ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND SYNTHETIC APPLICATIONS OF Fe_3O_4/HA/Ag NANOPARTICLES

M.Sc. THESIS

Gözde Mediha KAMER

Department of Chemistry

Chemistry M. Sc. Programme

Thesis Advisor: Prof. Dr. Birsen DEMİRATA ÖZTÜRK

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

Fe_3O_4/HA/Ag NANOPARÇACIKLARININ SENTEZİ VE SENTETİK UYGULAMALARI

YÜKSEK LİSANS TEZİ

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AĞUSTOS 2012

Gözde Mediha KAMER, a **M.Sc.** student of ITU **Institute of / Graduate School of Science** 509091047, successfully defended the **thesis** entitled "SYNTHESIS AND SYNTHETIC APPLICATIONS OF Fe_3O_4/HA/Ag NANOPARTICLES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Birsen ÖZTÜRK** İstanbul Technical University	....
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To my family,

FOREWORD

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Gözde Mediha KAMER
(Chemistry Teacher)

TABLE OF CONTENTS

Page

ABBREVIATIONS

App **:** Appendix
DLS **:** Dynamic Light Scattering
DVLO **:** Derjaguin, Verwey, Landau and Overbeek theory
EDS **:** Energy Dispersive Spectroscopy
EDXD **:** Energy Dispersive X-ray Diffraction
HA **:** Humic Acid
NOM **:** Natural Organic Matter
NP **:** Nanoparticle
SEM **:** Scanning Electron Microscope
TEM **:** Transition Electron Microscope
PVA **:** Polyvinyl Alcohol

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYNTHESIS AND SYNTHETIC APPLICATIONS OF Fe_3O_4/HA/Ag NANOPARTICLES

SUMMARY

Heavy metal pollution occurs as a result of industrial wastewater and it threats the life in soil and water. Recently in conclusion with the new regulations, the track and removal of heavy metal concentration in wastewater became an obligatory process. Silica, activated carbon, humic acid and magnetite are the examples of materials that have used for this purpose. Humic acid is a type of natural organic matter and it's been formed as a result of the decomposition of animal and plant residues in soil. Humic acid is the most widely found structure in Earth's crust. It contains oxygenated groups such as carboxylic acid and phenol. The charge of these groups allows heavy metal ions to bind on the surface of humic acid. This property makes it a very useful tool in terms of heavy metal removal process. They can also be used in different forms. Developments in nanoparticle technology and more eco-friendly synthesis methods made magnetic nanoparticles a very popular solution in heavy metal removal applications. There are many different types of magnetic nanoparticles and magnetite, Fe_3O_4, is one of them. A method for the synthesis of Fe_3O_4 nanoparticles is called co-precipitation. In this method a stoichiometric mixture of ferrous and ferric chloride mixtures are reduced in the presence of a reducing agent such as Polyvinyl alcohol (PVA). A disadvantage of these particles is their easy oxidation and agglomeration. In order to prevent this and increase the application field particles are being coated with different structures. As a result of the combination of different composite nanoparticle structures a new type of nanoparticle called multi-functional nanoparticles is formed.

The aim of this work is to find the removal percentage of copper and cadmium ions from synthetic solutions by using synthesized Fe_3O_4/HA/Ag multifunctional nanoparticles. In the structure magnetite represents the magnetic property, humic acid represents metal binding property and silver represents anti-bacterial property. During synthesis, first stage consists of the formation of magnetite structure and its coating with humic acid. In this stage Fe^{+2} and Fe^{+3} chloride solutions were heated up to 90 ^{0}C for 40 minutes, humic acid sodium salt solution is added and reduction was made in a 25% NH_3 solution. Later by using Tollen's reagent (ammoniacal silver nitrate solution) silver is reduced to cover the surface of synthesized particles. In this stage redox reaction between silver and tin was used. Synthesis was made in air atmosphere and particles were dried in 60 ^{0}C. Characterization of particles was made with Scanning electron microscope. In order to determine the parameter of removal percentage of heavy metal ions optimization was made and initial and final concentration of metal ions were found with Atomic Absorption Spectrometer. The concentration of magnetic nano-adsorbent was fixed at 20 mg particle/25 mL solution. Unless otherwise specified, the adsorption experiments were performed in aqeous solution at pH 9 and 300 K. Removal percentage of copper and cadmium was found between 92% and 97%, respectively.

