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Synthesis of Iron Oxide/TiO_2 with Citric Acid Nano-Composite to Remove Some Inorganic Pollutants from Kema Drain -Aswan-Egypt

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Abstract

MINPs are new nanomaterials with functional materials, which was great used in different applications in water treatment processes. This paper focuses on the preparation and characterization (structure and magnetic properties) of a novel adsorbent of magnetic iron oxide nano-particles coated with citric acid and TiO2, and their corresponding application in removing some inorganic pollutants from Kema drain – Aswan – Egypt. The characterization of the synthesized nano-composite was performed by XRD, SEM, particle size analysis and VSM, and the obtained results were discussed. The coating process of iron oxide nano-particles with citric acid and TiO_2 was elucidated from XRD analysis system, which indicates that the composite is well crystallized structure. While, SEM images for the iron oxide coated with citric acid TiO_2 confirms that magnetic iron oxide nano-composite are nano-fibrils and highly uniform in size with rod shape, as well as SEM image show that the TiO_2 particles coat the core magnetic iron oxide nano-particles with the homogenous distribution approximately. Also, particle size analysis indicated that the smallest size of nano-particles (70nm) formed due to the heterogeneous nucleation of new nano-composite of iron oxide with TiO_2 with multi-hydroxyls groups of citric acid. Finally, vibrating sample magnetometer (VSM) shows that the nano-composite particles have typical super-paramagnetic behavior, which is confirmed by the magnetic hysteresis loops. Also, the results showed that the synthesized nano-composite were dependent on pH, adsorbent dosage, contact time and temperature. The efficiency of iron and copper ions adsorption increases with increasing adsorbent dosage and temperature at certain limits of pH and contact time. The maximum removal percentage reached 92.85% and 85.03% for copper and iron removal, respectively, by using the magnetic iron oxide coated with citric acid and TiO2 nano-composite at pH 7, adsorbent dosage (0.1g) and temperature 300C after a contact time 35min and 25min for iron and copper, respectively.

Key words: Iron oxide nano-particles, TiO_2-anatase, citric acid, water treatment.

INTRODUCTION

Kema drain was constructed in the past at Aswan Governorate 60 years ago in south east - north direction of Aswan city as a reservoir for the floods in order so as a protect for Aswan city from the dangers of floods, where the flood water flows into Kema drain and from it to the Nile River directly. But it was exploited by the Kema Fertilizer Factory in Aswan, which it is the largest chemical fertilizer plant in the Middle East, by dumping its industrial wastes in the drain, which is discharged in turn directly in the Nile River (Fig.1). Also, the Sewage Authority in Aswan city participates in this problem by throwing sewage of Aswan city in the Nile water, which is about 12,0000m^3 of wastewater. As well as, the Kema drain was used by some offenders as a drain to get rid of sewage, where some people connect the drainage pipes to pour into the drain. This causes a foul smell hurt everyone who passes through this area. It is an environmental and health tragedy for the people of Aswan. Thus, over 60 years, there is still a source of disturbance and pollution of one of the most important tourist governorates (Aswan Governorate). By analyzing the Kema drain wastewater and some Nile River water samples that were taken after the outlet of Kema drain, it is advised that they contaminated by some inorganic pollutants (Table 1). Where, toxic heavy metals of water sources have become one of the main problems worldwide (Madaln and Suzuki, 2002). So, it must find a solution to this problem by treating the wastewater of the Kema drain before throwing it in the Nile River in a number of ways, including those used in this paper.

The removal of heavy metals, such as copper and iron has a great attention because of their harmful effects on the ecosystem and human health. Removal of heavy metals can be eliminated by different treatment methods. (**Pokhrel and Viraraghavan, 2008 & Vaclavikova et al., 2008)**. Adsorption processes are commonly applied and show a good efficiency to cost ratio for removing toxic metals. Sorption methods are the best method with less technical cost and removal efficiency percent. **(Vaclavikova et al., 2008).** Recently, magnetic materials have a high interest for removal of heavy metals. Generally, MINPs particle size has a main effect on removal toxic metals. **(Yavuz et al., 2006 and Deliyanni et al., 2010)**. Improve performance of nanoparticles to sorbent materials depends on nano-porous structures. (**Fryxell et al., 2004**). Large surface area of nanomaterials has very advantageous for removal of toxic metals from polluted water **(O'Handley, 2000)**. The morphological character of MINPs is crystalline and can be synthesized by chemical methods; a challenging task is nano range of particle size and morphology. Chemical precipitation, sol-gel, hydrothermal, emulsion-precipitation, electro-deposition, and microwave assisted hydrothermal technique. The sol – gel method is considered as a best method for preparing nanosized materials. **(Mary Jacintha et al., 2017).** A numerous phases of iron oxides, i.e., oxides, hydroxides or oxy-hydroxides are known to date. These are Fe $(OH)_3$, $Fe(OH)_2$, Fe_3O_4, FeO, five polymorphs of FeOOH and four of Fe_2O_3. Properties of this oxide contain mostly the trivalent phase of iron, low solubility and brilliant colors **(Cornell and Schwertmann, 1996).** Nano iron oxides have exhibited great effect as catalytic substance, wastewater treatment adsorbents, pigments, flocculants, coatings, gas sensors, ion exchangers, magnetic recording devices, magnetic data storage devices, toners and inks for xerography, magnetic resonance imaging, bio-separation and medicine. Fe_3O_4 and γ-Fe_2O_3 have vital magnetic properties for biomedical purposes. Iron hydroxides and oxy-hydroxides such as ferrihydrite, goethite, akaganeite, lepidocrocite are being evaluated for their applications in water treatment for remove toxic ions **(Mohapatra and Anand, 2010**). Nano-particle diameter ranged between from 1 to 100nm. Magnetic NPs have high magnetic properties such as super-paramagnetic, high coercivity, low curie temperature, high magnetic susceptibility, etc. MINPs have a large surface-to-volume ratio. So, it has high surface energies. These nanomaterials tend to aggregate; moreover, MINPs have high chemical activity and auto-oxidize. We need to keep the stability of magnetic iron oxide NPs, where MINPs loss some of magnetism and dispersibility by aggregation. Grafting or coating of different composite with MINPs such as silica, metal or nonmetal elementary substance, metal oxide or metal sulfide may be improve of removal different pollutants water **(Wu et al., 2008).** Fe_3O_4 has a black color and ferromagnetic properties with ferrous and ferric ions **(Cornell and Schwertmann, 2003).** The high magnetization behavior of MINPs gives availability in different applications. Also, magnetic nano-particles have attracted broad attention due to their potential applications; however, the main target of nanomaterials is to increase the surface to binding with different groups. **(Kumar and Mohammad, 2011and Pal et al., 2014 and 2015)**. The lowest magnetite diameter can be obtained by sol-gel method. Ungrafted MINPs show super-paramagnetic behavior. Iron oxide nano-particles were coated with citric acid and TiO_2 (**Yao et al., 2009**). Citric acid is an inorganic acid which has three carboxylate groups **(Gupta and Gupta, 2005 & Chomoucka et al., 2010).** Citric acid grafted on the surface of MINPs. In which the grafting with citric acid prevent agglomeration and oxidation of nano-particles **(Wu et al., 2008).** This work focus mainly on preparation and characterization of a novel magnetic nano-adsorbent of iron oxide nano-particles coated with different compounds such as citric acid that have several functional groups (tri-carboxylic acid and four hydroxyl groups) and TiO_2 as an antimicrobial substance by sol-gel and co-precipitation method with different surfactants. Also, use this new nano-composite in removing some heavy metals from Kema drain wastewater – Aswan – Egypt.

