

# Synthesis, Characterization of Magnetite Nanoparticles and Their Role in Lead Adsorption

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**Abstract-** Industrialization has revolutionized the quality of life but also led to the increase in environmental pollution in the form of industrial waste. The effluents released from the industries include toxic compounds which get accumulated in soil and persist for years if not treated properly. These persisting, non-degradable compounds include the heavy metals which are mostly released into the soil from electronic industries in the form of E-waste. Electronic industries are the fast growing industries and the amount of the waste released from them is considerably high. Most of the electronic goods are made of heavy metals like Lead (Pb), Cadmium (Cd), Zinc (Zn), etc., of which Lead is an important metal found in most of the electronic goods which is highly toxic. The metal leaches into the soil if not processed properly and leads to contamination of soil thereby affecting the lives of flora and fauna on earth. To prevent this the present study focused on the use of nanotechnology in the removal of Lead from contaminated soils. Magnetite nanoparticles are used for Lead adsorption. The unique property of high affinity of magnetite nanoparticles towards cations enables a better adsorption of Lead by the nanoparticles. The current study focuses on the application of Magnetite nanoparticles in reducing Lead toxicity by adsorption technique. The nanoparticles exhibited a higher rate of metal removal upto 2500ppm. X ray diffraction study revealed the size of the magnetite nanoparticle to be 4.3nm. The structure of the nanoparticle was determined by Scanning electron Microscope and Transmission electron microscope.

**Index Terms-** Magnetite nanoparticles, metal adsorption, and adsorption isotherm.

## I. INTRODUCTION

Soil is the basic source for life on earth. In recent years due to rapid industrialization soil is being polluted with various toxic compounds. The toxic compounds include different types of chemicals as well as heavy metals. These compounds leach into the soil because of improper treatment methods. Among the pollutants heavy metals pollution is the most challenging environmental problem globally [1]. It is a major threat for agriculture based countries like India where the contaminant free soil is of major importance. The presence of the heavy metals even in low concentrations could be harmful to the flora and fauna. Few of these compounds like Lead persist in soil for years without being degraded. So there is need for an efficient

treatment method for the heavy metals. The basic sources of these heavy metals are the electronic goods. The utility of the electronic goods has increased to a large extent in 21<sup>st</sup> century. At the same time the discard of these goods after their usage has also increased tremendously. The electronic goods are discarded in the landfills and remain in soil as electronic waste or e-waste for a long period due to improper treatment procedures. According to United Nations Environment Programme (UNEP) estimates the amount of E-waste produced globally is 50million tones annually and only 10% of it is recycled [2]. The E-waste from the developed nations is dumped into developing countries [3] as a part of free trade which is adding up to the difficulty in waste management. There are different methods available for E-waste management like mechanical separation, thermal treatment, hydrometallurgical treatment; electrochemical treatment [4]. But the employment of these methods requires more cost and expertise for their operation and also facilities for e-waste collection and treatment [5]. Because of inadequate facilities the e-waste is not being recycled properly and is getting accumulated in soil leading to environmental pollution. So there is a need for a new method which is cost effective and does not require much infrastructure. One of such methods is by adsorption mechanism using nano-based adsorbents. Nano-based adsorbents or Nanoparticles have small size and high surface area which enables greater adsorption of the cations onto them. Nano adsorbents such as Magnetite nanoparticles are generally used to remove Lead from soil. The magnetic property of the Magnetite nanoparticles enable easy separation of the adsorbent from the applied site as well as reusability [6]. So the present study focuses on the use of magnetite nanoparticles for Lead adsorption from soil samples containing high concentrations of Lead.

## II. MATERIAL AND METHODS

**1.1 Synthesis of magnetite nanoparticles:** Magnetite nanoparticles were synthesized by co-precipitation method [7]. 19.46 g of anhydrous FeCl<sub>3</sub> was completely dissolved in 150 ml distilled water (aqueous solution A). Potassium iodide solution (aqueous solution B) was prepared by dissolving 6.584g of potassium iodide in 50.0 ml distilled water. Both the solutions were mixed together at room temperature (RT) and allowed to stand for 1h to reach equilibrium. Iodine precipitate formed

was filtered out and then washed with distilled water. To the filtrate the washing was added. To the filtrate 25% ammonia solution was added drop-wise with continuous stirring at 1100rpm on a magnetic stirrer till a black precipitate was observed. Then the beaker was left to settle, filtered and washed with distilled water. After washing the sample was dried at 90°C.

