

Research on Copper Ions Removal from Wastewater Using Fe_3O_4 and Fe_3O_4 -PVP Hybrid Nanomaterials

CRISTINA ILEANA COVALIU^{1*}, OANA STOIAN¹, ECATERINA MATEI¹,
GIGEL PARASCHIV¹, EUGENIA TANASA¹, GINA ALINA CATRINA (TRAISTARU)²

¹University Politehnica of Bucharest, 313 Splaiul Independenței, 060042, Bucharest, Romania

²INCD ECOIND, 71-73 Drumul Podu Dambovitei Str., 060652, Bucharest, Romania

Abstract: Wastewater containing Cu (II) ions has become a huge environmental problem worldwide because ingestion of copper ions affects the human body leading to epigastric pain, nausea, vomiting, diarrhea and even death. The researches for new methods of treatment of wastewater polluted with heavy metals more efficient than the conventional ones led us to study Fe_3O_4 and his corresponding hybrid Fe_3O_4 -PVP as potential adsorbent nanomaterials for the removal of copper ions from industrial wastewater. First, the two nanomaterials were synthesized by precipitation method and characterized by XRD, FTIR and TEM analyses. Then, the two obtained nanomaterials were tested within the process of copper ions removal from wastewater and factors influencing the process including pH and contact time were investigated. The maximum wastewater treatment capacity reached up to 97 % under the optimal condition using Fe_3O_4 and 70% for Fe_3O_4 - PVP.

Keywords: magnetite nanomaterial, magnetic hybrid, copper ions removal, XRD, TEM

1. Introduction

It is known that without water no human or animal can live on earth, air and soil having the same importance like water, these being abundant resources for living beings. If these resources are polluted, the human health is in danger. Protection of water, air and soil is the most important concern in the whole world, especially in developed countries. Depollution is a challenge when we take into consideration the legislation, efficiency, recyclability, environmental impact and cost. The most common pollutants found in water are mainly inorganic pollutants like heavy metals, organic compounds such as pesticide, detergents or pharmaceuticals. For example, some of the heavy metal ions found in water are Pb^{2+} , Hg^{2+} , Cr^{6+} , Cd^{2+} , As^{3+} , As^{5+} , Co^{2+} , Cu^{2+} , Ni^{2+} . The pollution of water with heavy metals which are non-biodegradable in our bodies can lead to huge health problems, such as diarrhea, vomiting, stomach cramp, gastrointestinal distress, coma, jaundice and nausea [1,22].

The conventional methods (Figure 1) for the removal or decreasing of heavy metal ions from water are: adsorption [2,3], chemical precipitation [4], membrane filtration [5], ion exchange [6], coagulation and flocculation [7], reverse osmosis [8], irradiation [9], flotation and extraction [10], advanced oxidation processes, electrochemical treatment techniques [11] and biosorption processes [12]. Adsorption is the most utilized technique for removing heavy metals from wastewater. Also activated carbons [13], clay minerals [14] or natural zeolites [15] are often used to remove heavy metals from wastewater. They have disadvantages, such as low adsorption over time, unequal pore structure or regeneration issues [16]. The conventional adsorbents already used in the depollution process are hard to remove and those can affect seriously our health [17].

Chemical precipitation used in wastewater depollution is applied for removing ionic compounds from wastewater adding counter-ions to decrease the solubility. It is used for the metallic cations removal, but also for anions and organic molecules elimination form wastewater [4].

The adsorption is the method that makes the pollutant to pass from the industrial wastewater to the adsorbent material surface and links to it through the chemical and physical interactions [24].

*email: cristina_covaliu@yahoo.com

Ion exchange method using membranes can enable the passage of counter-ions (oppositely charged ions), while block co-ions (similarly charged ions) [30].

Filtration is a method that refers to solid-liquid separation, being a common method in wastewater depollution. The purpose of solid-liquid separation is to growth the solids concentration by using a driving strength for consolidation of the suspended solid phase [31].

Coagulation-flocculation is a common method in wastewater depollution for precipitating dissolved impurities and destabilizing colloids to make large aggregates, which can be eliminated from wastewater in further processes. The most used coagulants are iron(III) and aluminum(III) compounds [7].

Bio-sorption is a process that use biomass such as yeast, algae, bacteria, fungi for wastewater depollution, being a low cost method and removing heavy metal ions [32].

As regarding copper ions, once it reaches our bodies they are transferred in the intestine and then carried through blood to the liver and it links to albumin [23]. The catalytic role of copper can lead to osteoporosis, bone abnormalities, growth disorders, anemia, neutropenia, hypopigmentation or immunodeficiency. The toxic quantity of copper salt for animals is 30 mg/kg. Copper poisoning is not very often for humans because of the transport system in our bodies that speeds elimination of excess copper. These systems can be disabled by the proteins that carry the copper so it will lead to cirrhosis. [24].

