Application of a newly developed super paramagnetic magnetite Fe$_3$O$_4$ nanowafers nanoparticle in the removal of heavy metals from industrial wastewater submerging in the River Nile

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ABSTRACT

This study describes a super paramagnetic magnetite Fe$_3$O$_4$ nanowafers adsorbent, using for the completely removal of some heavy metals (Fe^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Pb^{+2}, and Cd^{+2}) from three discharge industrial wastewater samples which consider some pollution sources that submerging in the River Nile. For adsorbent the effect of various parameters such as the initial concentration (100 – 300 ppm), the mass of adsorbent (0.5 – 3 gm), the contact time (1-3 ml/min) and the solution pH (2-10) were determined of Cd metal ions by breakthrough determination. The maximum removal efficiency was found to be 100% in 1gm of SPMMFe$_3$O$_4$ NWNPs per 4572 ml at 25 mg/l (10 mg/l Fe^{+2}, 4 mg/l Mn^{+2}, 3 mg/l Ni^{+2}, 2 mg/l Cu^{+2}, 2 mg/l Zn^{+2}, 2 mg/l Pb^{+2}, and 2 mg/l Cd^{+2}) of industrial discharge wastewaters were collected from the El-Nasr Company for Coks, Chemicals, Egyptian Iron and Steel factory and Egyptian Sugar & Integrated Industries Company at pH= 7.However, the AMBERLITE IR 120 H resin obtains result 2914.65 ml at the same conditions, this means that the efficiency of super paramagnetic magnetite Fe$_3$O$_4$ nanoparticles on a resin (AMBERLITE IR 120 H) supportis greater with 36.25 %. The next step in this work will consist of testing this non-conventional adsorbent on a pilot industrial scale.

Keywords: Nanowafers, magnetite, heavy metals, wastewater, River Nile

INTRODUCTION

The Nile is the longest river in the world, at 4,180 miles. It is an extremely important source of water in Africa, Egypt in particular. Egypt is about 97% desert, and thus, the Nile's water is essential for its survival. The river is an important source of freshwater for both household and agricultural use. It is also a power source from the hydroelectric plant at Aswan, and a mean of transportation for people and trade. Only a very small percentage of Egypt is habitable; about 5%. Most of the inland population is located along the Nile (Goher *et al*., 2014; Goher and Toufeek, 2014; Ali *et al*., 2011). Industrial wastewaters are considered among the major sources of environmental pollution, endangering public health through direct use as well as feeding fish that live in the polluted streams. It is estimated that more than 400 factories continue to discharge more than 2.5 million m^3/day of untreated effluent into Egypt's waters (Abdel-Dayem, 1994; Myllyla, 1995). Industrial complexes have now become foci of environmental pollution. The emphasis now is thus on removal of toxic polluting chemicals (WHO 2011). The control of these toxic priority pollutants is to be based on the application of the best available technology economically achievable. Metals of particular concern in treatment of industrial wastewaters include

Fe^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Pb^{+2}, and Cd^{+2} which are toxic to living organisms at fairly low concentrations and tend to either biologically magnify or accumulate in plant and animal systems. Thus, the disposal of heavy metals bearing wastes into water bodies or on land is of great concern due to their adverse effects. The metal processing, plating and metal finishing industries, e -wastes etc are sources of such metal wastes. In general, to be removed from wastewater, the metals must be precipitated or otherwise attached to an insoluble form through nanoparticles adsorbents (Kurniawan, 2006). Nanotechnology for water remediation will play a crucial role in water security and consequently the food security of the world (Smith, 2006). Could summarize the applications of nanotechnology in the cleanup of contaminated water: 1. Nanoscale filtration techniques, 2. The adsorption of pollutants on nanoparticles and 3. The breakdown of contaminants by nanoparticle catalysts. Researchis underway to use advance nanotechnology in water purification for safe water. Nanotechnology is an emerging science with wide applications in the remediation of environmental pollutants. In recent years, a great deal of attention has been focused on the synthesis and application of nanostructure materials as adsorbents to remove toxic and harmful substances from industrial wastewater. Resurgence to synthesize and manipulate nanoparticles finds use in improving water quality in the environment. Reactive nanoparticles have a significant amount of surfaces and thus attract much interest to be applied as adsorbents in comparison to macromolecules. Various nanoparticles have been applied in removing heavy metals from industrial wastewater submerging in the River Nile. Metal oxides play a significant role in many fields of nanotechnology including super paramagnetic properties (Bao *et al*., 2001; Gao *et al*., 2001; Liang *et al*., 2004; Seto *et al*., 2005; Tian *et al*., 2005; Jeon *et al*., 2005, 2006). Iron-based magnetic nanomaterials have distinguished themselves by their unique properties, such as larger surface area-volume ratio, diminished consumption of chemicals, and no secondary pollutant. However, with another special property of this kind magnetic materials are realized and utilized in the context of environmental remediation. More and more magnetic separation has been combined with adsorption for the removal of heavy metals from contaminated water at laboratory scales (Mayo, 2007; Chen, 2005; Yavuz, 2006). Especially in industries, magnetic separation is desirable because it can overcome many drawbacks occurring in the membrane filtration, centrifugation, or gravitational separation and is easy to achieve a given level of separation just via external magnetic field (Neuberger *et al*., 2005;Teja, Koh, 2009).In addition, as the adsorption is sometimes reversible and adsorbent can be regenerated by suitable desorption process (Ai, 2008).Newly developed super paramagnetic magnetite Fe_3O_4 nanowafers adsorbent support on AMBERLITE IR I20 H Resinis synthesized with nanoparticle size ranging and the shape, porous and size were confirmed using SEM, XRD and FTIR. The magnetization property of super paramagnetic magnetite Fe_3O_4 (AMBERLITE IR 120 H) was confirmed using MSB to give the effective magnetic moment (Emara *et al*., 2016). The main objective of this study was to remove metals from industrial wastewater of El-Nasr Company for Coks & Chemicals, Egyptian Iron and Steel factory in El-Tebbin – Helwan city in Giza governorate and the Egyptian Sugar & Integrated Industries Company at north in El-Hawamdya city in Giza governorate,that discharged into the River Nile using Fe_3O_4nanowafers adsorbents. A detailed investigation on the initial concentration (100-300 ppm), the mass of adsorbent (0.5 – 3 gm), the contact time (1-3 ml/min) and the solution pH (2-10) on Cd metal ions removal from a solution was carried out.