Fig.1: Drainage of Kema drain in the Nile River.

MATERIALS AND METHODS

2.1. Water sample collection:

Some water samples were collected from the Kema drain wastewater outlet as well as from the Nile River water at distances from the Kema drain outlet for the treatment process, where the localities of these samples were identified by using a GPS instrument. These samples were analyzed at the laboratories of Desert Research Center to determine the concentrations of trace elements in them (Table 1 and Fig.2).

Table 1: The trace element concentrations in the Kema drain wastewater outlet and some Nile River water samples

Sample No.	Sample description	Al	B	Cd	Co	Cu	Fe	Mn	Pb	Zn
1	Kema drain outlet	6.413	0.787	0.028	0.093	26.16	13.72	0.337	0.0623	1.003
2	From Nile River at 100m from Kema drain outlet	1.096	0.494	0.002	0.019	24.82	5.838	0.285	0.036	0.452
3	From Nile River at front of Wadi El-Kobania	0.956	0.325	0.002	0.009	3.995	4.039	0.204	0.015	0.236
4	From Nile River under Aswan bridge	0.949	Nil	0.001	<0.001	2.975	1.024	0.143	<0.003	0.015

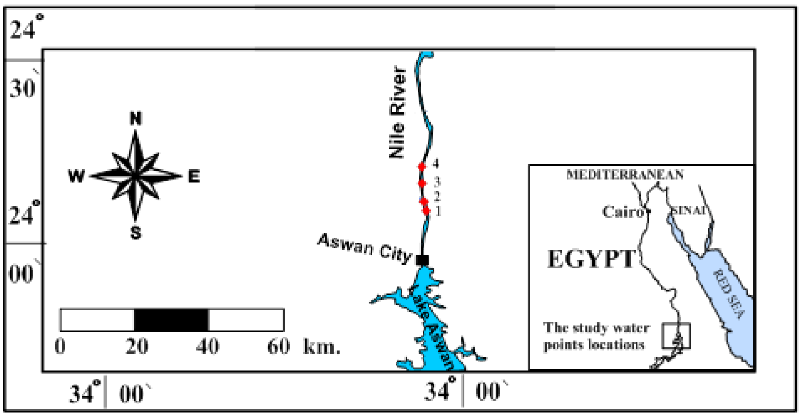


Fig. 2: the water sampling sites map.

2.2. Chemicals and instruments:

The materials were used for synthesis of magnetic iron oxide nano-particles coated with citric acid and TiO_2 were ferric chloride hexa-hydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetra-hydrate ($FeCl_2{\cdot}4H_2O$), citric acid anhydrous (CAA), titanium dioxide, sodium hydroxide (NaOH) and ammonium hydroxide. All chemical reagents used in this experiment were supplied from Sigma Chemical Companies (St. Louis, MO) and were of analytical grade. Distilled water was used throughout without further purification. A plasma-atomic emission spectrometer (ICP spectrophotometer Thermo Jarrel Ash model POEMS 3, made in England), used for detecting the concentrations of trace metal ions in the synthetic solutions and Nile River water as well as Kema drain wastewater samples. The precipitation technique is probably the simplest and most efficient chemical pathway to obtain iron oxide nano-particles coated with citric acid and TiO_2. Iron oxides (FeOOH, Fe_3O_4 or γ-Fe_2O_3) are usually prepared by the addition of alkali to iron salt solutions and keeping the suspensions for ageing. The main advantage of the precipitation process is that a large amount of nano-particles can be synthesized. However, the control of particle size distribution is limited, because only kinetic factors are controlling the growth of the crystal (Gong et al., 2012). In the precipitation process, two stages are involved; a short burst of nucleation occurs when the concentration of the species reaches critical super saturation, and then, there is a slow growth of the nuclei by diffusion of the solutes to the surface of the crystal (Tartaj et al., 2006). Size control of mono dispersed particles must normally be performed during the very short nucleation period, because the final particle number is determined by the end of the nucleation and it does not change during particle growth. A wide variety of factors can be adjusted in the synthesis of iron oxide nano-particles coated with citric acid and TiO_2 to control size, magnetic characteristics, or surface properties. A number of studies have dealt with the influence of these different factors among them; Tominaga et al., 2006.