Copper containing proteins have another purpose in our bodies for the carriage of electrons and oxygen, for procedures based on the fast transition from Cu^+ to Cu^{2+} . Oxygen is carried by the protein hemocyanin. The level of copper in our bodies is between 1.4 and 2.1 mg/kg of body weight. For the normal behavior of the body, the minimum daily dose of copper is 0.97 mg/day [23].

Because nanomaterials could have a great potential for retain heavy metals from wastewater, are currently studied. Because of their small size, nanomaterials have a high surface area, therefor improving adsorption capacities for the removal of heavy metals [25].

The advantages of using nanosized magnetic particles are that they could have high capacity of adsorption of cooper ions from wastewater compared with other conventional copper adsorbents, have high surface area, reduced cost and can be easily separate from wastewater using magnetic field at the end of the wastewater treatment process [18]. These nanosized magnetic particles have attracted a lot of consideration in the removal process of heavy metals from polluted water [19], such as As^{3+} , Pb^{2+} , Hg^{2+} , Cr^{6+} , Cd^{2+} which are recognized to cause great damage to living beings and to the environment [17,20].

Fe_3O_4 nanoparticles have been used for the elimination of some pollutants from wastewater. In the recent years, magnetite (Fe_3O_4) has been studied in the environmental depollution because of their strong adsorption capacities, magnetic properties and easily separation and collection [21, 26-29].

Some researchers discovered that the copper adsorption from a copper-ammonia water solution depends on $p\text{H}$, copper removal increases with increasing $p\text{H}$ (from $p\text{H}$ 2 to $p\text{H}$ 9). At $p\text{H}$ 8 the removal percentage was 100%. Also, the efficiency of $\text{NH}_3\text{-N}$ removal was about 26% at $p\text{H}$ 8. The adsorbent dosage also had an important role. The study consisted in testing of differ&ent magnetic ferrite dosages (0.2, 0.4, 0.6, 0.8 and 1g) into 200mL of Cu(II) ions wastewater [33]. Other researchers observed that initial solution $p\text{H}$ influence the Cu(II) ion adsorption on a Fe_3O_4 composites. They investigated $p\text{H}$ range between 3.0 - 11.0 and discovered that once increasing solution $p\text{H}$ from 3.0 to 7.0 the removal rate increase as well [34].

Poly(vinylpyrrolidone) has various applications because of its unique properties such as biological compatibility, environment friendly, complexing ability and film forming ability.

Table 1 presents the experimental conditions and efficiencies of removing copper ions from wastewater reported in the specialized literature.

**Table 1.** Copper ions adsorption from different synthetic water solutions using different materials

Solution	Adsorbent	Heavy metal conc. (mg/L)	Adsorbent dosage (g/L)	Ion solution (mL)	Temp (°C)	pH	Contact time (min)	Yield (%)	Model	q _{max} (mg/g)	Ref
Copper-ammonia	Fe ₃ O ₄	50	0.2	200	25	8	60	99.53	Langmuir Freundlich Temkin D-R	124.80	[33]
		100	0.2	200	25	8		99.82		-	
		150	0.2	200	25	8		99.68		112.17	
Copper ions	MCGON	100	0.01	50	25	7	70	-	Langmuir Freundlich Temkin Redlich-Peterson	217.40 - - -	[35]
Copper ions	Magnetic Fe ₃ O ₄ /CNT	100-900	-	20	30	5	150	87.5	Langmuir Freundlich D-R	9.36 - 14.02	[36]
Copper, nickel and zinc ions	SDS- Fe ₃ O ₄ NPs	10	0.01 Fe ₃ O ₄ 0.01 SDS	20	-	4	5	~ 42.00	Langmuir Freundlich	24.30 -	[37]
			0.01 Fe ₃ O ₄ 0.025 SDS					~ 45.00			
			0.02 Fe ₃ O ₄ 0.025 SDS					~ 40.00			
Copper and nickel ions	M	10	0.1	50	-	5	-	~ 80.00	Langmuir Freundlich	6.19 -	[38]
	MIA							~ 85.00	Langmuir Freundlich	48.78 -	
Cadmium and copper ions	PFM	50	0.01	50	25	6	720	15.23	-	30,285	[39]
			0.1					92.60			
			10					98.88			
			100					23.10			
		50				400	96.91				
Copper ions	GFMNPECABs	6	0.1	10	40	6	160	96.00	Langmuir Freundlich Temkin	120.10 - -	[40]
Cu(NO ₃) ₂	FGNs	30	1	50	20 ± 2	7	60	96.00	Langmuir Freundlich	103.22 -	[41]
Copper ions	Gly@MNP	10	0.0075	50	25	7	60	~ 98.00	Langmuir	~ 350	[42]
			0.2			6.5					

MCGON – magnetic chitosan/graphene oxide-based nanoparticles

CNT – carbon nanotubes

SDS- Fe₃O₄ NPs – sodium dodecyl sulphate-coated Fe₃O₄ nanoparticles

M - Fe₃O₄

MIA - Fe₃O₄ nanoparticles incorporated with hydroxyapatite nanorods

PFM – magnetic composite of polyacrylamide-modified Fe₃O₄/MnO₂

GFMNPECABs – glycine functionalized magnetic nanoparticle entrapped calcium alginate beads

FGNs – functionalized graphene nanosheets

Gly@MNP – glycine-functionalized maghemite nanoparticles

The limit of copper loading of industrial and municipal wastewater discharged into natural receptors is 0.1 mg/dm³ according to NTPA-001/2005 and the limit value of copper in wastewater discharged into the sewerage of localities is 0.2 mg/dm³ according to NTPA 002/2005.