## 2.2 Characterization of magnetite nanoparticles:

**2.2.1 UV-Vis spectra analysis:** UV-Vis spectral analysis was done using UV-Vis absorption spectrophotometer (Systrosnis 2100). Small aliquot of the sample was diluted in distilled water and measured at wave length between 200-600nm.

**2.2.2 X-Ray Diffraction(XRD):** The crystallographic structural information of the magnetite nanoparticles was analyzed by X-ray diffraction(XRD).The analysis of sample in diffraction patterns were recorded from  $10^0$  to  $70^0$  with a diffractometer (CuK $\alpha$ , 40 kV, 30 mA and  $k = 1.54056 \text{ \AA}$ ) (Indian Institute of Chemical Technology, Hyderabad).

**2.2.3 Scanning Electron Microscopy:** The morphology of the synthesized Magnetite nanoparticles was assessed by Scanning Electron Microscope (ZEISS). The samples were placed on a round cover glass of 1.2 cm diameter each, deionized water was used to wash and dried in a desiccator at RT. The cover glass was then mounted on a SEM stub and coated with gold for SEM analysis.

**2.2.4 Transmission electron microscopy:** The samples were observed under TECNAI FE12 TEM instrument operating at 120 kV using SIS imaging software. The magnetite nanoparticles were dispersed in methanol and a drop of each sample was placed on formvar-coated copper grid and air dried.

**2.2.5 Selected area diffraction:** The crystal structure of the nanoparticles was determined by Selected area (electron) diffraction ( SAD or SAED) which is determined inside a transmission electron microscope (TEM).

**2.3 Preparation of Lead stock solution:** Stock solution of Lead (Pb II) was prepared by dissolving 300mg of metal in 300ml sterile distilled water (3000ppm). From this different concentrations of the metal were made ranging from 5ppm to 2500ppm by dilution.

**2.3.1 Preparation of nanosuspension:** 1g of Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (dried) was dissolved in 100ml distilled water to make Magnetite particle suspension. For uniform dispersion of the nanoparticles in distilled water ultrasonic disruption (25 KHz, Model: Enertech) was carried on [8].

**2.3.2 Metal adsorption studies:** 25ml of metal solution of different concentrations were taken in a conical flask and 5ml of magnetite nanoparticle suspension was added to each flask. The flasks were incubated at 37°C for 24h. After the incubation period the amount of metal present in each concentration was determined by Atomic Absorption Spectrophotometer. The amount of metal (mg) adsorbed onto 1g of magnetite

nanoparticles was determined by mass balance equation which is given as [9].

$$Q_e = \frac{C_o - C_e}{m} V$$

Where C<sub>o</sub> is the initial metal ion concentration (mg L<sup>-1</sup>), C<sub>e</sub> is the final concentration of the metal.

V is the sample volume (L), and m is the mass of Fe<sub>3</sub>O<sub>4</sub> nanoadsorbent (g).

**2.3.3 Adsorption isotherm studies:** The amount of adsorbate on the surface of an adsorbent with respect to pressure for gases or concentration for liquids at constant temperature is explained by adsorption isotherms. Langmuir and Freundlich models are the two adsorption isotherms used to determine the adsorption phenomenon of Lead ions onto the surface of 1g of magnetite nanoparticles.

**Freundlich- Langmuir Isotherm:** This adsorption isotherm model explains heterogeneous system [10] which is expressed as  $X/m = KCe^{1/n}$

Where: x is the amount of adsorbate adsorbed

m=mass of adsorbate

Ce=equilibrium concentration of adsorbate

K= Freundlich constant

n=no. of layers of metal adsorbed on the surface layers of nanoparticles.

