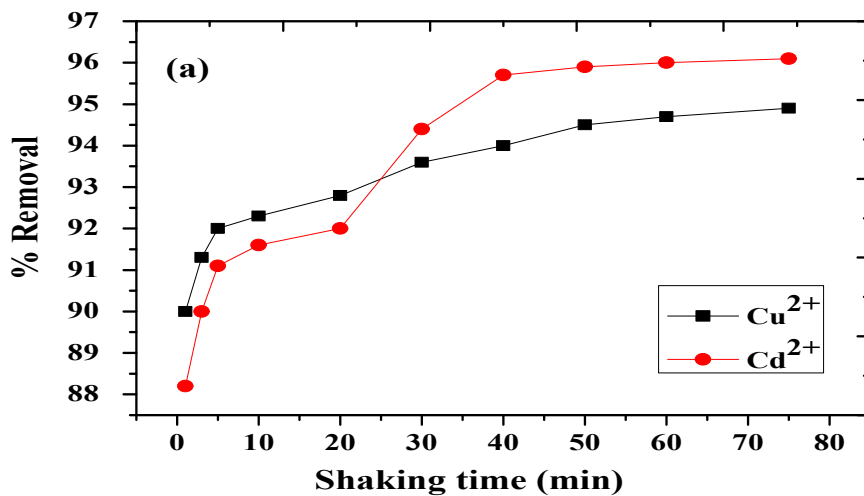


Fig. 7. Effect of shaking time on the removal of Cd²⁺ and Cu²⁺ onto ZnFe₂O₄/PUF adsorbent at C_i=0.8 ppm and m/v =0.1gm /25 mL

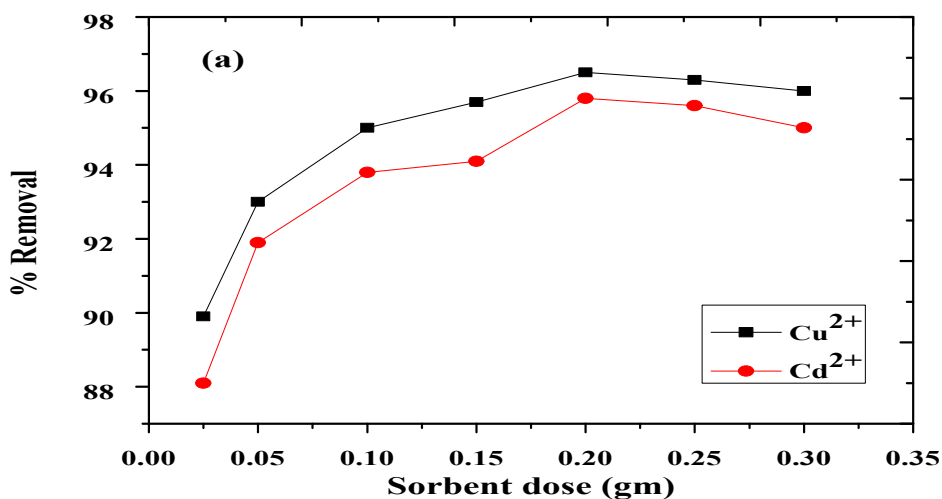


Fig. 8. Effect of sorbent dose on the removal of Cd²⁺ and Cu²⁺ ions onto ZnFe₂O₄/PUF adsorbent respectively at C_i=0.8 ppm and v =25 mL

Extraction isotherm and Sorbent capacity: Effect of metal ions concentration

The relationship between the amount of a metal ions extracted at a constant temperature and its initial concentration in the equilibrium solution is called the adsorption isotherm. The capacity of the sorbent is an important factor because it determines how much solid phase is required quantitatively to remove a specific amount of the studied ions from the solution. The capacity Q ($\mu\text{g/g}$) of adsorbed ion at 25°C

was calculated using equation (2). Extraction isotherm studied for individual ions by the static mode, by shaking 25 ml metal ions solution containing metal ion concentration varying from 10 to 100 μg at the optimized pH. The uptake capacity values were determined by increasing the initial metal ion concentration till the plateau values were obtained at Fig (9), it is clear that the extraction capacity of Cd (II) and Cu (II) ions probably differ due to their ionic size, the value of their binding constant with the

composite, and the degree of hydration. The results indicate also that Cd (II) and Cu (II) ions are directly coordinated on the composite of foam phase, probably by using donor atoms, without other transfer mechanism (Prasad et al., 2006; Liu et al., 2004). The gradual increase in the metal ions extracted with increasing the sample concentration reveals the gradual saturation of the sorbent binding sites. When complete saturation of binding sites is fully occupied, no further uptake occurs.