The purpose of this study is to use Fe₃O₄ and his corresponding hybrid Fe₃O₄ –PVP as adsorbent nanomaterials for copper ions removal from wastewater. Some influential parameters for the wastewater treatment process of copper ions such as contact time, nanomaterials dose and pH value were investigated.

2. Materials and methods

Ferric chloride (FeCl₃ · 6H₂O), copper chloride (FeCl₂ · 6H₂O), sodium alginate (ANa) and polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH) were supplied from Sigma Aldrich and were used as received.

The preparation of magnetite nanomaterial tested in the wastewater process was done by precipitation method. The precipitation was accomplished using 0.7 mol L^{-1} aqueous solution of sodium hydroxide and the reaction pH was 12. The molar ratio $\text{Fe}^{2+} : \text{Fe}^{3+} : \text{ANa} : \text{PVP}$ unit was 1:2:5:5. The precipitate was separated by centrifugation and washed several times with water. Finally, Fe_3O_4 powder was obtained by precursor calcination at 400°C for 2 h.

The hybrid (Fe_3O_4 -PVP) was obtained by dispersing an amount of Fe_3O_4 powder in 40% solution of PVP. The Fe_3O_4 -PVP powder was separated by centrifugation and dried at room temperature.

The X-ray diffraction (XRD) analysis was obtained using a X'PERT PRO MPD with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$), the transmission electron microscopy (TEM) investigation was done on FEI Tecnai TMG²F30 S-TWIN with EDAX energy dispersive X-ray spectrometer and the results of the wastewater treatment process were determined with the PhotoLab S12 photometer.

Adsorption experiments were done using 100 mL of the synthetic wastewater having different concentrations of copper ions, at different pH values and using the two magnetic nanomaterials (Fe_3O_4 and a Fe_3O_4 -PVP). For experiments were used three concentrations of Cu^{2+} ions in water of 0.7, 1 and 1.2 mg/L concentration and 0.2g of adsorbent as in Figure 1. The pH was settled at 4.8 and 11.5.

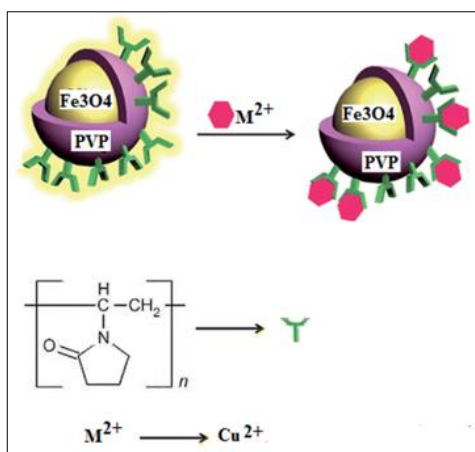


Figure 1. The representation of the wastewater treatment experiment

The system containing copper wastewater solutions and nanomaterials used as adsorbent were homogenized using a ultrasonic bath. All the experiments were done at room temperature. All concentrations were measured at PhotoLab S12. Yields were calculated with the formula (1).

$$\% \text{ Yield} = \frac{c_i - c_f}{c_i} * 100 \quad (1)$$

where:

c_i - the initial concentration (mg/L) of Cu^{2+} ;

c_f - the final concentration (mg/L) of Cu^{2+} .

The experimental results were determined in accordance with ISO 8466-1 and DIN 38402 A51 (10-mm cell) with a measuring range of 0.10-6.00 mg/L Cu^{2+} .

3. Results and discussions

3.1. X-ray diffraction

The nanopowder and corresponding hybrid obtained from synthesis were analyzed by XRD. The XRD pattern of oxide powder has proved the formation of single phase compound with inverse spinel structure and cubic symmetry for Fe_3O_4 (Figure 2a). The average crystallite size was 14 nm.

The XRD pattern of the hybrid material sample showed that the crystalline structure of the oxide nanoparticles is preserved after the coating procedure (Figure 2b).