2.3. Synthesis of Iron oxide (NPs) coated with citric acid and TiO_2:

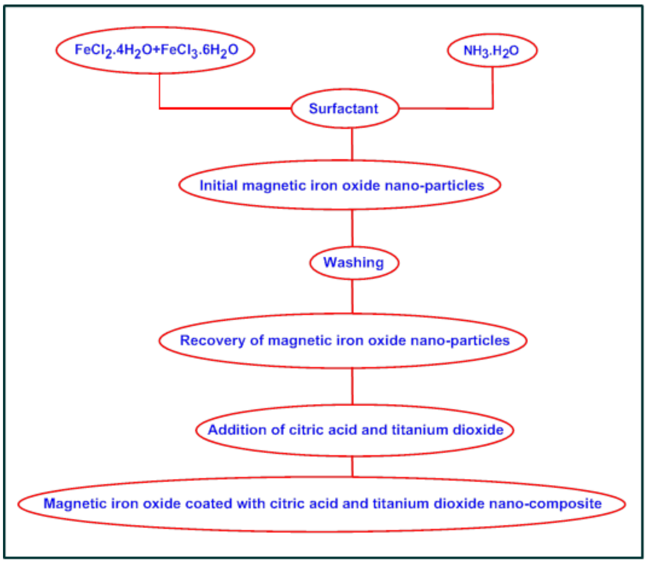
Magnetic iron oxide nano-particles, Fe_3O_4, were prepared by co-precipitating Fe^{2+} and Fe^{3+} ions by ammonia solution and treated under hydrothermal conditions (Liao and Chen, 2001 & Chen and Liao, 2002). The ferric and ferrous chlorides (molar ratio 2:1) were dissolved in water at a concentration of 0.3M iron ions. Chemical precipitation was achieved at 25°C under vigorous stirring by adding NH_4OH solution (29.6%). During the reaction process, the pH was maintained at about 10 and then adds citric acid anhydrous (CAA) and titanium dioxide at certain amounts to the precipitation formed in the solution. The mixture was ultrasonically agitated and then centrifuged. In order to obtain iron oxide nano-particles coated with citric acid and TiO_2, the residual mass was dried at 450°C to evaporate water and organic material to the maximum extent (Jana et al., 2009).
In general, the formation of magnetic iron oxide nano-particles followed this reaction;

$$Fe^{2+} + 2Fe^{3+} + 8NH_3{\cdot}H_2O \longrightarrow Fe_3O_4\downarrow + 8NH_2 + 4H_2O \quad (1)$$

Noteworthy to mention that when ammonia is added to the $FeCl_2$ and $FeCl_3$ solutions, $Fe(OH)_2$ is initially formed (Eq.2), which is then oxidized to Fe_3O_4 (Eq.3). The formation mechanisms of Fe_3O_4 magnetic NPs and iron oxide nano-particles coated with citric acid and TiO_2 can be summarized as follows:

$$Fe^{2+} + 2NH_3 + H_2O \rightarrow Fe(OH)_2 + 2NH_4^+ \quad (2)$$

$$3Fe(OH)_2 + 1/2O_2 \rightarrow Fe_3O_4 + 3H_2O \quad (3)$$



Scheme 1: Procedure for the preparation of magnetic iron oxide coated with citric acid and titanium dioxide nano-composite by the controlled chemical co-precipitation method.

The suggested mechanism for synthesis of magnetic iron oxide coated with citric acid and TiO_2 nano-composite can be deduced as in Fig.3;

Noteworthy to mention that, the interaction of the ligand with the iron oxide surface is either a hydrogen bonding interaction through the OH group (under acidic conditions) or a direct Fe-carboxylate linkage (at more alkaline pH values as in this study), (Ulman, 1991). During the synthesis, magnetite in the dry state is oxidized to maghemite by air. It is known that ultrafine crystals of magnetite change over years from black to the brown of maghemite even at room temperature (Cornel and Schwertmann, 1996). This method has widely been used because of the ease and reproducibility of the synthesis, as well as the uniformity, high crystallinity, and mono-dispersity of the product. Also, because of the dependence of photocatalytic and photoelectrochemical properties on the nano-particle size, significant efforts have been concentrated on the precise control of particle size distribution (Torimoto et al., 2000 and Calza et al., 2007).The suggested mechanism for removing the pollutants (iron and copper) from water solution by the synthesized magnetic iron oxide coated with citric acid and TiO_2 nano-composite can be deduced as in Fig.4;

RUSELT AND DISCUSSION

3.1. Nano-composite characterization:

The synthesized nano-composite was prepared using X-ray diffraction (XRD, Philips X'Pert PRO) with secondary mono-chromator, using Cu-Ka radiation (λ=1.54A^0) at 50kv and 40MA as well as scanning speed 0.02°/Sec. Also, the morphology of the prepared nano-composite was investigated by (SEM) Model; Quanta 250 FEG (Field Emission Gun). As well as, the size of the synthesized particles was obtained by PSA (ZETA-SIZER, MALVERN Nano-ZS90). Finally, magnetic characters of the nano-composite was assessed with (VSM, Homade 2 tesla) at room temperature. A magnet (Φ 17.5×20mm, 5500Oe) was utilized for the collection of magnetic particles. Basing on the results of measurements, both the coercivity, remanence and saturation of samples have been determined.