MATERIALS AND METHODS

1- Sampling

Industrial discharge wastewaters were collected from the El-Nasr Company for Coks & Chemicals, Egyptian Iron and Steel factory in El-Tebbin – Helwan city in Giza governorate and the Egyptian Sugar & Integrated Industries Companyat north in El-Hawamdya city in Giza governorate (Fig. 1).The selected sampling stations depended mainly on the points discharged into the River Nile water stream of the three companies, the analytical characteristics of three samples taken on seasonally and the period of investigation starting from February 2013 to February 2014 are shown in Table 1. The chemicals and solutions used in this study are of the highest available purity from Sigma–Aldrich analytical grade. The stock solution was further diluted to the required experimental concentration following standard method procedures (APHA, 2005). The effluents are average samples characteristic of that day's activity.

Fig.(1):Location Map of studied area

Table 1 : Heavy metals concentrations of three industrial discharge wastewaters				
Parameters	Law No. 44 /2000 for Allowable range for industrial wastewater	El-Nasr Co. for Coks& Chemicals	Egyptian Iron and Steel factory	Egyptian Sugar & Integrated Industries Co.
Fe mg/1	1.0	2.845	6.175	2.180
Mn mg/1	0.5	0.960	2.012	0.706
Ni mg/1	0.1	0.22	0.49	0.11
Cu mg/1	1.0	0.89	1.04	0.60
Zn mg/1	1.0	0.548	0.795	0.11
Pb mg/1	0.05	0.055	0.081	0.032
Cd mg/1	0.01	0.048	0.181	0.099

2- Materials

A stock solutions containing CuCl$_2$·2H$_2$O, ZnCl$_2$, Cd (NO$_3$)$_2$·4H$_2$O, Pb (NO$_3$)$_2$, FeCl$_3$, MnCl$_2$ and NiCl$_2$ were used as sources of Cu^{+2}, Zn^{+2}, Cd^{+2} , Pb^{+2}, Fe^{+2}, Mn^{+2} and Ni^{+2} respectively, was prepared by dissolving a known quantities of materials in deionized water. The residual metals in solution were analyzed, using GBC atomic absorption reader (Model Savant AA AAS with Flame and GF 5000 Graphite Furnace). The pH adjustments were done using 1.0 MNaOH and 1.0 MHCl. By used Cd^{+2} metal ions we determined the influence of different experimental parameters and conditions on the removal process, namely the initial concentration of Cd^{+2}, contact time, adsorbent mass and finally pH of the contact solution was coveredby breakthrough determination.

3- Characterization Technique

Fixed-bed column runs were carried out using glass columns a small (in - out) constant flow water pump connected to a power supply of 9 volts. Then water goes into Fixed-bed column runs were carried out using the constructed system Figures (2&3) which consists of a glass column (11 mm in diameter) and The flow-rate for all runs was adjusted to be 2 ml/min and it remained practically constant during the whole experimental time. A 5 liter feed solution containing a single pollutant or mixture of pollutants under investigation was prepared from grade reagents and deionized water. A 5 ml aliquot from the effluent was analyzed regularly by the GBC

atomic absorption reader until the breakthrough is reached. The calculations were based on bed volumes and number of bed volumes. This methodology will help determine the adsorbent capacity of removing the pollutants (Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2}) under investigation depending on how much mls of water passed through the $SPMMFe_3O_4$ NWNPs bed to calculate the bed volume, the following equation(1) was used:

$$B.V = \pi r^2 h \qquad (1)$$

Where B.V = Bed volume, π = 3.14, r = radius of column = 5.5mm and h =height of exchanger in the column. In addition, the number of bed volumes can be calculated as follows equation (2):