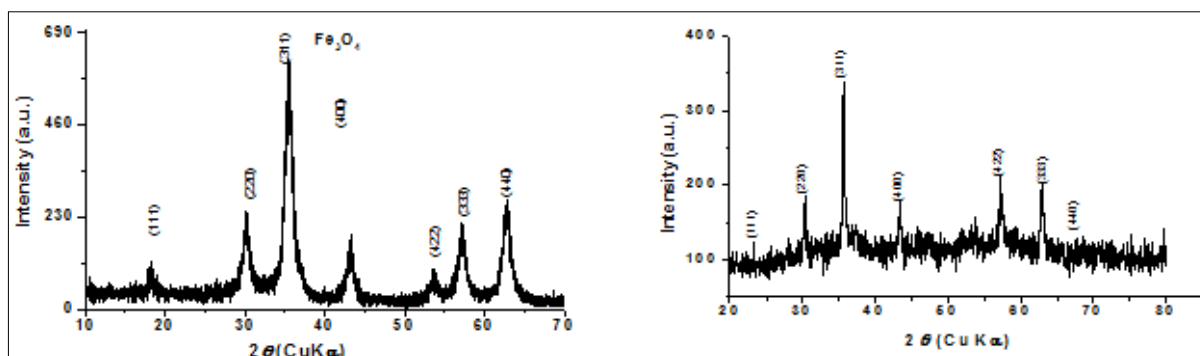


Figure 2. XRD patterns of: (a) Fe_3O_4 powder and (b) Fe_3O_4 -PVP hybrid

3.2. FT-IR spectroscopy

The FT-IR spectrum of the Fe_3O_4 - PVP hybrid and PVP polymer are displayed in Figure 3. By comparing the FT-IR spectra of Fe_3O_4 - PVP (Figure 3a) and PVP polymer (Figure 3b) were found the following: a) the peaks found at 2958 cm^{-1} and 2945 cm^{-1} are due to the asymmetric stretching vibration of CH_2 group of PVP from the pyrrolidone group; b) the symmetric CH_2 stretching vibration is placed at 2894 cm^{-1} and 2885 cm^{-1} ; c) the peaks placed at 1659 cm^{-1} and 1652 cm^{-1} correspond to stretching vibration of $\text{C}=\text{O}$ in the pyrrolidone group; d) the bands placed at 1429 cm^{-1} in both spectra correspond to the CH deformation modes from the CH_2 group [43,44]. In Figure 3a the band at around 1288 cm^{-1} is owing to $\text{C}-\text{N}$ bending vibration from the pyrrolidone structure of Fe_3O_4 -PVP while in PVP spectrum is placed at 1285 cm^{-1} [43].

The FTIR spectrum of Fe_3O_4 -PVP show two main iron-oxygen bands, the highest vibration one, in $600\text{-}550\text{ cm}^{-1}$ range, which is assigned to intrinsic stretching vibrations of the iron from the tetrahedral sites and the lowest vibration band placed in $450\text{-}400\text{ cm}^{-1}$ range corresponding to stretching vibrations of the iron from the octahedral sites (Figure 3a) [45].

As suggested by previously published data a shift of the $\text{C}=\text{O}$ group in hybrid spectrum in comparison with that of PVP spectrum can be attributed to the change of p - π conjugation associated with the amide group arising from the dissociation of PVP chains due to the interaction with the metals ions from the ferrite nanomaterial (Figure 3a) [43,45].