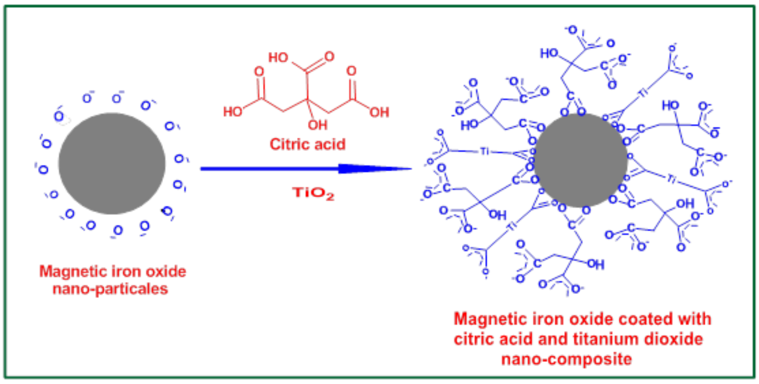


Fig. 3: The synthesis of the magnetic iron oxide coated with citric acid and TiO_2 nano-composite.

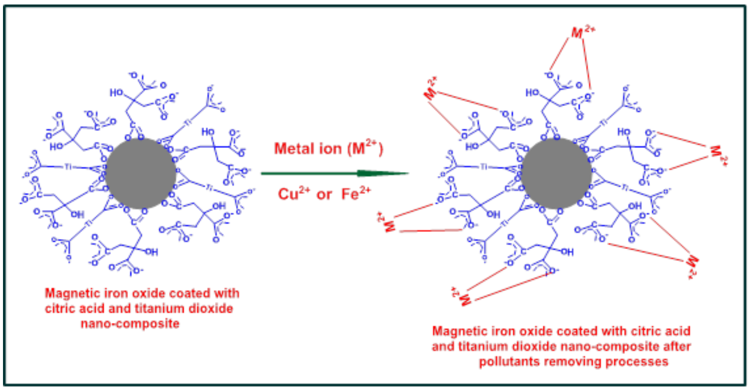


Fig. 4: The removal processes of the heavy metals from a polluted solution using magnetic iron oxide coated with citric acid and TiO_2 nano-composite.

3.2. Structural analysis (X-ray diffraction instrument):

The crystal content and phase clarity of synthesized nano-composite spinel magnetic iron NPs coated with citric acid and TiO_2 was characterized by the X-ray diffraction (XRD) and depicted in Fig.5. The nano-composite is believed to be the major crystalline phase as identified by the diffraction peaks in the XRD pattern at 2θ of 23.9°, 27.5°, 33.5°, 35.5°, 41° & 44.5°, 49.5° and 55.5° which corresponding well to the diffractions values of crystal faces of citric acid, TiO_2, Fe_3O_4 (magnetite), Fe_3O_4-CAA, α-Fe_2O_3 (hematite), α-Fe_2O_3-composite and γ-Fe_2O_3 (maghemite) spinal structure (Patri et al., 2009). All these peaks confirm the cubic spinel lattice of magnetic iron oxide coated with citric acid and TiO_2 nano-composite. The XRD pattern at 2θ of 23.9°, 27.5°corresponding to the diffractions of crystal faces of citric acid anhydrous and TiO_2 anatase structure. The situation and relative densities of the reflection peak of α-Fe_2O_3 (hematite), γ-Fe_2O_3 (maghemite) and Fe_3O_4 (magnetite) accept with XRD peaks of standard Fe_2O_3 samples (Mahdavi et al., 2013), indicating that the black-colored magnetic powders are a mixture of hematite and magnetite nano-particles and by complexing with TiO_2 in the presence of citric acid gave a brown colored. Sharp peaks also suggest that the iron oxide nano-particles formed have well crystallized structure. Noteworthy mentioning that, the diffraction peak value at 35.5° may be assigned to the citric acid and Fe_3O_4 combination, while the peak at 49.5° may be assigned to the α-Fe_2O_3 and composite combination. Thus, the appearance of the two peaks is a strong indicator for the formation of the magnetic iron oxide nano-composite. This indicates that the synthesized magnetic iron oxide nano-composite of good crystalline with no impurity phase (no impurity peak was detected), demonstrating the high purity of the prepared nano-composite.

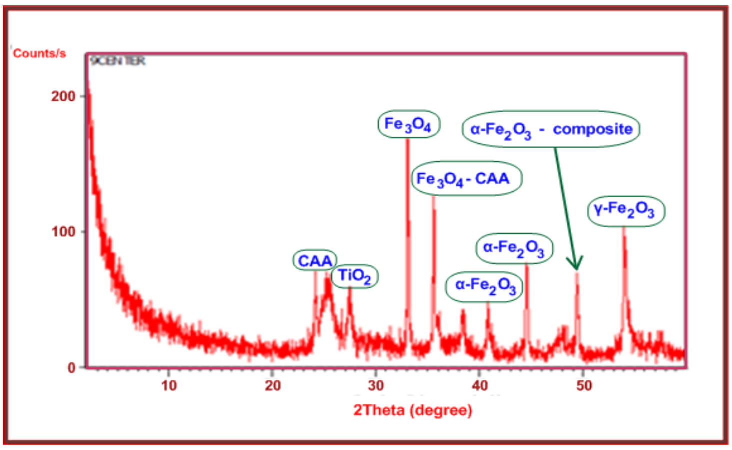


Fig. 5: The XRD pattern of the synthesized magnetic iron oxide coated with citric acid anhydrous and titanium dioxide nano-composite.