Fe_3O_4/HA/Ag NANOPARÇACIKLARININ SENTEZİ VE SENTETİK UYGULAMALARI

ÖZET

Ağır metal kirliliği günümüzde sanayi atıkları ile birlikte oluşmakta, toprakta ve suda birikerek canlı hayatı tehdit etmektedir. Son yıllarda yasal düzenlemelerin yapılması ile birlikte sanayi atıklarında ağır metal konsantrasyonlarının takibi ve giderilmesi zorunlu hale getirilmiştir. Bu amaçla sentezlenen ve kullanılan malzemelere aktif karbon, silika, hümik asit ve magnetit örnek olarak verilebilir. Hümik asit (HA) doğada hayvan ve bitki atıklarının bozunması sonucu oluşmaktadır. Sahip olduğu oksijen içeren karboksilik ve fenolik grupların yüklerine bağlı olarak doğadaki metaller ile kompleks oluşturma kapasitesine sahiptirler. Bu özellikleri dolayısı ile de ağır metal temizliğinde farklı şekillerde kullanılmaktadırlar. Nanoparçacık teknolojisinin gelişmesi ve çevre dostu sentez yöntemlerinin kullanılması ile birlikte ağır metal temizliğinde magnetik nanoparçacıklar rağbet gören bir çözüm yolu olmuştur. Magnetik nanoparçacıkların boyutu biyoteknoloji uygulamalarında da kullanılmalarını sağlamaktadır. Oksitlenme ve kümelenmedir geniş yüzey alanı/hacim oranı sebebi ile magnetik nanoparçacık sentezinde en fazla görülen sorunlardır.Bunun giderilmesi içinde yüzeyin uygun ve amaca yönelik bir madde ile kaplanması tercih edilmektedir. Kaplama işlemi bu sorunları gidereceği gibi, kompozite yapının daha fazla fonksiyona sahip olmasına da olanak sağlayacaktır. Kaplama amaca uygun olarak organik veya inorganik maddeler ile yapılabilmektedir. Kaplama sonucu oluşturulabilen yapılardan biri de çekirdek/kabuk yapılardır. Çekirde/kabuk yapılarda kabuğun oluşturulması için ortamın polar veya apolar olma durumu önemlidir. Ancak polar ortamlarda kabuk yapının oluşması başarıya ulaşmaktadır. Farklı komposit nanoparçacık yapılarının birbirleri ile oluşturdukları yeni yapılara çok fonksiyonlu nanoparçacıklar adı verilir. Bu tür yapılar, ek olarak kabuğun üzerine farklı maddelerin tutturulması ile oluşturulurlar.

Kompozit yapıların kimyasal sentez yollarından biri çöktürme ile sentezdir. Bu yöntemin diğer kimyasal sentez yöntemlerine göre avantajlarının yanında dezavantajları da olabilmektedir. Bu yöntemde sentez dakikalar içerisinde ve çok yüksek sıcaklık değerlerine çımadan gerçekleştirilebilmektedir. Çözücü olarak su kullanılmaktadır. Dolayısı ile sentez diğer yöntemlere göre daha kolaydır. Şekil kontrolünü sağlamak ise diğer yöntemlere kıyasla daha zordur. İstenilen büyüklüklerin sağlanması için ortam koşullarının optimum seviyeye ayarlanması gerekmektedir.

Parçacıklar sentezlendikten sonra uygulanabilecek karakterizasyon yöntemleri yüzeyin elemental analizine de uygun olarak seçilmelidir. Bu açıdan EDX ile desteklenmiş Taramalı elektron mikroskopu tercih edilebilir. Taramalı elektron mikroskobunda numunenin iletkenliği önemlidir, numunenin iletken olmadığı durumlarda ise ayrı bir kaplama yapılmaktadır. Taranan alandaki maddenin iletkenliğine göre cihazdan gönderilen ışının yansıması değişmekte ve sentezlenen yapının görüntüsü iletken kısımlara göre daha parlak veya daha koyu olmaktadır. Numunenin cihaza verilişinde farklı şekiller mevcuttur, bunlardan bir tanesi mekanik öğütme yöntemidir. Bu yöntemde parçacıklar mümkün olan en ince şekilde öğütülerek bir yüzeye yapıştırılır ve cihaza verilir. Taramalı elektron mikroskopunda verilen numune kalınlığının bu sebepten 10 nm'yi geçmemesi gerekmektedir. Taramalı elektron mikroskopu, diğer mikroskobik yöntemlere göre daha düşük