$$No. of\ B.V = (Volum\ of\ water\ passed\ x\ Flow\ rate)/(B.V) \qquad (2)$$

All experimental data are plotted in Figures between the concentration ratio (C/C_0) of the pollutant under investigation against No. of B.V or Time (min)as X-coordinate, where C_0 =is the starting concentration before passing through bed and C is its concentration after passing through bed at varies intervals are shown in Figures 2&3. The break through value refers to the total number of bed volumes passed through the $SPMMFe_3O_4$ NWNPs exhausted to reach the half value of the starting pollutant concentration under investigation. This can be easily determined from plotting the concentration ratio (C/Co) of pollutant against bed volume, and then evaluating the bed volume corresponding to 0.5 (Miyoung, 2007).
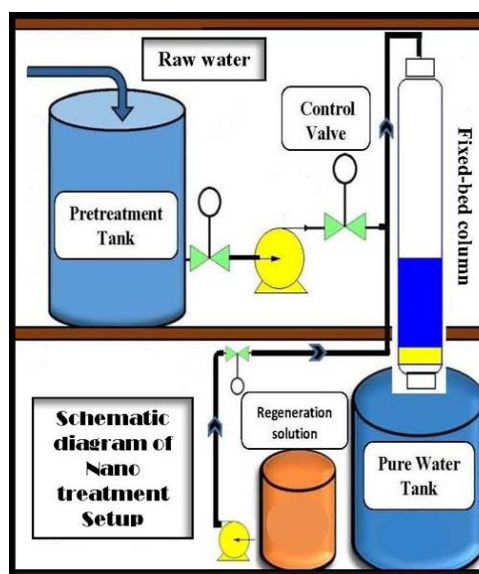

Fig. 2: Fixed-bed column set-up.

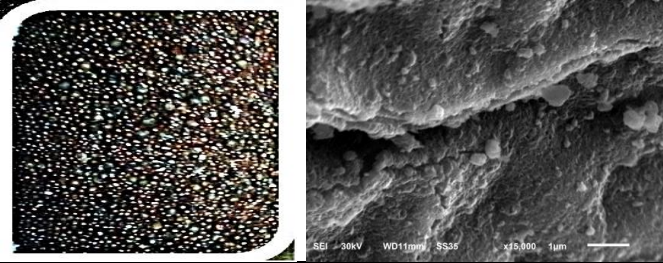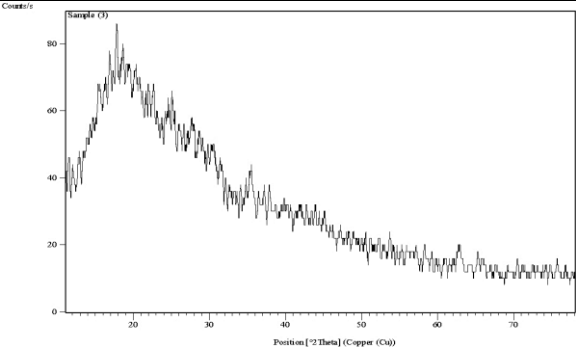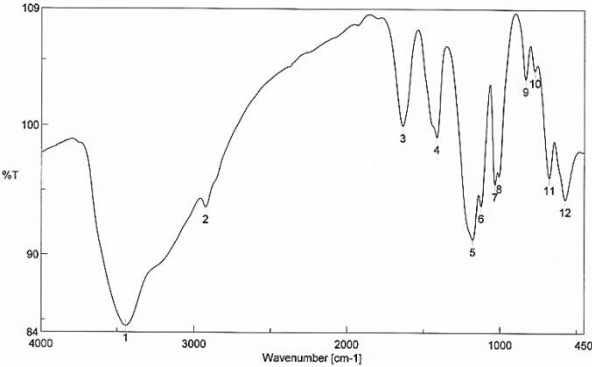Fig. 3: A schematic diagram of Fixed-bed column set-up

Upon completion of the given contact time (in minutes) between adsorbent and adsorbate, the solution was filtered. The removal percentage (R %) was calculated using the following equation (3): $R\ \% = \frac{(C_0 - C_e)}{C_0} X\ 100 \qquad (3)$

Where C_0 and C_e are concentration (mg/l) of metal ions in the initial and equilibrium solutions, respectively.

Characterization of adsorbent

The characteristics of super paramagnetic magnetite Fe_3O_4 nanowafers nanoparticles adsorbent are shown in Tables 2 (Emara *et al.*, 2016).

Tables 2: The characteristics of SPMMFe$_3$O$_4$ NWNPs.

No.	Characterization	Super paramagnetic magnetite Fe$_3$O$_4$Nanowafersnanoparticlesadsorbent	
1	Technique of synthesis	Simple	
2	Yield	High/scalable	
3	SEM (Shape control)		Excellent
4	XRD		Specify the presence of Fe$_3$O$_4$
5	Size Distribution	Very narrow	
6	Size Control average (nm)	2.9-33.2	
7	FTIR		Fe$_3$O$_4$ is represents four absorption bands
8	Magnetization property of Super paramagnetic magnetite Fe$_3$O$_4$	μ_{eff} = 31.31 emu.mol^{-1}	

RESULTS AND DISCUSSION

The application of Super paramagnetic magnetite Fe$_3$O$_4$nanowafers on AMBERLITE IR 120 H resin support to removal of Cadmium ions (Cd^{+2}) with study the effect of various parameters such as the initial concentration (100 – 300 ppm), the mass of adsorbent (0.5 – 3 gm), the contact time (1-3 ml/min) and the solution pH (2-10) were determined by breakthrough determination. The aim is to study application of SPMM Fe$_3$O$_4$ NWNPs for removal of emerging pollutants from industrial wastewater, where Can super paramagneticmagnetite Fe$_3$O$_4$ nanoparticles be used for the selective removal of heavy metals pollutants Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2} .

Factors affecting the Cd(II) adsorption onto nanomaterial

Several factors can be affected to the adsorption process, such as initial contaminant concentration solution, Flow rate, adsorbent dosage and pH value, and presence of other co-existing ions. In addition to these factors, the nanoparticle size and shape also affect to the adsorption performance (Qiu, et al., 2009) higher adsorption capacities can be obtained by optimizing above parameters. To determine these factors we used of SPMM Fe_3O_4 NWNSs for aqueous Cd(II) removal with used breakthrough determination. The effect of some of these factors is discussed below.