In general, 1/n is less than 1. Therefore, above equation can be written as

$$\text{Log}x/m = \text{log}K + 1/n \text{ log}C_e$$

The Freundlich coefficient can be determined from the plot of log x/m versus log C<sub>e</sub>

## III. RESULTS AND DISCUSSION

### Characterization of magnetite nanoparticles:

The accumulation of electronic waste because of improper recycling techniques is posing a major threat to the environment. Electronic waste constitute heavy metals like lead, mercury, copper which are toxic to the environment if they leach directly into soil without proper recycling. Due to lack of appropriate technologies the increase in the volumes of the scrap is witnessed after informal recycling [11]. So there is a need to design a method by which the volumes of the toxic metals that are leached into the soil can be minimized without causing any harm to the environment. Though there are many methods employed in their treatment the use of nanosized particles as environmental remediants is drawing the attention of current researchers as they provide cost-effective solutions for most of the environmental pollutants [12]. Nanosized Iron particles (Magnetite) are widely employed in the removal of common environmental pollutants like organic contaminants [13, 14, 15] as well as heavy metals [16, 17]. The literature reveals that Magnetite nanoparticles synthesized by co-precipitation method are used for the treatment of water contaminated with metals like lead, copper, Zinc and Manganese [18]. The magnetite nanoparticles functionalized with carboxyl (succinic acid), amine (ethylenediamine) and thiol (2,3-dimercaptosuccinic acid) groups were used for the removal of toxic metal ions (Cr(III), Co(II), Ni(II), Cu(II), Cd(II), Pb(II))

and As(III) and bacterial pathogens (*Escherichia coli*) from water [19]. The unique property of magnetite nanoparticles which enables their use as adsorbent of Lead ions is the larger surface area and presence of hydroxy groups as reactive sites [20].

The validation of the synthesized magnetite nanoparticles was done by UV-Visible spectroscopic analysis. The absorption band was observed at 316.8nm (Fig1) which is according to the previously reported literature [13]. The absorbance band in the visible range between 330-450nm indicates the formation of particles of nanodiameter [21]. The crystal structure was verified using x-ray diffraction (XRD) and the size of the magnetite nanoparticles analyzed using Deby - Scherrer equation [22] and was found to be 4.3nm (Fig 2). The data obtained is very close to the JCPDS card no.89-0691 which will prove that the prepared nanoparticles was made of iron oxide [23]. The XRD pattern of Magnetite nanoparticles obtained by co-precipitation method shows the characteristic peaks at 35.2°(311), 43.1°(400), 53.4°(422), 57.1°(511) and 62.8°(440) were observed which indicate the crystalline nature and phase purity of the synthesized magnetite nanoparticles. The literature shows that the magnetite

nanoparticles of size less than 30nm exhibit a greater paramagnetic property which enables easy separation from the applied regions in presence of external magnetic field [24]. Magnetite nanoparticles synthesized by co-precipitation method using different reagents like  $FeCl_3 \cdot 6H_2O$ ,  $FeCl_2 \cdot 4H_2O$ , propylene glycol and ammonium hydroxide had a mean particle size diameter of 8nm [25]. The small size of the nanoparticles determines their nanocrystalline nature [26]. The morphology of the magnetite nanoparticles was determined using SEM (Fig3). The figure shows the spherical magnetite nanoparticles synthesized by co-precipitation method. The magnetite nanoparticles agglomerated to a little extent because of their small size and more surface energy. The size is approximately >10nm indicating the synthesis of homogenous nanoparticles. TEM analysis confirmed the size of the magnetite nanoparticles to be below 10nm(Fig4.a). From the SAED pattern it can be inferred that as observed in XRD, SAED also shows characteristics patterns which explain the phase purity of the magnetite nanoparticles (Fig4.b).