3.3. Morphological analysis (Scanning electron micrograph analysis):

Scanning electron microscope (SEM) is responsible for scanning surface morphology of materials without entering to matter depth so it shows the external shape with final edging of nano-particles. The morphological characterization samples are realized through SEM imagery analysis. Fig.6 Shows the SEM images for the synthesized iron oxide coated with citric acid and TiO_2 which confirms that magnetic iron oxide nano-composite are nano-fibrils and highly uniform in size with rod shape. Also, SEM image shows the TiO_2 particles coat the core magnetic iron oxide nanoparticles with the homogenous distribution approximately.

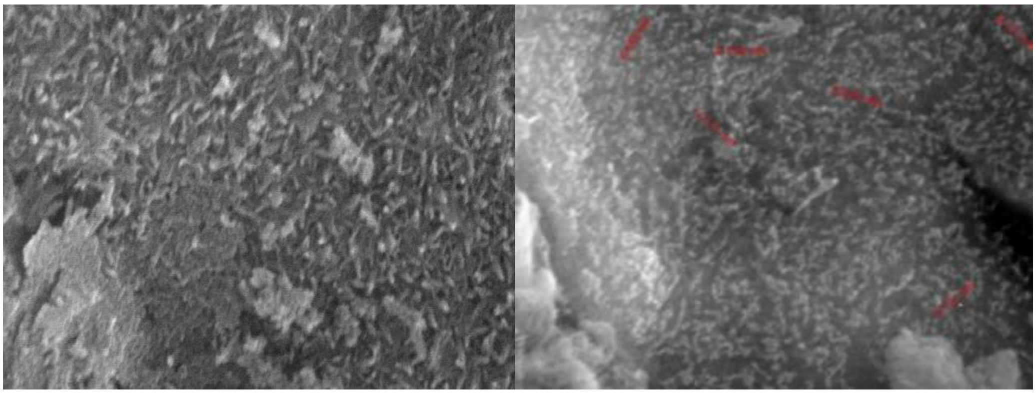


Fig. 6: The SEM micrograph of magnetic iron oxide coated with citric acid and TiO_2 nano-composite.

3.4. Particle size analysis of iron nano-composite with TiO_2 and CAA:

Fig.7 showed the magnetic iron oxide coated with citric acid anhydrous and titanium dioxide nano-composite intensity weighting was 145.2nm, volume weighting was 46.4nm and number weighting was 20.8nm. The smallest size of nano-particles formed due to the heterogeneous nucleation of new nano-composite of iron oxide with TiO_2 and multi-hydroxyls groups of citric acid. The mean average diameter of iron oxide nano-composite is 70.8nm. The reading value meant that results of reduction percent of synthesized iron nanomaterials depend on the dimension of dispersant nanomaterials.

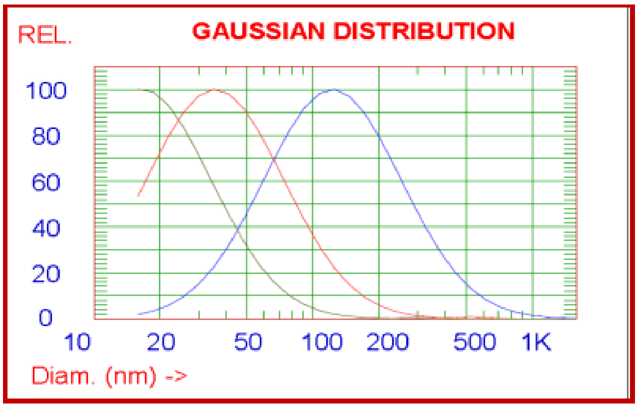


Fig.7: Particle size distribution of magnetic iron oxide coated with citric acid and TiO_2 nano-composite.

3.5. Vibrating Sample Magnetometer (VSM) and magnetic properties:

VSM technique for measuring a magnetization characters (expressed by the measured magnetization curve) of spinel magnetic iron oxide coated with citric acid and TiO_2 nano-composite sample was recorded and the results of hysteresis (the M–H loops of the sample) are shown in Fig.8. The hysteresis loop of the nano-composite, which was measured in the powder state (Fig.8) indicating that there was no hysteresis in the magnetization of a sample, provided evidence that the synthesized magnetic iron oxide nano-composite was super-paramagnetic at room temperature, this can be attributed to the small size of the synthesized nano-composite (Pradhan et al., 2006, Güner et al., 2015 and Stoia et al., 2017). In other words, when the magnetic nano-composite size is smaller than a certain size, the particles will exhibit super-paramagnetism (Guo et al., 2010). Basing on the results of measurements, the coercivity, remanence and saturation of samples have been determined, from each powder sample a certain amount of the sample has been portioned out, put into another container and weighted. The obtained values of saturation magnetization (Ms) and coercivity (Hc) at 300K are 46.998emu/gm and 34.865Oe for magnetite. Noteworthy, the magnetization (Ms) is significantly less than that of the bulk magnetization, which is Ms (bulk) = 92emu/g. The decreasing of saturation index is connected to nano-size materials. The increasing in magnetization of magnetite expressed excellent crystallite. Magnetization quantity of INPs grafted by citric acid and TiO_2 has less than pure magnetite nano-particles; therefore the magnetization has lowest value after grafting of TiO_2 with CAA onto the surface of magnetite and Fe_2O_3. The existence of diamagnetic shell surrounding the magnetite nano-particles is responsible for magnetic moment (Qu et al., 2010). In general (Hc) of a nanocomposite is a measure of magnetic anisotropy (Joy et al., 2000). It looks like to come from the alternate anisotropy, due to unorganized rotation. As a result of increasing the surface-to-volume ratio, we expect the presence of different sizes of MINPs. (Kasapoglu et al., 2007). Magnetite Fe_3O_4, hematite α-Fe_2O_3 and maghemite γ-Fe_2O_3 nano-particles have added to grafted substances.