Effect of initial contaminant concentration

The effect of initial Cd(II) ions concentration at different concentrations (100, 150, 200 & 300ppm) were prepared from a pure reagent $Cd(NO_3)_2 \cdot 4H_2O$. Only 1.00 gram of SPMM Fe_3O_4 NWNSs was used and the flow rate was adjusted to be 2ml/min. An influent solution with no pH adjustment (pH =6.83 at Temp. = $25^{\circ}C \pm 1$) passed through a fixed bed column containing SPMM Fe_3O_4 NWNPs (see figs.2, 3). The experimental data obtained in Table 3.

Table 3: No. of B.V. for 100% removal and breakthroughs values for removal of different concentration of Cd(II) ions

No.	Concentration of Cd^{2+} (ppm)	No. of B.V. at 100% Removal values (ml)/Time (min:sec)	No. of B.V. at Breakthroughs values (ml)/Time (min:sec)
1	100	1504/571:00	2057/781:30
2	150	1199/455:30	1453/552:00
3	200	947/360:00	1217/462:30
4	300	608/231:00	703/267:00

Figure 4 shows the high efficiency of the SPMM Fe_3O_4 NWNPs clearly appear in the complete removal of Cd(II) Ions. We observed that No. of B.V. at 100% Removal values (ml) which record 1504 bed volumes in case of 100 ppm Cd (II), 1199 bed volumes in case 150 ppm Cd (II), and 947 bed volumes in case of 200 ppm Cd (II) and finally 608 bed volumes in case of 300 ppm Cd(II) ions confirming the high sorption capacity of the sorbent for each four target concentrations (Fig. 4).
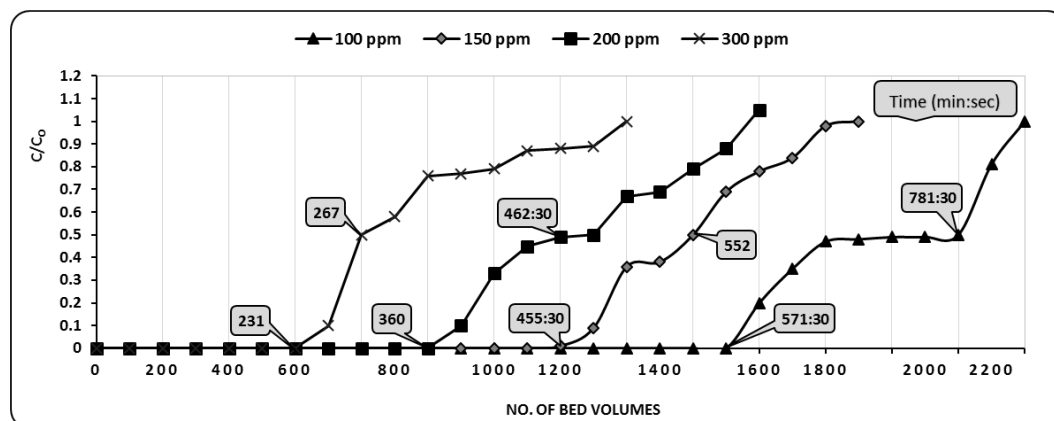

Fig. 4: Effect of initial Cd(II) concentration for removal of different concentration100, 150, 200 & 300ppm Cd(II) ions using SPMM Fe_3O_4 NWNPs each in a fixed bed column run.

In case of 100 ppm Cd(II), the breakthrough reached after 2057 bed volumes, while that in case of 150 ppm Cd(II) was reached after 1453 bed volumes, in case of 200 ppm Cd(II) was reached after 1217 bed volumes and that of 300 ppm Cd(II) after 703 bed volumes. This shows that the increasing of Cd(II) concentration increases the

rate of attaining breakthrough as it has expected, also from this observation it can predicted that SPMM Fe$_3$O$_4$ NWNPs can efficiently remove Cd(II) ions from low concentration Cd(II) bearing water streams. Effect of initial contaminant concentration is a main parameter, which can directly affect to the adsorption capacity of an adsorbent. This factor must be taking into consideration when comparing the adsorption capacities of different adsorbents. According to Adegoke, Amoo Adekola, the amount of Cd(II) ions adsorbed onto the SPMM Fe$_3$O$_4$ NWNPs having different morphologies, increased with increasing Cd(II) concentration. This may be due to the fact that, lack of available adsorbent sites at higher concentrations, and hence, the percentage adsorption of Cd(II) decreases (Srivastava, Sharma, 2013). It should be carefully noted that, the actual amount of Cd(II) adsorbed per unit mass of SPMM Fe$_3$O$_4$ NWNSs increased with the increase of initial concentration as the two terms "percentage of removal" and "actual amount of removal" are sometimes leading to confusions.

Flow Rate ml/min (Retention time):

This is a main factor has a great influence on the adsorption process and It is well known that the contact time. Investigation of changing contact time on the removal of Cd(II) ions was studied using only one concentration (200 ppm) from the previously studied concentrations. An influent solution with no pH adjustment (pH =6.83 at Temp. = 25°C ± 1) passed through a fixed bed column containing 1.00 gram of SPMM Fe$_3$O$_4$ NWNPs (see figs. 2, 3)at different rates (1 ml/min, 2 ml/min, and 3ml/min) and the data obtained were in Table 4.