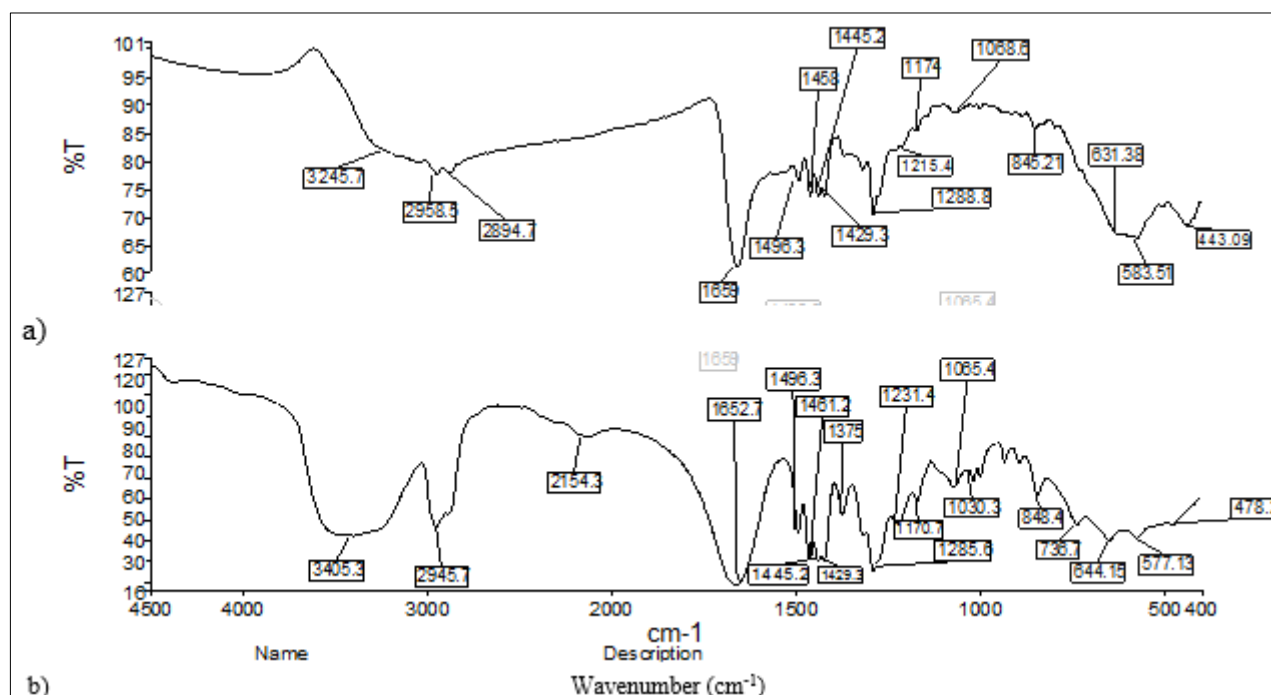


Figure 3. The spectra of: a) Fe_3O_4 -PVP and b) PVP polymer

3.3. TEM analysis

The morphology of the obtained hybrid material was investigated by TEM. The Fe₃O₄-PVP hybrid material exhibit a narrow size distribution, the mean particles size being 12 nm, respectively (Figure 4).

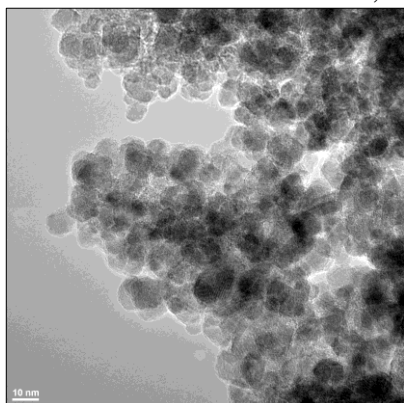


Figure 4. TEM image of Fe₃O₄-PVP hybrid material

3.4. Copper ions removal using Fe₃O₄ and Fe₃O₄-PVP nanomaterials

The results obtained for testing magnetite material for copper ions removal from the synthetic wastewater are presented in Table 2 and 3. The highest treatment efficiency was obtained at pH of 8 and 11.5 of wastewater for all three concentrations of copper ions.

Table 2. Variation of concentrations of Cu (II) measured in time, for different initial concentration of Cu (II) the presence of Fe₃O₄ nanomaterial

Initial Cu ²⁺ concentration (mg/L)	Wastewater solution pH	Concentration of Cu ²⁺ (mg/L), t=1140 min	Concentration of Cu ²⁺ (mg/L), t=1440 min	Concentration of Cu ²⁺ (mg/L), t=2520 min
0.70	4	0.48	0.63	0.45
0.70	8	0.14	0.02	0.02
0.70	11.5	0.02	0.02	0.02
1.00	4	1.05	0.87	0.90
1.00	8	0.03	0.03	0.03
1.00	11.5	0.04	0.03	0.03
1.20	4	1.27	1.22	1.11
1.20	8	0.04	0.04	0.04
1.20	11.5	0.04	0.04	0.04

The pH value of wastewater is very important for pollutant-adsorbent system. We made tests on different pH values (4, 8 and 11.5). We observed that at the pH 4, the pollutant is adsorbed, then desorbed (Table 2) and the yield does not increase more than 35% (Table 3). For the other two cases (pH 8 and 11.5) the yield of adsorption got up to 97.14% in less than 24h (Figure 5, 6).

Table 3. Variation of wastewater treatment yields for different copper ions concentrations measured in time, in the presence of Fe₃O₄ nanomaterial

Initial Cu ²⁺ concentration (mg/L)	pH	Wastewater treatment yield after 1140 min (%)	Wastewater treatment yield after 1440 min (%)	Wastewater treatment yield after 2520 min (%)
0.70	4	31.43	10.00	35.71
0.70	8	80.00	97.14	97.14
0.70	11.5	97.14	97.14	97.14
1.00	4	0.00	13.00	10.00
1.00	8	97.00	97.00	97.00
1.00	11.5	96.00	97.00	97.00
1.20	4	0.00	0.00	7.50
1.20	8	96.67	96.67	96.67
1.20	11.5	96.67	96.67	96.67

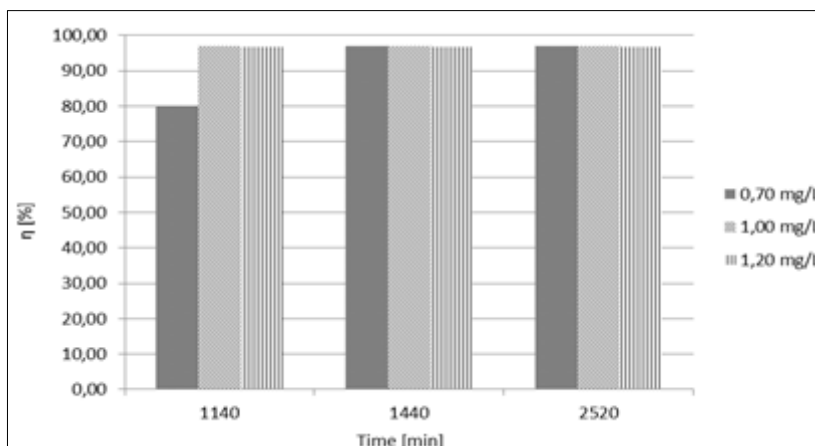


Figure 5. Variation of wastewater treatment yield in time, at pH 8, in the presence of Fe_3O_4 nanomaterial