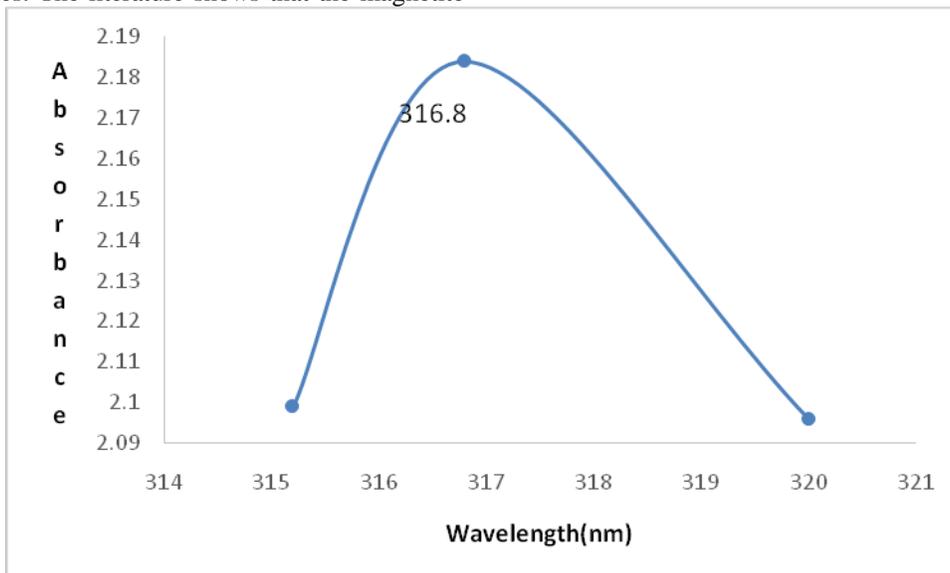
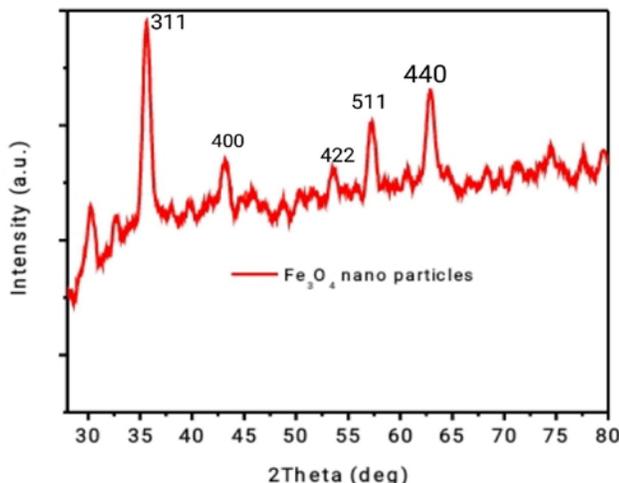
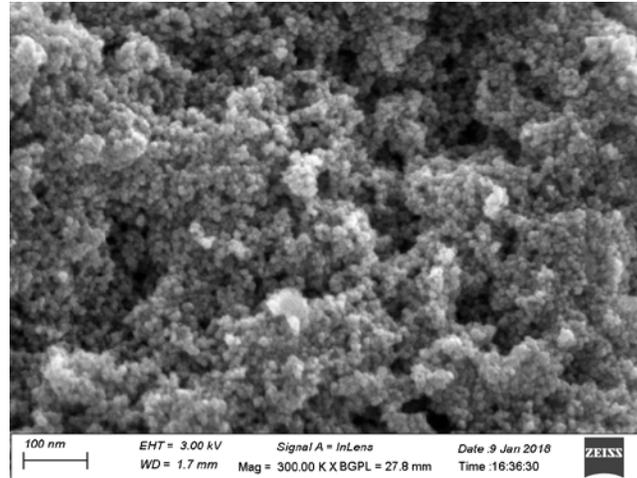


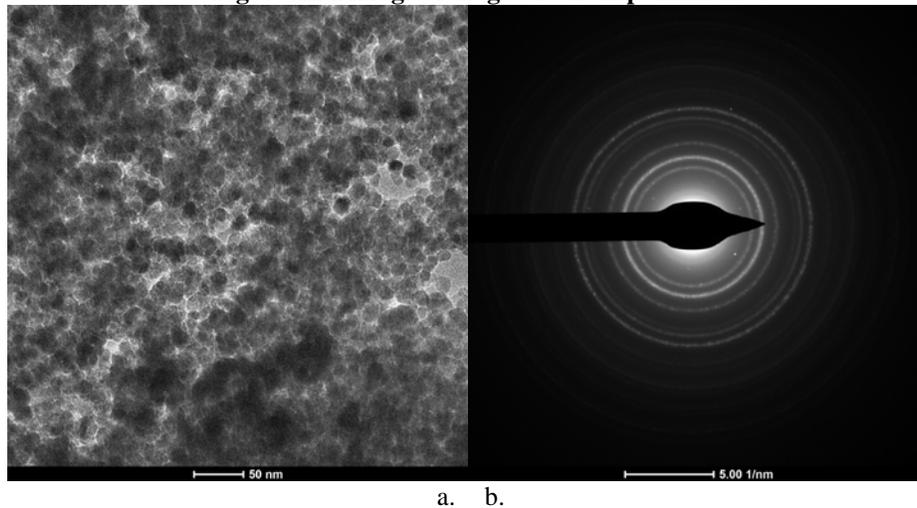
Fig.1: UV-VIS absorption spectra of magnetite nanoparticles