Table 4: No. of B.V. for 100% removal and breakthroughs values for removal of 200 ppm of Cd(II) ions at different flow rates 1 ml/min, 2 ml/ml, & 3 ml/min using SPMM Fe$_3$O$_4$ NWNPs

No.	Flow Rate (ml/min)	No. of B.V. at 100% Removal values (ml)/Time (min:sec)	No. of B.V. at Breakthroughs values (ml)/Time (min:sec)
1	1	1003/1524:00	1241/1886:00
2	2	947/360:00	1217/462:30
3	3	636/107:20	681/115:00

From Figure 5 the following observations obtained, Firstly, changing of flow rate was found to be strongly affecting the attaining of breakthrough in such a way that when the contact time is reduced, the possibility of Cd ions adsorption is lowered. Consequently, when the flow rate was adjusted at 1 ml/min the No. of B.V.at 100% Removal value was 1003 and breakthrough was observed after 1241 bed volumes, the No. of B.V. at 100% Removal value was 947 and breakthrough was observed after 1217 bed volumes at 2ml/min and that at flow rate of 3 ml/min was observed after 636 bed volumes at 100% Removal value and breakthrough was observed after 681 bed volumes . Secondly, we can conclude the lower the flow rate the higher will be the number volumes obtained for the removal Cd(II) ions. Based on the above results the best breakthrough was observed with a flow rate of 1 ml/min and that the lowest one was observed in case of flow rate of 3 ml/min.
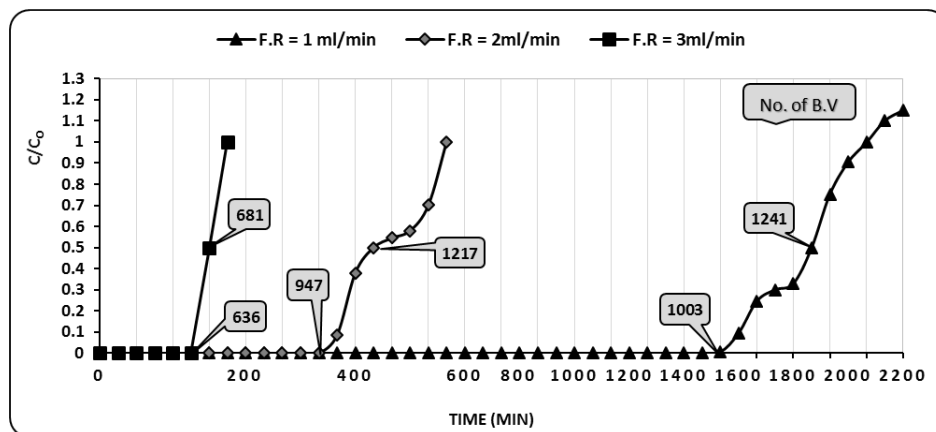
Fig. 5: Effect of Flow Ratefor removal of 200 ppm of Cd(II) ions at different flow rates 1 ml/min, 2 ml/ml, & 3 ml/min using SPMM Fe_3O_4 NWNPs.

Mass of adsorbent (SPMM Fe_3O_4 NWNPs)

Investigation of the effect the SPMM Fe_3O_4 NWNPs mass on the removal Cd(II) ions from water has been studied to get the optimum conditions for the removal process. For this purpose different masses of SPMM Fe_3O_4 NWNSs(0.5 gm, 1 gm, and 1.5 gm, 2 gm& 3gm) were applied for the removal of Cd(II) ions using solutions of the same concentration (200 ppm) and the flow rate was adjusted to be 2ml/min. An influent solution with no pH adjustment (pH =6.83 at Temp. = $25^oC \pm 1$) each in a fixed bed column run (Fig.6) and the data obtained were in Table 5.

Table 5: No. of B.V. for 100% removal and breakthroughs values for removal of 200 ppm of Cd(II) ions at different Masses of adsorbent (SPMM Fe_3O_4 NWNPs) 0.5 gm, 1 gm, and 1.5 gm, 2 gm& 3gm.

No.	Mass of adsorbent (SPMM Fe_3O_4 NWNPs) (gm)	No. of B.V. at 100% Removal values (ml)/Time (min:sec)	No. of B.V. at Breakthroughs values (ml)/Time (min:sec)
1	0.5	730/156:00	1041/222:30
2	1.0	947/360:00	1217/462:30
3	1.5	1017/604:30	1274/757:00
4	2.0	907/732:00	1183/955:00
5	3.0	704/836:30	1209/1436:30

Figure 6 depict the data obtained for different masses of SPMM Fe_3O_4 NWNPs. The following data has been recorded. Firstly, when solution with Cd(II) ions of (200 ppm) flow throughout a fixed bed column with SPMM Fe_3O_4 NWNSs weight of 0.5 gm the No. of B.V. at 100% Removal value was 730 and breakthrough was observed after 1041 bed volumes, the No. of B.V. at 100% Removal value was 947 and breakthrough was observed after 1217 bed volumes at 1.0 gm of SPMM Fe_3O_4 NWNSs and that weight of 1.5 gm was observed after 1017 bed volumes at 100% Removal value and breakthrough was observed after 1274 bed volumes. The weight of 2.0 gm of SPMM Fe_3O_4 NWNSs was observed after 907 bed volumes at 100% Removal value, breakthrough was observed after 1183 bed volumes, that weight of 3.0 gm was observed after 704 bed volumes at 100% Removal value, and breakthrough was observed after 1209 bed volumes. Secondly, From these observations we can say that the variation in mass of SPMM Fe_3O_4 NWNPs affect the removal of Cd(II) ions in such a way that as the mass of the SPMM Fe_3O_4 NWNSs