görüntü çözünürlüğüne sahiptir. Bu sebepten farklı karakterizasyon yöntemleri ile muhakkak desteklenmesi gerekmektedir. Bu çalışmada görüntüyü destekleyen diğer yöntemler zeta potansiyel analizi ve dynamic light scattering (DLS) yöntemidir. Zeta potansiyel analizinde kolloidal sistemin yüzeyinde yüklerin potansiyeli mV cinsinden ölçülmektedir. Çıkan değerin -30 ve +30 mV arasında olması önemlidir. Değerin pozitif veya negatif olması yüzeydeki yüklerin cinsini göstermektedir. DLS yönteminde brown hareketinde dayanarak parçacıkların büyüklüğü analiz edilir.

Nanaoparçacıklar çok çeşitli alanlarda uygulamaya sahiptirler. Çevre uygulamaları da bunlardan biridir. Magnetik ayırma teknikleri genel olarak magnetik nanoparçacıkların metal kirliliği olan ortama uygulanmasından sonra basit bir magnet yardımı ile toplanmalarına dayanmaktadır. Hızlı ve sonuç veren bir yöntemdir. Ayırma ile birlikte ortam konsantrasyonunu artırma amacı ile de kullanılabilmektedir.

Çalışmamızda Fe_3O_4 magnetit nanoparçacıklar Fe^{+2} ve Fe^{+3}'ün kimyasal çöktürme yöntemi kullanılarak sentezlenmektedir. Parçacıkların çabuk oksitlenmeleri ve kümelenme yapmalarını önlemek amacı ile de parçacık yüzeyi farklı bir materyal ile kaplanarak hem daha dayanıklı hale getirilir, hem de uygulama alanı artırılır.

Bu çalışmanın amacı kimyasal çöktürme yöntemi ile sentezlenen Fe_3O_4/HA/Ag çok fonksiyonlu nanoparçıkların sentetik hazırlanan bakır(II) ve kadmiyum(II) çözeltilerini temizleme yüzdesini hesaplamaktır. Fe_3O_4'in magnetik özelliği, hümik asit'in ağır metal temizleme kapasitesi, gümüşün ise antibakteriyel özellikleri kompozit oluşturmada göz önüne alınmıştır. Sentez aşamasında 1. kısım Fe_3O_4 yapısının oluşturulması ve bu yapının hümik asit ile kaplanmasıdır. Bu kısımda Fe^{+3} ve Fe^{+2} içeren çözeltiler 90 ^{0}C'ye ısıtılmış, 100 ppm hümik asit sodyum tuzu çözeltisi ortama ilave edilmiş ve indirgeme 10 mL %25 NH_3 çözeltisi ortamında yapılmıştır. Bu sayede Hümik asit kaplı magnetit yapısı oluşturulmuştur. İkinci kısım gümüşün yapıya bağlanmasıdır, bağlanmanın gerçekleşmesi için öncelikle mevcut kompozit yapı Kalay(II)klorür çözeltisinde bekletilmiş ve ultrasonik banyo işleminden sonra Tollen's reaktifi (Amonyaklı gümüş nitrat çözeltisi) süspansiyona eklenmiştir. Tollen's reaktifi çabuk bozulduğundan her denemede tekrar hazırlanmaktadır. Burada amaç kalay ve gümüş arasındaki redoks reaksiyonundan faydalanarak gümüşün önceden olutşturulan yapıya kolaylıkla bağlanmasını sağlamaktır. Sentezlenen parçacıklar 60^{0}C'de kurutulmuştur.