Sorbent capacity

The total extraction capacity Q ($\mu\text{g/g}$) of the composite ($\text{ZnFe}_2\text{O}_4/\text{PUF}$) was determined by the recommended method. The total extraction capacity Q was calculated from equation $Q = [(C_0 - C) \times V] / m$, Where C_0 and C are the concentration of the analyte ion in the initial and final solution, respectively ($\mu\text{g/ml}$), V is the sample volume of aqueous phase (ml) and m is the weight of the composite $\text{ZnFe}_2\text{O}_4/\text{PUF}$ (grams). The total uptake capacity ($Q \pm \text{SD}^*$) of the $\text{ZnFe}_2\text{O}_4/\text{PUF}$ composite are $251.50 \pm 0.33 \mu\text{g/g}$ and $381.01 \pm 0.20 \mu\text{g/g}$ for Cd^{2+} ion and Cu^{2+} ion, respectively.

Pre-concentration and concentration factor

In order to explore the possibility of pre-concentrate low concentration of metal ions

from large sample volume, the effect of the sample volume on the recovery of Cd (II) or Cu (II) ions was investigated at **Fig (10)**. The capability of $\text{ZnFe}_2\text{O}_4/\text{PUF}$ composite to collect the tested metal ions quantitatively from large volumes was explored by the batch procedure. The sample pH and shaking time at the optimum values was adjusted. It was observed that the uptake percent value reaches from 95.7 to 96.5% and from 94.9 to 95.8% for Cu (II) and Cd (II) respectively up to 1000ml of sample volume and then decreased slowly. The maximum volume of the sample which reveals quantitative recovery of the element is utilized to calculate the pre-concentration factor. The pre-concentration factor is the ratio between the volume of the metal ion in the sample to its volume in the eluate. From the data obtained in **Table (1)**, it is clear that 20 μg of each metal ion could be pre-concentrated from sample volume up to 1000ml under the optimum conditions without any loss of the analyte. The pre-concentration factor of $\text{ZnFe}_2\text{O}_4/\text{PUF}$ in case of the largest studied sample volume (1000 ml) and eluate volume (10 ml) is calculated and was found to be 100 for the two studied metal ions. From these results, the extraction of Cd (II) and Cu (II) ions onto 0.2g of $\text{ZnFe}_2\text{O}_4/\text{PUF}$ is not affected by the sample volume till 1000 ml.

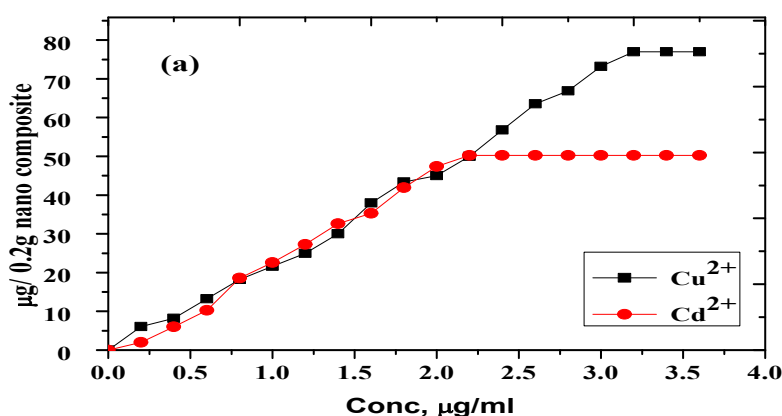


Fig. 9. Extraction isotherm of Cd^{2+} and Cu^{2+} by the $\text{ZnFe}_2\text{O}_4/\text{PUF}$ composite at 25°C