3.6. Sorption experiments:

Iron present in two forms Fe(II) and Fe(III) and present in natural water. Fe(II) is a vital substance for transport and storage oxygen in hemoglobin and myoglobin. The water bearing formation can consider as one of the sources for Fe (II) in the study area. Contamination of water by (Fe^{2+}) ions is a major eco-problem, whereas (Fe^{2+}) is known as poisonous. Copper has enormous application in the industry. It is used in the electroplating, paint and pigment industry, electrical, and fertilizer. Due to a wide range of application of copper can be accumulated in the environment which makes the water more pollute. For the batch sorption experiments, a constant volume (100ml) of the synthesized polluted water or real wastewater was mixed with a fixed mass of sorbent iron oxide coated with citric acid and TiO_2 nano-composite into a conical flask. The pH was adjusted by 0.1M HCl acid and/or 0.1M NaOH. Make shaking at different times, to get on the optimal condition. Then, the adsorbent was separated by external magnetic field. Iron oxide coated with citric acid and TiO_2 washed with deionized water to neutrality. The concentrations of metal ions were measured by ICP. The effects of pH (5–8), sorbent dosage (0.025, 0.05, 0.1 and 0.2mg/l), contact time (5–50min) and temperature (20, 25, 30 and 35°C) were studied.

The Fe(II) and Cu(II) removal (%) could be calculated with the following equation:

$$\text{Removal } \% = \frac{\text{Conc. A.T- Conc. B.T}}{\text{Conc. B.T}} \times 100 \qquad (4)$$

Where, Conc. A.T is the concentration of solution after treatment and Conc. B.T is the concentration of solution before treatment.

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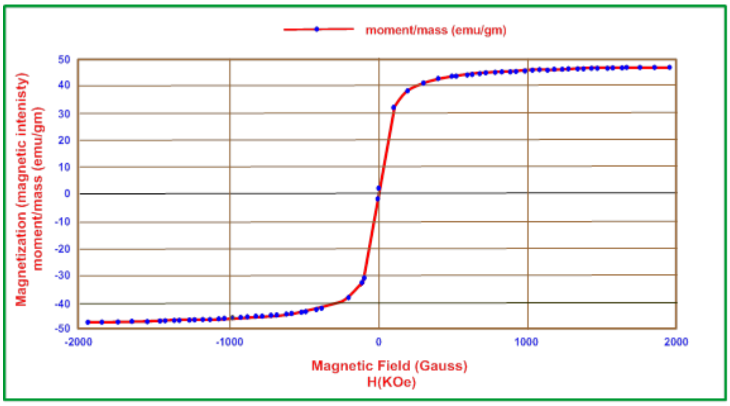

Fig. 8: Magnetic properties of the synthesized iron oxide coated with citric acid and TiO_2 nano-composite dependence of the magnetization at room temperature.

3.7. Effect of pH on Fe(II) and Cu(II) adsorption:

pH represents the most critical parameter affecting on adsorption process for removal Fe(II) and Cu(II). The removal of Fe(II) and Cu(II) by magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite was studied at different initial pH ranging between 5 and 8; dosage 0.1g; temperature, 30°C and contact time 35 and 25min for iron and copper, respectively. The results are shown in Fig.9. A maximum removal (%) was observed at pH 7. Fig.9 showed the effect of pH on reduction percent. pH has a significant effect on the removal (%) by the MINPs coated with citric acid and TiO_2 nano-composite, where there is an increase in the removal (%) with increasing pH of the medium until it reached to pH 7 (maximum removal) and then decreases. The lowest value of removal efficiency showed at low pH values. This may be due to, the sterric hindrance of different metal cations as Fe(II) and Cu(II) ions with hydrogen ions in reaction medium on the surface of nanoparticles. At higher pH, such positive charge density, which accumulated on the surface of magnetic iron nano-composite decreases, allowing the metal ions to approach the sorbent surface which result in higher adsorption values. At high pH more than 7, metal hydroxide ions would precipitate and less value of reduction percent. It is known that at high pH values Fe(II) and Cu(II) ions exist as cationic species of the type $Fe(OH)_2$ and $Cu(OH)_2$, while the favored species for adsorption of trace Fe(II) and Cu(II) are ions form.

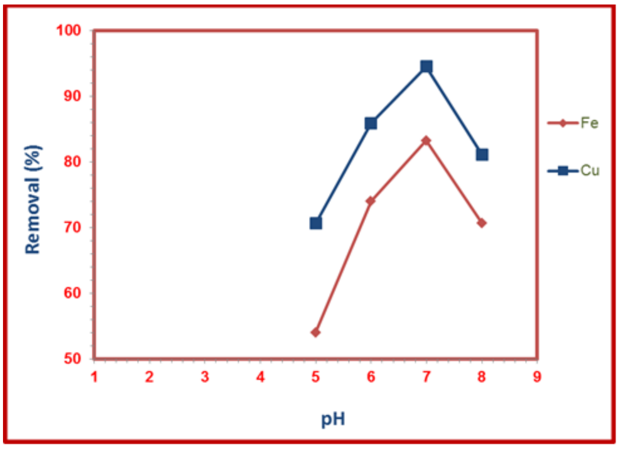

Fig.9: Effect of pH on Fe(II) and Cu(II) adsorption using magnetic iron oxide coated with citric acid and TiO_2 nano-composite at given conditions; dosage 0.1g; temperature 30°C and contact time 35 and 25min for iron and copper, respectively.

3.8. Effect of magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite dosages on Fe(II) and Cu(II) adsorption:

Adsorption of iron and copper by magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite was studied at different dosages ranging from 0.025 to 0.2g; pH 7; temperature, 30°C and contact time 35 and 25min; for iron and copper, respectively. Fig.10 illustrate the removal (%) of Fe(II) and Cu(II) as a function of the magnetic iron oxide nano-particles coated with citric acid and TiO_2 dosages. The Fig.10 revealed that the removal (%) was low at dosages 0.025 and 0.05g and progressively increased at dosage 0.1g and then decreases other once. Many parameters can interfere with adsorbent concentration.