increase, the number of adsorption sites increase and consequently the removal of Cd(II) ions is improved. However, we observe that when the number of bed volumes taken in consider the process was found to become a height dependent in such a way that the increase in the mass was deleted by the effect of SPMM Fe$_3$O$_4$ NWNSs height. The percentage of contaminant removal increases with the increase of adsorbent dosage. This may be due to the availability of adsorption sites which adsorbate used attached. The determination of effect of adsorbent dosage gives an idea about the minimum amount of adsorbent need to be used for adsorption process. This value is useful in the viewpoint of cost.
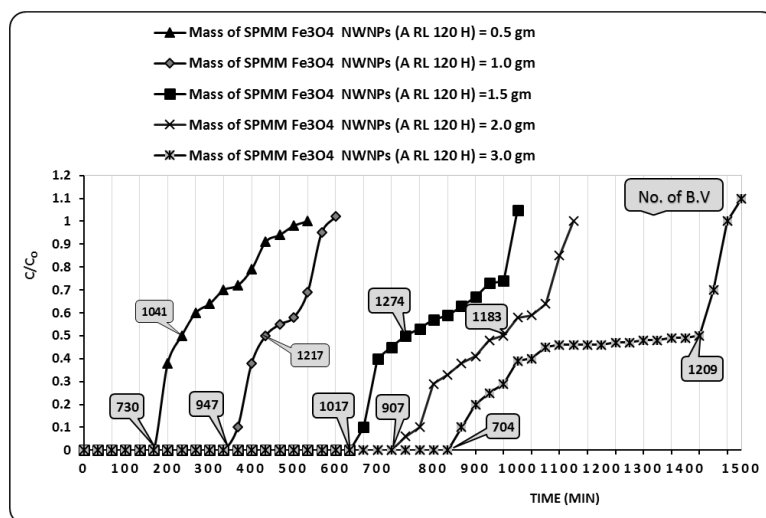

Fig. 6: Effect of Mass of adsorbentfor removal of 200 ppm of Cd(II) ions at different Masses of adsorbent (SPMM Fe$_3$O$_4$ NWNPs) 0.5 gm, 1 gm, and 1.5 gm, 2 gm& 3gm.

Effect of solution pH

The pH of the solution is an important parameter, which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surface charge of the adsorbent. Therefore investigating the effect of pH on the adsorption is essential in adsorption experiments. We studied the pH effect on the removal process of Cd(II) ions. Different influent solutions were prepared from a pure reagent Cd(NO$_3$)$_2$·4H$_2$O at pH = 2, 4, 6.83, 8 and pH = 10. However, the prepared solutions flew throughout a fixed bed column using 1gm of SPMM Fe$_3$O$_4$ NWNPs and the flow rate was adjusted to be 2ml/min. An influent solution with no temperature adjustment (Temp. = 25°C $\pm$ 1) each in a single state and the following results were obtained: Firstly, when a pH adjusted to be = 2.0 the No. of B.V. at 100% Removal value was 434 and breakthrough was observed after 487 bed volumes, the No. of B.V. at 100% Removal value was 601 and breakthrough was observed after 751 bed volumes at pH = 4 and that pH = 6.83 was observed after 947 bed volumes at 100% Removal value and breakthrough was observed after 1217 bed volumes. when pH = 8 was observed after 1014 bed volumes at 100% Removal value, breakthrough was observed after 1284 bed volumes, that pH = 4 was observed after 713 bed volumes at 100% Removal value, and breakthrough was observed after 983 bed volumes. The results are presented in Table 6 and Figure7.

Table 6: No. of B.V. for 100% removal and breakthroughs values for removal of 200 ppm of Cd(II) ions at different pH = 2, 4, 6.83, 8 and pH = 10.

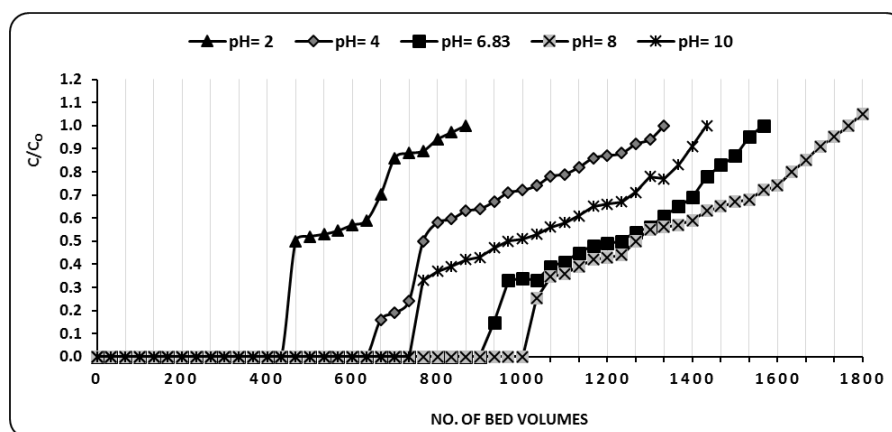| No.	pH Value	No. of B.V. at 100% Removal values (ml)/Time (min:sec)	No. of B.V. at Breakthroughs values (ml)/Time (min:sec)
1	2	434/165:00	487/185:00
2	4	601/228:30	751/286:30
3	6.83	947/360:00	1217/462:30
4	8	1014/385:30	1284/488:00
5	10	713/271:00	983/373:30

Fig. 7: Effect of pH valefor removal of 200 ppm of Cd(II) ions at different pH = 2, 4, 6.83, 8 and pH = 10.