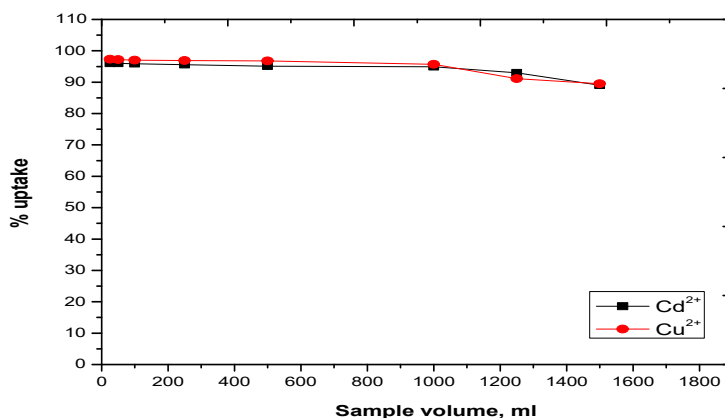


Fig. 10. Effect of sample volume on extraction of Cd²⁺ and Cu²⁺ using ZnFe₂O₄/PUF composite under optimum conditions.

Table 1. Pre-concentration factor (CF) of Cd²⁺ and Cu²⁺ ions with ZnFe₂O₄/PUF composite

	Metal Ion	Initial volume (ml)	Final Volume (ml)	Recovery (%)	CF
ZnFe ₂ O ₄ /PUF	Cd ²⁺	1000	10	94.9	100
	Cu ²⁺	1000	10	95.7	100

Desorption and reusability of ZnFe₂O₄/PUF composite

It determines the feasibility of applying the adsorbent systems in large-scale operations. To assess the desorption characteristic of ZnFe₂O₄/PUF composite for Cd²⁺, using 10 ml of 0.5 mol.L⁻¹ of HCl solution as eluting agent. To check the reusability performance of ZnFe₂O₄/PUF composite adsorbent, seven successively adsorption-desorption cycles have been conducted at the same adsorbent samples and experimental conditions and the results are presented in Fig (11). It was clear that the adsorption percent removal of

ZnFe₂O₄/PUF composite materials for Cd (II) remains almost as the same even after 5 regeneration cycles. A slight decrease after the fifth cycle is observed indicating that ZnFe₂O₄/PUF composite could retains its functionality more than 5 cycles without significant loss of original adsorptive capacity. These results indicated that ZnFe₂O₄/PUF composite could be regenerated and further reutilized, which considerably supports the practical application of the prepared composite materials as adsorbent.

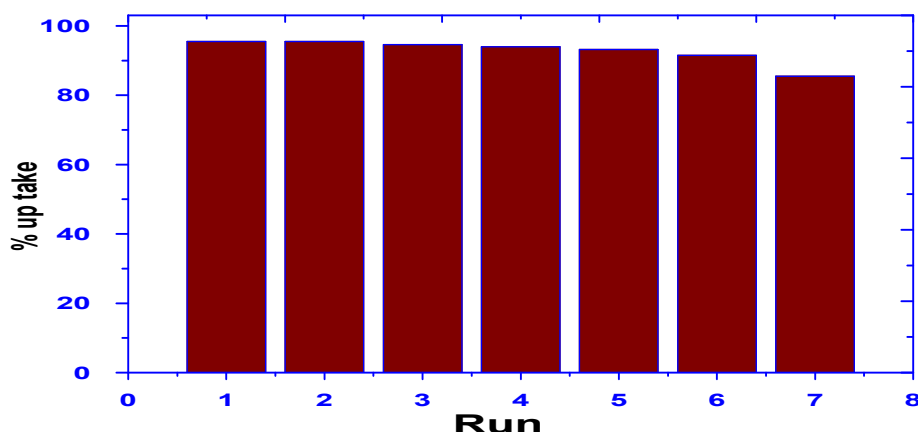


Fig. 11. Adsorption cycles of ZnFe₂O₄/PUF composite materials for Cd²⁺ under the optimum experimental condition (pH=6, metal ion concentration=0.8ppm, sorbent dose 0.2gm and contact time=60 min).