**Fig .2: X-Ray diffraction patterns of magnetite nanoparticle**

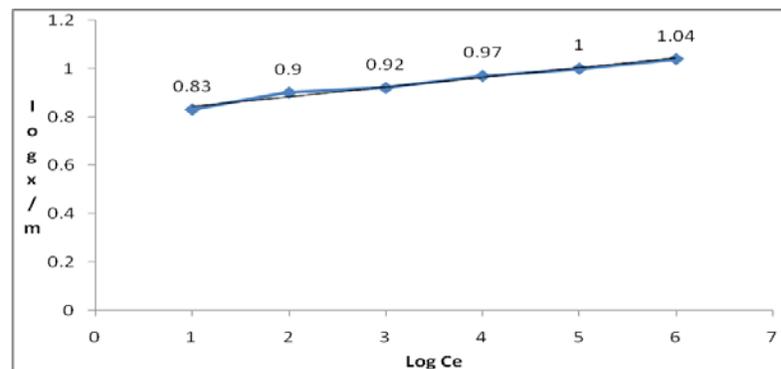


**Fig 3: SEM image of magnetite nanoparticles**



**Fig 4. TEM image of Magnetite nanoparticles (a),SAED pattern of magnetite nanoparticles(b)**

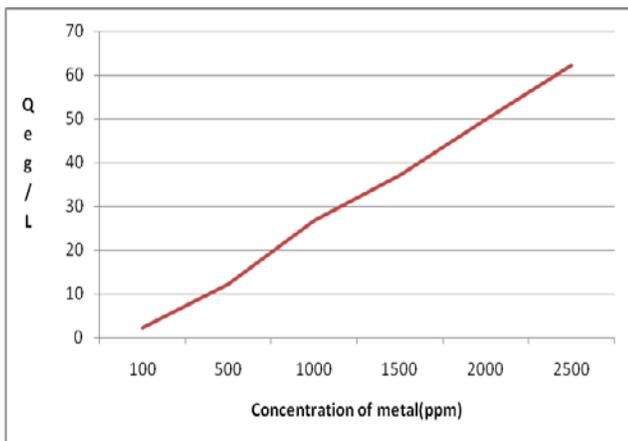
**Adsorption isotherms:** Freundlich- Languimer adsorption isotherm model was used to determine the monolayer formation or the heterogeneity of the adsorbate onto the surface of the adsorbent. Different concentrations of Lead solution were taken ranging from 100ppm to 2500ppm. The experimental data obtained from adsorption of Lead ions onto the surface of magnetite nanoparticles are presented (Fig6). The correlation coefficient of the Languimer -Freundlich isotherm was above 1 which indicated a deviation from the monolayer adsorption of the Lead ions onto the magnetite nanoparticles. The literature shows that if the  $1/n$  values are less than unity it indicates the significant adsorption at low concentration and as the concentration increases the amount adsorbed becomes less significant [27]. The non-linearity may be because of the hydrophobic nature of Lead ions and presence of polar functional groups which compete with water molecules for adsorption sites [28].



**Fig 6: Languimer–Freundlich adsorption isotherm of Lead adsorbed onto magnetite nanoparticles.**

**Metal adsorption by Magnetite nanoparticles:** The amount of metal adsorbed by the magnetite nanoparticles was determined using Atomic absorption spectrophotometer (Fig 5). A range of metal concentrations were taken from 100ppm to 2500ppm. It was observed that as the concentration of metal increased the amount of metal (g) deposited on the surface of