3.9. Effect of contact time on Fe(II) and Cu(II) adsorption:

The sorption of iron and copper ions was carried out at different times ranging from 5-50min; pH 7; dosage 0.1g and temperature 30°C for iron and copper. About 0.1g of the adsorbent was mixed with 100ml of the both Fe(II) and Cu(II) solution. Fig.11 shows the effect of reaction time on the adsorption of the iron and copper by magnetic iron oxide nanoparticles coated with citric acid and TiO_2 nano-composite. A rapid kinetic reaction of Fe(II) and Cu(II) removal occurred within the first 20 and 30min for copper and iron, respectively, and the adsorption equilibrium was achieved at 25 and 35min for copper and iron, respectively, and a remarkable decrease was observed in the removal (%) with longer contact times. As evidenced from Fig.11, the removal (%) of all the sorbents reached saturation at 25 and 35min for copper and iron, respectively, i.e., the equilibrium time is a crucial parameter for an optimal removal of both metal ions from the polluted water.

3.10. Effect of temperature on the adsorption process:

The adsorption was conducted at different temperatures ranging from 20 to 35°C; pH 7; dosage 0.1g and contact time 35 and 25min for iron and copper, respectively. Fig.12 showed the relationship between temperature and the amount of Fe(II) and Cu(II) ions adsorbed onto magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite. As seen in Fig.12, adsorption of Fe(II) and Cu(II) on the concerned adsorbent increased when the temperature was increased until reach to 30°C for copper and iron, i.e., the adsorption is favored by high temperature. Adsorption of both copper and iron increases by increase the temperature, this is may be a result of increase in mobility of the Cu(II) and Fe(II) ion with temperature. Increasing temperature may produce a swelling effect within the internal structure of the adsorbent enabling metal ions to penetrate further (Dôgan and Alkan, 2003).

Citation: Yasser Abdulhady and Yahia Gedamy, Water Resources Management Using Satellite Remote Sensing (Case study in Lake Tana and Lake Nasser). Australian Journal of Basic and Applied Sciences, 12(7): 89-97.

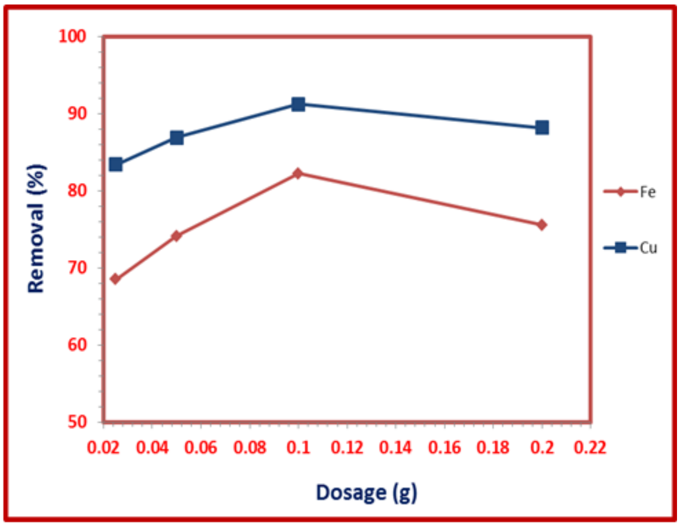

Fig.10: Effect of magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite dosage on Fe(II) and Cu(II) adsorption at given conditions; pH 7; temperature 30^{o}C and contact time 35 and 25min;for iron and copper, respectively.

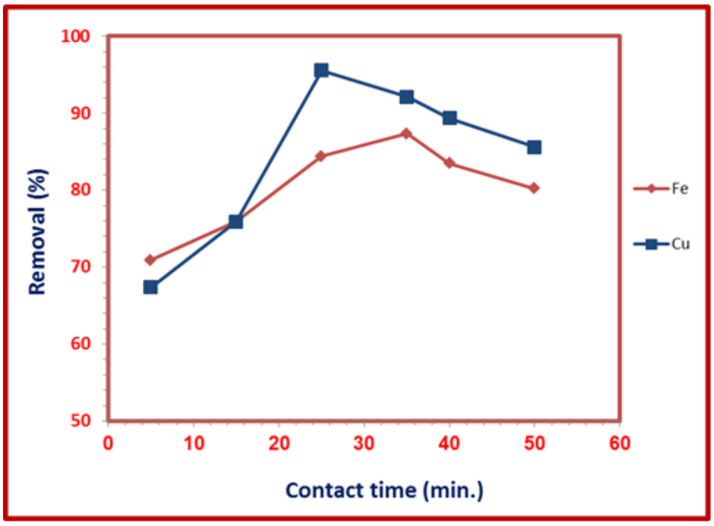

Fig.11: Effect of contact time on Fe(II) and Cu(II) adsorption using magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite at given conditions; pH 7; dosage 0.1g and temperature 30^{o}C for both iron and copper.