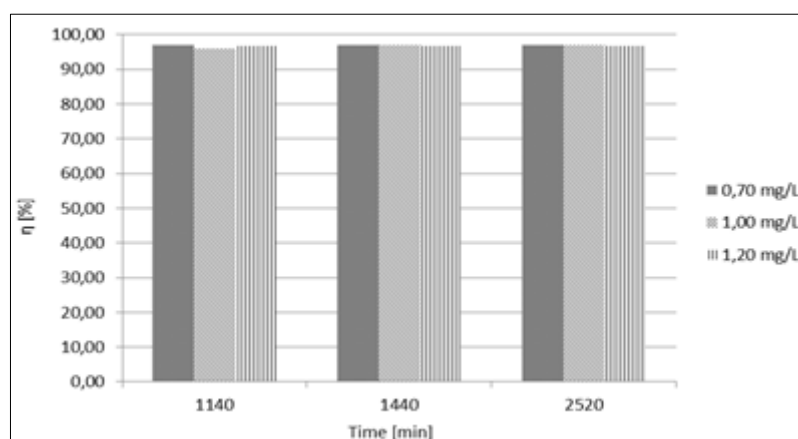


Figure 6. Variation of wastewater treatment yield in time, at pH 11.5, in the presence of Fe_3O_4 adsorbent

The removal of copper ions present in wastewater in different concentrations (0.70; 1.00 and 1.20 mg/L respectively) is represented in Figures 5 and 6. Using Fe_3O_4 as an adsorbent nanomaterial for the removal of copper ions from wastewater with pH 8 (Figure 5) it was observed that the treatment efficiencies reached 97.14; 97.00 and 96.67% respectively in case of the three studied Cu^{2+} concentrations removal. In case of wastewater with pH 11.5 (Figure 6), the same values of treatment efficiencies were obtained as in the case of pH 8 in order to remove 0.70; 1.00 and 1.20 mg/L Cu^{2+} , respectively, except that, in the case of the initial concentration of copper ions 0.70 mg/L, it is observed that the process was faster at pH 11.5.

The pH value also had an important role for the copper ions removal using Fe_3O_4 -PVP hybrid and it is observed in Table 4. The acidic environment (pH 4) has a negative impact on the adsorption process. The yield is only 1.45% after 1200 min. When the pH values were 8 and 11.5, we noticed changes of the wastewater treatment yield to 56.92% for pH 8 (Figure 7) and 70.00% for pH 11.5 after 48 h (Figure 8).

Table 4. The experimental results of copper ions removal from wastewater using Fe₃O₄ -PVP hybrid material

Time (min)	pH	Initial Cu ²⁺ conc. (mg/L)	Read Cu ²⁺ conc. (mg/L)	Yield (%)	pH	Initial conc. (mg/L)	Read conc. (mg/L)	Yield (%)	pH	Initial conc. (mg/L)	Read Cu ²⁺ conc. (mg/L)	Yield (%)
120	8	0.65	0.55	15.38	8	1.05	0.90	14.29	8	1.20	1.07	10.83
1200			0.49	24.62			0.85	19.05			1.03	14.17
2880			0.28	56.92			0.83	20.95			0.96	20.00
120	11.5	0.70	0.48	31.43	11.5	0.96	0.91	5.21	11.5	1.20	1.10	8.33
1200			0.43	38.57			0.88	8.33			1.06	11.67
2880			0.21	70.00			0.75	21.88			0.97	19.17

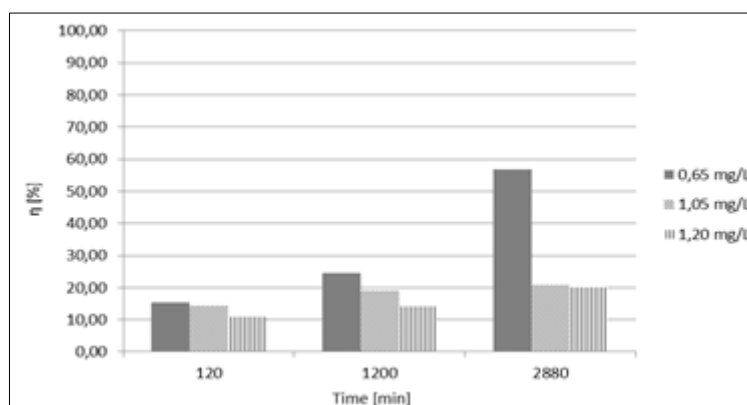


Figure 7. Wastewater treatment variation of copper ions removal at pH 8 using Fe₃O₄-PVP hybrid material as adsorbent