magnetite nanoparticles also increased. The maximum amount adsorbed on 1g of magnetite nanoparticle at 2500ppm concentration of metal was 62.189g. According to earlier studies Magnetite nanoparticles. Previous studies reveal that Magnetite nanoparticles can adsorb maximum upto 2.072ppm of Lead ions [29]. From the study it was observed that the concentration of the metal adsorbed onto the surface of the nanoparticle increased with increase in the concentration of the metal ions, this may be due to the formation of multilayers on the surface of the adsorbent enabling higher intake of metal. The small size of the nanoparticles favours the diffusion of metal ions from a bulk solution onto the active sites of the adsorbent at a higher rate [30]. The amount of Lead removed by magnetite nanoparticles increases with the increase in the contact time between the metal and the adsorbent [31, 32, 33]. The uptake of Lead ions by magnetite nanoparticles is by physico-chemical interactions between the adsorbent and the adsorbate [27]. In aqueous solutions the hydrated ionic radius of Lead ions is low which enables highest adsorption capacity towards the protons on the adsorbent [34]. So there is greater adsorption of the metal observed onto the magnetite nanoparticles.



**Fig 5: Concentration of metal(g) adsorbed on the surface of nanoparticles**

#### IV. CONCLUSION

The current work concludes the use of magnetite nanoparticles synthesized by co-precipitation method with a size of 4.3nm as effective adsorbents of Lead ions (Pb II). The magnetite nanoparticles had maximum adsorption capacity upto 2500ppm which enable their use in highly contaminated Lead soils. The ease in the recovery and reuse of the magnetite nanoadsorbents from the applied sites reduces the economical burden.

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#### REFERENCES

- [1] M. Fujita, Y. Ide, D. Sato et al. "Heavy metal contamination of coastal lagoon sediments: fongafale islet, Funafuti atoll, tuvalu," *Chemosphere*, 2014. vol. 95, pp. 628–634.
- [2] *Bulletin Waste Management World*, Undercover investigations into e-waste smuggling, May 16, 2011.
- [3] *Toxics Link*. E-Waste in Chennai Time is running out. www.toxicslink.org accessed on 14th June, 2006.
- [4] Ruchi Chauhan, Kanjan Upadhyay, Removal of Heavy metal from E-Waste: A review, 2015.
- [5] Gurcharan Dass, E-Waste management: Solid waste management in India, 2016.
- [6] Pragnesh N. Dave and Lakhan V. Chopda, Application of Iron Oxide Nanomaterials for the Removal of Heavy Metals, *Journal of Nanotechnology*, 2014, pp.1-14.
- [7] Mutasim I. Khalil, Co-precipitation in aqueous solution synthesis of magnetite nanoparticles using iron(III) salts as precursors *Arabian Journal of Chemistry*, 2015, 8, 279–284.
- [8] Yufei Li, Xiaoyu Du, Chao Wu, Xueying Liu, Xia Wang and Ping Xu, *Nanoscale Research Letters*, 2013, 8:522
- [9] L. Giraldo, A. Erto, Napoli Federico II, C. Moreno-Piraján, Magnetite nanoparticles for removal of heavy metals from aqueous solutions: synthesis and characterization *Adsorption* 2013, 19:465–474
- [10] Freundlich, H.M.F, Uber Die Adsorption in Losungen. *Zeitschrift für Physikalische Chemie*, 1907, 57, 385 – 470.
- [11] Rashmi Kumar, Dahyalal. J. Shah (2014) Review: Current Status of Recycling of Waste Printed Circuit Boards in India, *Journal of Environmental Protection*, 5, 9-16.
- [12] Tungittiplakorn W, Lion LW, Cohen C, Kim JY (2004), Engineered polymeric nanoparticles for soil remediation. *Environ Sci Technol*, 38:1605–1610.
- [13] Zhang, W.(2003), Nanoscale iron particles for environmental remediation: An overview. *J. of Nanoparticle Res.* 5: 323–332.
- [14] Shan GB, Zhang HY, Cai WQ, Xing JM, Liu HZ(2005). Improvement of biodesulfurization rate by assembling nanosorbents on the surface of microbial cells. *Biophys J*, 89:L58–L60.
- [15] Shan GB, Xing JM, Zhang HY, Liu HZ(2005): Biodesulfurization of dibenzothiophene by microbial cells coated with magnetic nanoparticles. *Appl Environ Microbiol*, 71:4497–4502.
- [16] R. El-kharrag1, A. Amin1, Y. E. Greish(2011) Synthesis and Characterization of Mesoporous Sodium Dodecyl Sulfate-Coated Magnetite Nanoparticles *Journal of Ceramic Science and Technology*, Vol. 2, No. 4
- [17] Wang X, Zhao C, Zhao P, Dou P, Ding Y, Xu P(2009) Gellan gel beads containing magnetic nanoparticles: an effective biosorbent for the removal of heavy metals from aqueous system. *Bioresour Technol*, 100:2301–2304.
- [18] Ponder SM, Darab JG, Mallouk TE(2000) Remediation of Cr(VI) and Pb(II) aqueous solutions using supported nanoscale zero-valent iron. *Environ Sci Technol*, 34:2564–2569.
- [19] Liliana Giraldo, Alessandro Erto, Juan Carlos Moreno-Piraján (2013), Magnetite nanoparticles for removal of heavy metals from aqueous solutions: synthesis and characterization *Adsorption* 19:465–474.
- [20] S. Singh, K.C. Barick and D. Bahadur (2011), Surface engineered magnetic nanoparticles for removal of toxic metal ions and bacterial pathogens, *Journal of Hazardous Materials* 192, 1539-1547.
- [21] Koutzarova T., Kolev, S., Ghelev, C., Paneva, D., Nedkov, (2006) *I. Phys. Stat. Sol. (c)*, 3 (5) 1302.
- [22] Berrington de Gonzalez A.; Darby S. *Lancet*. 363 (2004) 345.
- [23] D. Princess Jeba et al.(2018), Synthesis and Characterisation of Fe<sub>3</sub>O<sub>4</sub> Nanoparticles *International Journal of Recent Research Aspects Special Issue: Conscientious Computing Technologies*, pp. 808-810
- [24] Y.T. Zhou, H.L. Nie, C. Branford-White, Z.Y. He and L.M. Zhu (2009) Removal of Cu<sup>2+</sup> from aqueous solution by chitosan-coated magnetic nanoparticles modified with α-ketoglutaric acid, *Journal of Colloid and Interface Science* 330 29-37.
- [25] Y. F. Shen, J. Tang, Z. H. Nie, Y. D. Wang, Y. Ren, and L. Zuo, "Preparation and application of magnetic nanoparticles Fe<sub>3</sub>O<sub>4</sub> for water purification," *Separation and Purification Technology*, vol. 68, pp.312-319, 2009.