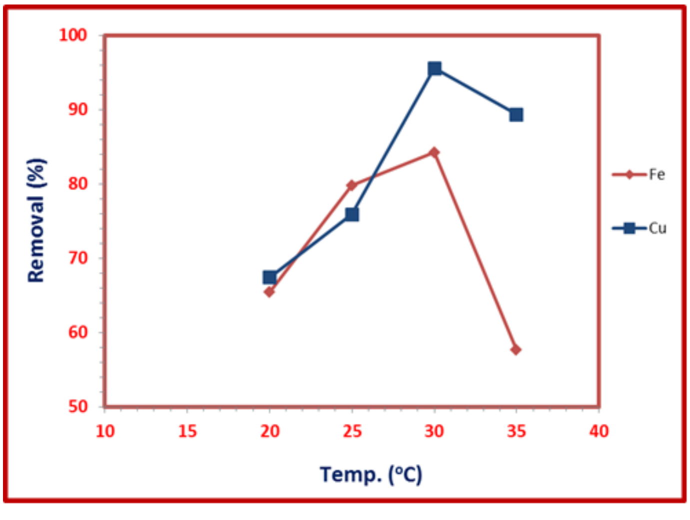

Fig. 12: Effect of temperature on the adsorption processes of Fe(II) and Cu(II) using magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite at given conditions; pH 7; dosage 0.1g and contact time 35 and 25min for iron and copper, respectively

In general, from the previous discussions it is obvious that the concerned adsorbent (magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite) has high efficiency for removal of both copper and iron from them synthetic solutions, this may be due to increase free oxygen attached to iron oxide nano-particles as core ion, therefore, increase of electrostatic bonding with different heavy metals. The carboxylic groups of citric acid were increasing the electronegativity surrounded to synthesized nano-composite that increases removal efficiency content. The action effectiveness of TiO_2 particle in nano-sized coated to iron oxide nano-particles were investigated as an antimicrobial agent and the chemical reaction occurred with the new nucleation process made shifting of TiO_2 wavelength from UV-band to visible –band.

Field study:

The suitability of magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite was tested with water samples that collected from the Kema drain wastewater outlet and from Nile River after the outlet of the Kema drain at different distances. This was done by adding 0.1g of sorbent to 100ml of the collected water sample and the contents were shaken at constant time (25 and 35min for Cu^{2+} and Fe^{2+}) at room temperature. The results are presented in Table 2. There is a significant reduction in the level of Fe(II) and Cu(II). It is evident from the results that the concerned adsorbent (magnetic iron oxide nano-particles coated with citric acid and TiO_2) can be effectively employed for removing Fe(II) and Cu(II) from wastewater of the Kema drain, where the removal (%) ranges from 88-93% and 80-85%, for both copper and iron, respectively, as follows;

Table 2: The trial results for an adsorption process of Fe^{2+} and Cu^{2+} (mg/L) from collected water samples represented for the Kema drain wastewater outlet and Nile River water after the outlet of the Kema drain using magnetic iron oxide nano-particles coated with citric acid and TiO_2 nano-composite.

Kema drain wastewater sample No.	Copper concentration before treatment as mg/L	Copper concentration after treatment as mg/L	Removal (%)	Iron concentration before treatment as mg/L	Iron concentration after treatment as mg/L	Removal (%)
1	26.16	3.066	88.28	13.72	2.04	85.09
2	24.82	1.77	92.85	5.83	1.08	81.45
3	3.99	0.33	91.73	4.03	0.69	82.85
4	2.97	0.25	91.60	1.024	0.21	79.96

Conclusion:

This study investigated the synthesis of new and more efficient adsorbent as iron oxide nano-composite (magnetic iron nano-particles coated with tri-carboxylic groups citric acid and TiO_2) compounds prepared by a co-precipitation method. The largest problem of Kema drain pollution was making toxicity of Nile River, which is the main source of healthy drinking water in Egypt. Our vision in this article was improved the water quality of water drain by using nanotechnology process. The using of iron nanoparticles with composites as a safe nanomaterials used in water treatment. The aim of achieving in this study was removal of copper and iron (polluted metals) from collected water samples of Kema drain wastewater outlet and Nile River after the Kema drain at different distances by nanotechnology. The results of the characterization of the synthesized nano-composite indicate that there is a coating process of iron oxide nano-particles with citric acid and TiO_2 at homogenous distribution approximately was carried out, which indicates that the composite is well crystallized structure, and the magnetic iron oxide nano-composite was nano-fibrils and highly uniform in size with rod shape. Also, particle size analysis indicated that the smallest size of nano-particles (70nm) formed due to the heterogeneous nucleation of new nano-composite of iron oxide with TiO_2 with multi-hydroxyls groups of citric acid. Finally, the synthesized nano-composite particles have typical super-paramagnetic behavior. Also, the results showed that the synthesized nano-composite were dependent on pH, temperature, contact time and adsorbent dosage. The efficiency of iron and copper ions adsorption increases with increasing adsorbent dosage and temperature at certain limits of pH and contact time. The lowest economic cost of prepared iron oxide nano-composite not needs to make the regeneration process of our nano-materials. This study has shown that magnetic iron oxide nano-particles with a surface functionalization have effective for removal toxic metals, which bind on iron oxide lattices. The nano-particles are a highly function as good dispersant materials in solutions. MINPs nanocomposite has ability to attract to magnetic field and can be separated from solution. The maximum removal (%) reached 92.85% and 85.03% of copper and iron removal, respectively, by using iron oxide/TiO_2 with citric acid nano-composite at pH 7 and adsorbent dosage 0.1mg after a contact time 25 and 35min and also temperature 25 ^{0}C and 30^{0}C for copper and iron respectively. This study investigated the synthesis of new and more efficient adsorbent as iron oxide nano-composite (magnetic iron nano-particles coated with tri-carboxylic groups citric acid and TiO_2) compounds prepared by a co-precipitation method. The aim of achieving in this study was removal of copper and iron (polluted metals) from collecting water samples of Kema drain wastewater outlet and Nile River water after the Kema drain outlet at different distances by nanotechnology.

Recommendations:

It is worth mentioning that to get rid of a large quantity of contaminants from the Kema drain wastewater before being delivered in the Nile River water, it must be repeated the treatment processes of Kema drain wastewater more than once.

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