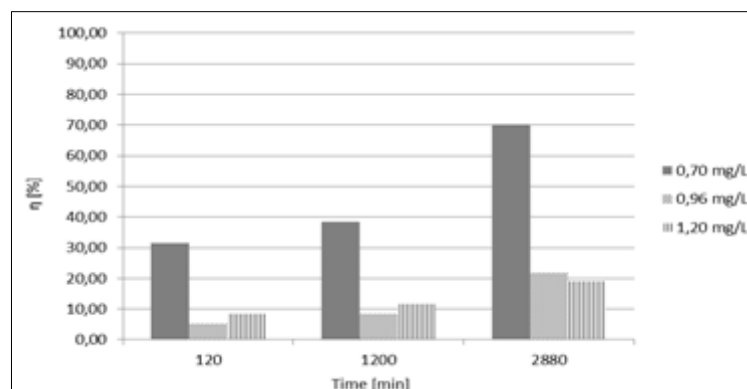


Figure 8. Wastewater treatment variation of copper ions removal at pH 11,5 using Fe₃O₄-PVP hybrid material as adsorbent

Langmuir isotherm model was used for characterization of the copper ions adsorption onto Fe₃O₄ and Fe₃O₄ - PVP nanomaterials. Langmuir isotherm is presented as Eq. (2).

$$q_e = \frac{Q^0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

where:

q_e represent the quantity of metal adsorbed/gram of adsorbent at equilibrium (mg/g);

Q⁰ represent maximum monolayer coverage capacity (mg/g);

K_L represent the Langmuir isotherm constant (L/mg);

C_e represent the equilibrium concentration of adsorbate (mg/L).

The equilibrium parameter R_L is calculated with the following equation:

$$R_L = \frac{1}{1+(1+K_L*C_0)} \quad (3)$$

where:

K_L represent the Langmuir constant, R_L value indicates that adsorption is unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

C_0 represent initial concentration

The adsorption process was also characterized by Freundlich isotherm model.

Freundlich adsorption isotherm is presented as Eq. (4)

$$q_e = K_F * C_e^{1/n} \quad (4)$$

where:

q_e represent the quantity of metal adsorbed/gram of adsorbent at equilibrium (mg/g);

K_F represent the Freundlich isotherm constant (mg/g);

C_e represent the equilibrium concentration of adsorbate (mg/L);

n represent the adsorption intensity;

The scientific literature describe the characteristics of adsorption being favorable if R_L is greater than zero but less than one [46,47]. Table 5 shows the adsorption isotherms constants for Fe_3O_4 and Fe_3O_4 - PVP used as adsorbents. Constants were calculated using the plots below (Figures 9-14).

Table 5. Langmuir and Freundlich adsorption isotherm constants [43, 44]

Adsorbent	Langmuir isotherm			Freundlich isotherm			
	K_L (L/mg)	R_L	R^2	$1/n$	n	K_F (mg/g)	R^2
Fe_3O_4	24.54	0.05	0.99	0.77	1.28	82.82	0.99
Fe_3O_4 -PVP	0.35	0.44	0.92	-0.11	-8.94	7.63	0.91