Secondly, from these observations we can say that the variation pH parameter showed remarkable effect on the removal process. The following discussion provides a concise explanation in this regard. Figure 8 illustrates the distribution of the three surface functional groups of HFO (e.g., $FeOH^{2+}$, FeOH, and FeO^-) with respect to pH; there can be three cases as follow:

$4 \leq pH \leq 9.0$: this pH range allows selective sorption of transition metal cation (Lewis acids) and ligands (Lewis acids) through the formation of inner sphere complexes. Therefore, the removal efficiency of cadmium increased in a great deal Note that other ions present in the solution (e.g. Sodium, Chloride) form only outer sphere complexes through electrostatic interactions and yield poor sorption affinities.

$pH \leq 4.0$: positively charged $FeOH_2^+$ is the most predominant surface functional group. Thus, transition metal cationsare desorbed efficiently at $pH \leq 4.0$. The removal efficiency is lower at high acidic pH. It seems that the positive charge on the adsorbent is created in the acidic pH.So, there is an electrostatic repulsion between the adsorbent and cadmium ions in solution. The hydrogen ions instead of cadmium ions are placed in to the adsorbent sites when the amount of hydrogen ions increases in solution, and so the removal efficiency decreases.

$pH \geq 11.0$: negatively charged Feo^- is the predominant surface functional group. All Anionic ligand are excluded because of donnan exclusion effect, leading to regeneration.

Comparative application of resins (AMBERLITE IR 120 H) as synthesized beforeand synthetic super paramagnetic magnetite Fe_3O_4 nanoparticles on a resins (AMBERLITE IR 120 H) supportfor the removal of Cadmium ions ($Cd^{+2)}$.

Table (7) and Figure 8: Comparison of the No. of B.V. for 100% Removal and Breakthroughs values for removal of 200 ppm of Cd(II) ions at different pH = 6.83 andflow rate = 2ml/min at Temp. = $25^oC \pm 1$ using AMBERLITE IR 120 H resin

and Super paramagnetic magnetite Fe_3O_4 nanoparticles on a resin (AMBERLITE IR 120 H) supportoptained that the efficiency of AMBERLITE IRI 20 H resin is increase after modification with 36.25 %.

Table 7: Comparative application data of resins (AMBERLITE IR 120 H) as synthesized before and SPMM Fe3O4 NPs on resin (AMBERLITE IR 120 H) support for the removal of Cadmium ions (Cd+2).

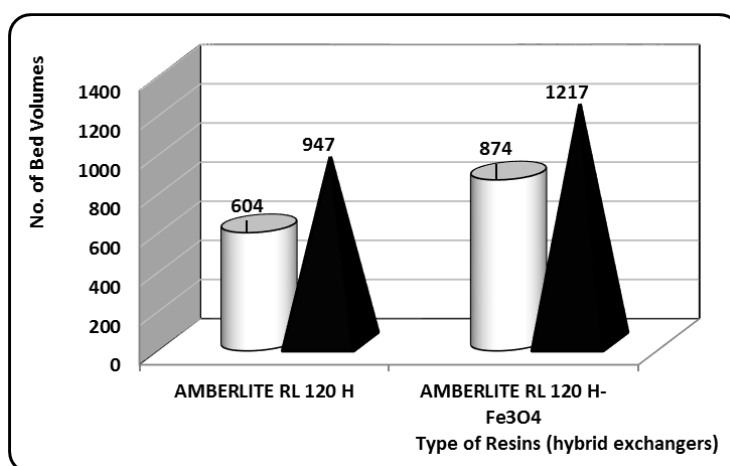| % Removal	Concentration of Cd^{+2} (ppm)	AM IR 120 H-Fe_3O_4/AM IR 120 H
No. of B.V. at 100% Removal (ml)	200	947/604
No. of B.V. at Breakthroughs values(ml)	200	1217/874

Fig. 8: Comparison of the efficiency of AMBERLITE IR 120 H andsuper paramagnetic magnetite Fe_3O_4.

Application of Super paramagnetic magnetite Fe_3O_4 nanowafers nanoparticles in the Removal of Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2} from industrial wastewater submerging on River Nile: The selected sampling stations depended mainly on the points discharged into River Nile water stream of the three companies. El-Nasr Company for Coks& Chemicals, Egyptian Iron and Steel factory in El-Tebbin - Helwan city in Giza governorate and the Egyptian Sugar & Integrated Industries Company at north in El-Hawamdya city in Giza governorate. The obtained results of metal ions removal are presented in Table 8. Were treated at1 gm/l dosage of SPMM Fe_3O_4 NWNPs, neutral pH = 7, Temp. = $25^oC \pm 1$ and the flow rate was adjusted to be 2ml/min. It is noted that analyzed metals, Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2}, were completely removed from all tested industrial wastes are obtained in Table 8.