- [26] L. Sophie, F. Delphine, P. Marc, R. Alain, R. Caroline, V. E. Luce, and N. M. Robert (2008), "Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterization, and biological applications," *Chem. Rev.*, vol. 08, pp.2064-2110.
- [27] Ho, Y.S., McKay, G.(1998), Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* 70, 115–124 .
- [28] Technical report 123, Adsorption-desorption distribution (Kd) and organic carbon-water partition (KOC) coefficients, European Centre For Ecotoxicology and toxicology of Chemicals
- [29] L. Giraldo, Bogota, A. Erto, J. C. Moreno-Piraján (2013) Magnetite nanoparticles for removal of heavy metals from aqueous solutions: synthesis and characterization, *Adsorption*, 19:465–474.
- [30] Areej. A. Jarullah, Mahasin. F. Alias and Karim H Hassan (2014), "Purification of aqueous solution from Ni(II) ions using commercial and Bitter Orange leaves activated charcoal", *Journal of Al-Nahrain University Science*, 17, 1, 32-40.
- [31] X.S. Wang et al. (2010), Adsorption of Lead(II) Ions onto Magnetite nanoparticles / *Adsorption Science & Technology* Vol. 28 No. 5 .
- [32] Z.Cheng, A.L.K.Tan, Y.Tao, D.Shan, K.E.Ting, and X.J.Yin (2012), "Synthesis and Characterization of Iron Oxide Nanoparticles and Applications in the Removal of Heavy Metals from Industrial Wastewater", *International J Photoenergy*, 1-5.
- [33] A. Imtiaz and U.Rafique (2011). "Synthesis of Metal Oxides and its Application as Adsorbent for the Treatment of Wastewater Effluent", *International Journal of Chemical and Environmental Engineering*, 2, 6, 399-405.
- [34] Ko, D.C.K., Cheung, C.W., Keith, K.H., Choy, Porter, J.F., McKay, G (2004).: Sorption equilibria of metal ions on bone char. *Chemosphere*, 54, 273–281

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