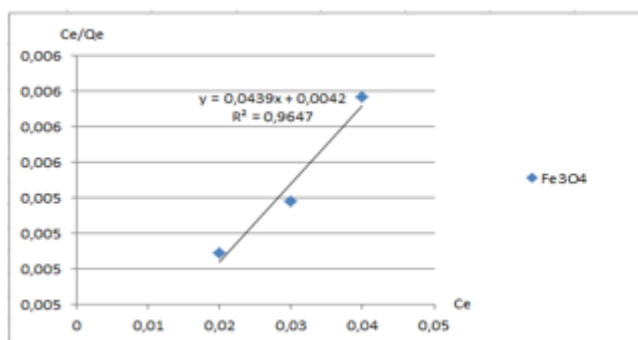


Figure 9. C_e vs C_e/Q_e plot for Fe_3O_4

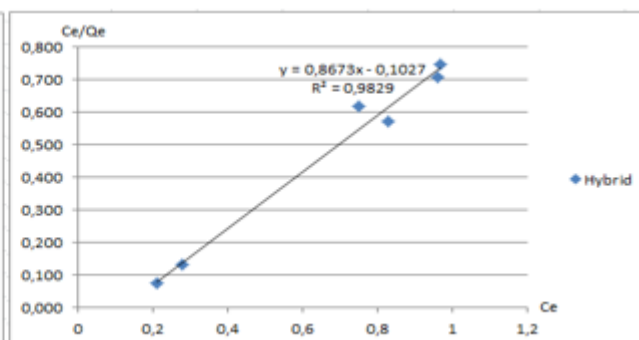


Figure 10. C_e vs C_e/Q_e plot for Fe_3O_4 -PVP hybrid

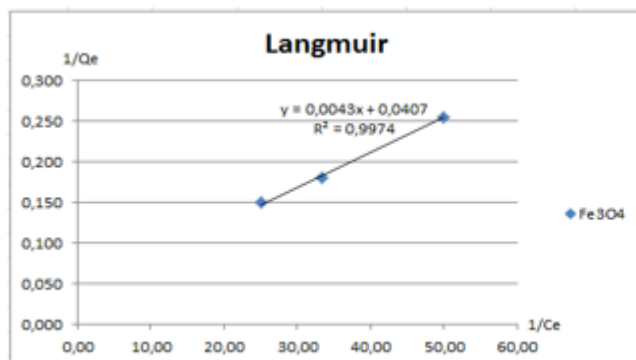


Figure 11. Langmuir plot for Fe_3O_4

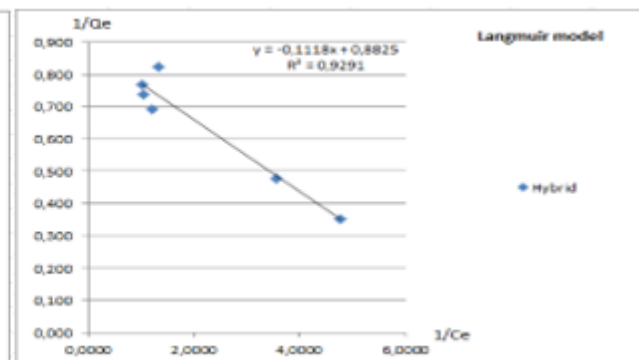


Figure 12. Langmuir plot for Fe_3O_4 -PVP hybrid

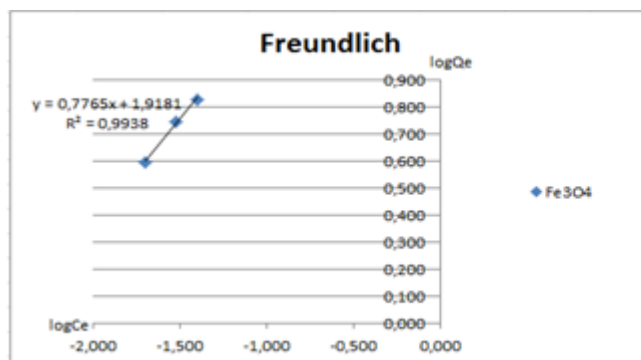


Figure 13. Freundlich plot for Fe_3O_4

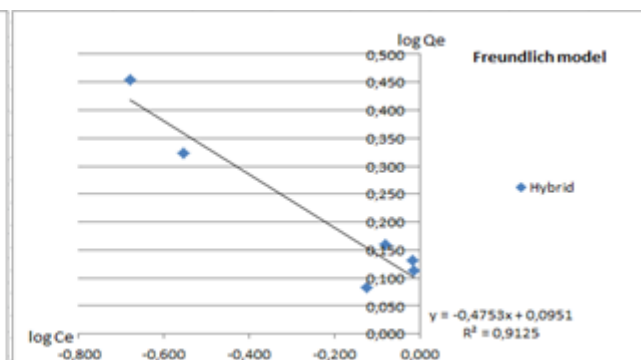


Figure 14. Freundlich plot for Fe_3O_4 -PVP hybrid

Two widely used models, represented by Langmuir and Freundlich, were used to model the adsorption at equilibrium. Adsorption isotherms were chosen to show whether the adsorption process takes place in a single layer or in a multilayer. The most appropriate model was chosen based on the correlation coefficient (R^2) determined from the equations of the linearized forms of the two models made after using the two adsorbent materials in the treatment process, Fe_3O_4 and Fe_3O_4 - PVP hybrid (Figures 9, 10).

In Table 5 it is observed that the R_L values are between 0 and 1 both in the case of using the Fe_3O_4 nanomaterial and in the case of the hybrid material Fe_3O_4 - PVP, this means that the adsorption went favorably in the studied experimental conditions. The Langmuir isotherms for the two materials used are shown in Figures 11 and 12. From these plots it is observed that the correlation coefficients R^2 are 0.9974 and 0.9291, respectively. Comparing with the values of the correlation coefficients R^2 resulting from the plots presented in Figures 13 and 14 which represent the Freundlich isotherms for each material (R^2 : 0.9938 respectively 0.9125 for the use of Fe_3O_4 and Fe_3O_4 - PVP as adsorbent materials) we can see that the R^2 values in the case of Langmuir isotherms are higher than in the case of Freundlich isotherms, which means that the adsorption process of copper ions from wastewater adapts better to the Langmuir model. This model considers that the surface of the adsorbent is homogeneous and the adsorption is monolayer.

4. Conclusions

The need to find more effective ways of water depollution compare with conventional methods justifies the intense researches that are made in this domain.

In this regard, the study that was made was based on the use of Fe_3O_4 and Fe_3O_4 -PVP nanomaterials in order to remove copper ions from wastewater.

Magnetite nanomaterial tested in this research demonstrated high efficiency on removing copper ions from wastewater at pH 8 and 11.5. The wastewater treatment yields obtained at 8 and 11.5 pH values using Fe_3O_4 as adsorbent were 97% and the maximum percent at pH 4 was 35.71%, the nanomaterial being instable in wastewater. In case of Fe_3O_4 -PVP adsorption at pH 4 the obtained wastewater treatment yield was of only 1.45%, reaching at higher values of 70% at 11.5 pH of wastewater.

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