Table 8: Ratio of metals removal for three sources of industrial wastewater by used SPMM Fe_3O_4 NWNPs

Adsorbent	Heavy metals		Source of pollution		
			El-Nasr Co. for Coks & Chemicals	Egyptian Iron and Steel Co.	Egyptian Sugar & Integrated Industries Co.
SPMM Fe_3O_4 NWNPs	Fe	C_0	2.845	6.175	2.18
		C_e	ND	ND	ND
		R %	100	100	100
	Mn	C_0	0.96	2.012	0.706
		C_e	ND	ND	ND
		R %	100	100	100
	Cu	C_0	0.89	1.04	0.6
		C_e	ND	ND	ND
		R %	100	100	100
	Zn	C_0	0.548	0.795	0.11
		C_e	ND	ND	ND
		R %	100	100	100
	Ni	C_0	0.22	0.49	0.11
		C_e	ND	ND	ND
		R %	100	100	100
	Pb	C_0	0.055	0.081	0.032
		C_e	ND	ND	ND
		R %	100	100	100
	Cd	C_0	0.048	0.181	0.099
		C_e	ND	ND	ND
		R %	100	100	100

CONCLUSION AND RECOMMENDATION

Super paramagnetic magnetite Fe_3O_4Nanowafers are synthesized with particle size ranging 2.9-33.2 nm<100nm.The shape, porous and size of these nanoparticles were confirmed using SEM, XRD and FTIR. The magnetization property of super paramagnetic magnetite Fe_3O_4 was confirmed using MSB to give the effective magnetic moment (μ_{eff}) whichequal 31.31 emu.mol^{-1}.Successful exploitation of metallic nanoparticles lies in the successful conjugation of their active surface structure. Thus, size and shape play a role in terms of variable surface energy. The removal of Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+2} with SPMM Fe_3O_4 NWNPs is affected by a number of operational parameters. The obtained results indicate that the above-mentioned SPMM Fe_3O_4 NWNPs can be used as an effective, economic and favorable for the removal of Fe^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Pb^{+2}, and Cd^{+}. As for the column studies the maximum removal efficiency was found to be 100% in 1gm of SPMMFe_3O_4 NWNPs per 4572 ml at 25 mg/l (10 mg/l Fe^{+2}, 4 mg/l Mn^{+2}, 3 mg/l Ni^{+2}, 2 mg/l Cu^{+2}, 2 mg/l Zn^{+2}, 2 mg/l Pb^{+2}, and 2 mg/l Cd^{+2}) of industrial discharge wastewaters were collected from the El-Nasr Company for Coks, Chemicals, Egyptian Iron and Steel factory and Egyptian Sugar & Integrated Industries Company at pH= 6.83.however, the AMBERLITE IRI 20 H resin obtains result 2914.65 ml at the same conditions, this means that the efficiency of AMBERLITE IRI 20 H resin increases after modification with 36.25 % . The next step in this work will consist of testing this non-conventional adsorbent on a real industrial scale.

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ARABIC SUMMARY

استخدام مادة الماغنتيت Fe_3O_4 (أكسيد الحديد الأسود المغناطيسي) النانونية،عالية المغناطيسية المحضرة حديثا في إزالة المعادن الثقيلة من مياه الصرف الصناعي التي تصب في نهر النيل

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يتناول هذا البحث استخدام مادة الماغنتيت Fe_3O_4 (أكسيد الحديد الأسود المغناطيسي) النانونية، عالية المغناطيسية في الإزالة التامة لبعض المعادن الثقيلة (الحديد، المنجنيز، النيكل، النحاس، الزنك، الرصاص، الكادميوم) من ثلاثة عينات من مياه الصرف الصناعي (شركة النصر للكيماويات الأساسية وفحم الكوك و شركة الحديد والصلب والشركة المصرية للسكروالصناعات التكاملية) في منطقة الحوامدية بالجيزة والتبين بحلوان والتي تعتبر من مصادر التلوث التي تصب في نهر النيل. تم التطبيق على هذه المادة باستخدام تقنية معملية لدراسة تأثير المتغيرات المختلفة مثل التركيز الإبتدائي (100-300 جزء في المليون) وكمية المادة (0.5-3 جرام) ومعدل السريان (1-3 ملي / دقيقة)، وتركيز أيون الهيدروجين (2-10) والتي تم تعيينها باستخدام أيونات الكادميوم وتعيين نقطة الاختراق وهي عند نصف قيمة تركيز أيونات الكادميوم الإبتدائية في المياه المعالجة. ومن خلال هذه النتائج كانت كفاءة إزالة الملوثات 100 % عند تركيز 25 جزء في المليون (الحديد 10 جزء في المليون، المنجنيز 4 جزء في المليون، النيكل 3جزء في المليون، النحاس 2 جزء في المليون، الزنك 2 جزء في المليون، الرصاص 2 جزء في المليون، الكادميوم 2 جزء في المليون) باستخدام 1 جرام من مادة الماغنتيت Fe_3O_4 (أكسيد الحديد الأسود المغناطيسي) النانونية، عالية المغناطيسية وعند تركيز أيون الهيدروجينيساوي 7 كانت كمية المياه المعالجة تماما 4572 ملي /جرام من هذه المادة. بالمقارنة بكمية المياه المعالجة تماما باستخدام مادة الأمبريليت 120 قبل معالجتها بمادة الماغنتيتFe_3O_4 كانت 2914.65 ملي/جرام عند نفس ظروف المعالجة. وبهذا تكون كفاءة مادة الماغنتيتFe_3O_4 (أكسيد الحديد الأسود المغناطيسي) النانونية، عالية المغناطيسية في الإزالةالتامة لهذه المعادن الثقيلة أعلي بنسبة 36.25%. ومن هذه الدراسه اختبار غير تقليدي لهذه المادة على نطاق صناعي.