Analytical applications of the method to real Samples

To test the analytical applicability of the prepared ZnFe₂O₄/PUF composite for cadmium and copper ions, pre-concentration and recovery percent of three natural water samples; Qaroun lake water, tap water and Bahr Youssef water are collected from Fayoum government were measured. The three tested water samples are spiked with 20 µg of each metal ion and mixed together with

ZnFe₂O₄/PUF adsorbent. Results obtained that, as shown in **Table (2)**, recoveries (%) of the spiked ions to water samples were quantitatively removed. R (%) was calculated as follows: $R (\%) = ([C_{\text{found}} / C_{\text{add}}] \times 100)$

Where C_{found} is the total value of the metal ions in the spiked sample, and C_{add} is the amount of the metal ion spiked. All the % R values are in the acceptable range. These results indicate good accuracy of the method in the precision point of view.

Table 2. The Recovery percent for spiked Qaroun Lake water samples, Tap water samples and Bahr Youssef water samples (n=3)

Sample type	Sorbent	Metal ion	Added (µg/ml)	Found (µg/ml± SD*)	Recovery (%)
Qaroun lake water	ZnFe ₂ O ₄ /PUF	Cd ²⁺	0.2	0.231±0.003	115.5
		Cu ²⁺	0.2	0.235 ±0.004	117.5
Tap water	ZnFe ₂ O ₄ /PUF	Cd ²⁺	0.2	0.221 ±0.004	110.5
		Cu ²⁺	0.2	0.219 ±0.003	109.5
Bahr Youssef water	ZnFe ₂ O ₄ /PUF	Cd ²⁺	0.2	0.233 ±0.002	116.5
		Cu ²⁺	0.2	0.225 ±0.003	112.5

Conclusion:

- The high crystallinity and purity of the spinel phase synthesized of ZnFe₂O₄ nanoparticles were observed in the XRD

data. Also, the average crystallite size of all nanoparticles in the range 16-25 nm.

- VSM measurements showed that the saturation magnetization (Ms) values of ZnFe₂O₄ is 4.179 emu/g
- The HR-TEM images observed that the nanoparticles are scattered in the PUF and / or agglomerated together inside the PUF. This is due to the magnetic nature of the ferrite nanoparticles leads to form agglomerations inside the PUF. The average particle size of the prepared nanoparticles in PUF ranged from 5.3 to 25 nm.
- The microstructure of the prepared composites observed the spongy structure (spherical shaped) and higher porosity of the prepared ZnFe₂O₄/PUF composite.
- It clear that the optimal pH, at which the maximum percentages of removal reached, for Cd (II) and Cu (II) ions removal with the composite are 6 and 5, respectively.
- The optimum shaking time required to reach maximum removal percent is ~ 60

minutes, at which equilibrium attained, which is considered a short period.

- The maximum percentages of removal were obtained at a sorbent weight of 0.2g.
- The maximum percentages of Cd (II) and Cu (II) ions removal on ZnFe₂O₄/PUF composite materials are 95.8% and 96.5% at the optimal conditions.
- The pre-concentration factor of ZnFe₂O₄/PUF in case of the largest studied sample volume (1000 ml) and eluate volume (10 ml) was calculated and found to be 100 for the two studied metal ions
- Desorption and reusability of ZnFe₂O₄/PUF composite shown that the percent of adsorption removal of the ZnFe₂O₄/PUF composite remains as the same even after 5 regeneration cycles. A slight decrease after the fifth cycle is observed indicating that ZnFe₂O₄/PUF composite could retains its functionality more than 5 cycles without significant loss of original adsorptive capacity.

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المخلص العربي

استخدام مركب النانو زنك فرايت بولي يورثان فوم (PUF/ZnFe₂O₄) لازالة ايونات الكاديوم والنحاس من المحاليل المائية

¹فاطمه حسن يوسف، ²محمد محمد صلاح وحش، ¹نجوي برهام برهام، ¹سامي محمد عبد العظيم

¹ كلية العلوم – جامعه الفيوم – قسم الكيمياء، ² المركز القومي للبحوث بالدقي – قسم السيراميك والحرارات ومواد البناء

تم تحضير المادة النانومترية (ZnFe₂O₄) بطريقه السيترات جيل modified citrate sol gel method في شكل مسحوق نانومتري. ثم اضافته هذه المادة اثناء عمليه البلمره والتكوين للبولي يورثان فوم بنسبة 0.33% مما يؤدي الي تحسين قدرة ماده البولي يورثان فوم على استخلاص المعادن الثقيلة وسهولة ازالته بعد إنتهاء عمليه الاستخلاص باستخدام مغناطيس خارجي.

تم دراسة التطور الطوري (Phases) والخصائص المغناطيسية للماده النانومترية (ZnFe₂O₄) المحضرة باستخدام كلا من جهاز حيود الاشعة السينيه (XRD) وجهاز قياس الصفات المغناطيسيه (VSM). كذلك دراسة حجم الحبيبات النانومترية المضافة داخل البولي يورثان فوم والبنية المجهرية الدقيقة للمتراكبات النانومغناطيسيه/ بولي يورثان فوم باستخدام كلا من جهاز الميكروسكوب النافذ الالكتروني (TEM) وجهاز الميكروسكوب الماسح الالكتروني (SEM). ثم ، دراسة كفاءة هذه الماده في استخلاص ايونات الكاديوم الثنائي والنحاس الثنائي في نطاق معلمي وتطبيقها على كلا من مياه الصنبور ومياه فرع النيل بمحافظة الفيوم (بحر يوسف) ومياه بحيرة قارون .

- تم دراسة التطور الطوري (Phase composition) للماده النانومترية (ZnFe₂O₄) واوضحه الدراسة تكوين معدن الاسبينيل (Spinel) مما يدل على كفاءة التحضير وجوده الكريستالات المتكونه وكما اظهرت النتائج ان متوسط حجم الكريستالات (crystallite size) المتكونه بين 16-25 نانو متر.
- تم دراسته تأثير درجه الاس الهيدروجيني : وتم التوصل الي درجه الاس الهيدروجيني التي يحدث عندها اعلي نسبة استخلاص وتركيز وازاله لعنصري الكاديوم والنحاس وهي بالنسبه لعنصر الكاديوم (pH=6) اما بالنسبه لعنصر النحاس كانت (pH=5) وكانت نسبة الاستخلاص 97%.
- دراسته تأثير زمن الرج: تم دراسته فترات زمنية مختلفه وتم التوصل الي ان عند time= 60 min تحدث عمليه الاتزان وعندها اعلي نسبة استخلاص لعنصري الكاديوم والنحاس.
- دراسته تأثير وزن الماده المازة : وفيها تم استخدام اوزان مختلفه من الماده المازة تتراوح بدايه من 0.025 g/25 ml to وكانت اعلي نسبة استخلاص للماده المازة عند وزن 0.2gm مما يدل علي قله كميته الماده المازة المستخدمه وذلك يؤدي الي تقليل عمليه التكلفة اثناء عمليه الاستخلاص.
- دراسته سعه استخلاص الماده المازة : تم استخدام تركيزات مختلفه من ايونات الكاديوم والنحاس وتم حساب سعه الاستخلاص باستخدام

$$Q = [(C_0 - C) \times V] / m$$

- دراسته اعاده استخدام الماده المازة (PUF/ZnFe₂O₄) لعده مرات ووجد انه يمكن استخدام هذه الماده لعدد مرات تصل الي خمس مرات بنفس كفاءه الاستخلاص التي يتم الحصول عليها في استخدام اول مره .
- دراسته تطبيق استخدام هذه الماده المازة (PUF/ZnFe₂O₄) في استخلاص بعض الكاتيونات تحت الدرسته في عينات حقيقيه من مياه طبيعيه مثل مياه الصنبور وفرع نهر النيل بالفيوم (بحر يوسف) وبحيرة قارون. وقد اظهرت النتائج أنه يمكن استخدام (PUF/ZnFe₂O₄) في تركيز وتقدير تلك الكاتيونات السابق ودراستها بكفاءة عاليه.
- **الكلمات الداله:** المواد النانومترية; زنك فرايت; بولي يورثان فوم; ازاله العناصر الثقيله; تلوث المياه.