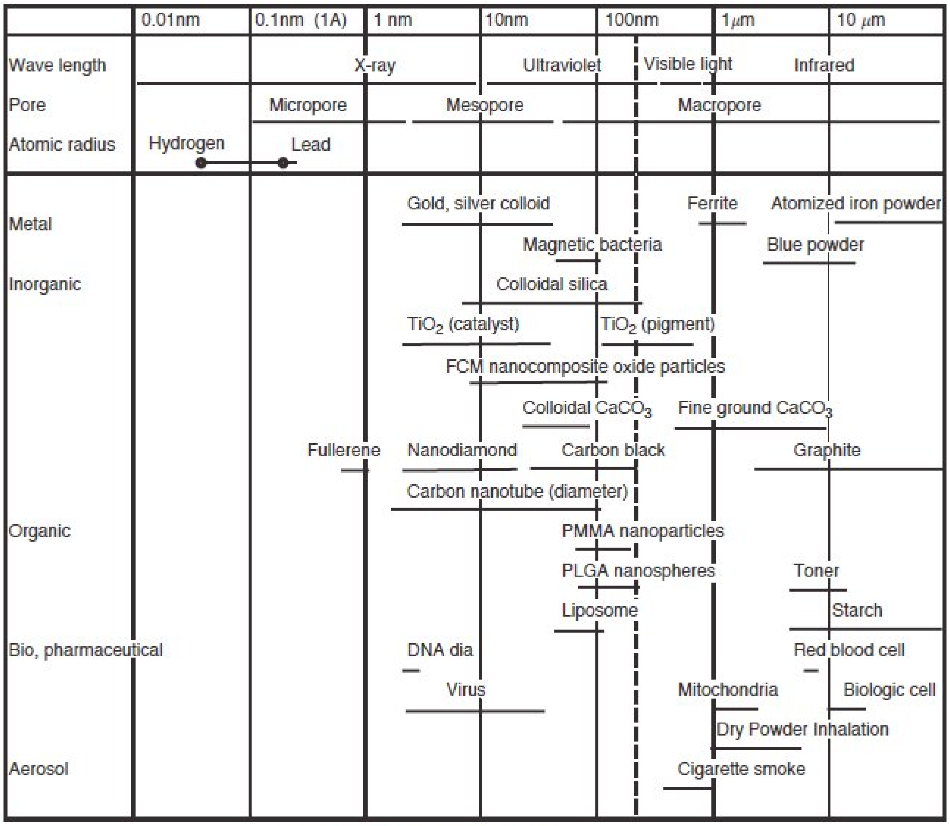
Parçacıkların karakterizasyonı için Taramalı Elektron Mikroskopu kullanılmıştır. Taramalı elektron mikroskobunda çözünürlük çok fazla olmadığında görüntülerde x50000 büyütmeden öteye gitmek mümkün olmamıştır ancak görüntülerde gri kısımlar hümik asiti beyaz kısımlar ise gümüşü göstermektedir. Taramalı elektron mikroskopunda yer alan elemental analiz programı (EDX) yapının seçilen bölgelerinin ayrıca elemental analizinin yapılmasına da olanak sağlamıştır. EDX sonuçlarıda ortamda gümüşün başarılı bir şekilde bağlandığını ve Kalay gideriminin gerçekleştiğini göstermektedir. Taramalı elektron mikroskobu sonuçları zeta potansiyel analizi ve DLS ile desteklenmiştir. Zeta potansiyel analizi koloidal yapı yüzeyinin -23.09 mV yani negatif yüklü olduğunu gösterdi. DLS sonuçları ise kolloidal parçacık büyüklüğünün 291 nm olduğunu göstermiştir. Bu sonuçlar sentezlenen yapının magnetik ayırma yöntemi için uygun olduğunu ve istenen amaçla kullanılabileceğini göstermektedir.

Sentezlenen ve özellikleri belirlenen parçacıkların ağır metal giderimi parametrelerinin berlirlenmesi amacı ile optimizasyon çalışmaları yapılmıştır. Bu çalışmalar sırasında optimum parametreler pH, nanoparçacık miktarı ve süre olarak belirlenmiştir. Çalkalama yöntemi ile yapılan çalışmalarda metal iyonu çözeltilerinin başlangıç ve çözeltide kalan konsantrasyonları Atomik Absorbsiyon cihazı kullanılarak ölçülmüştür. pH belirleme çalışmasında pH 3, 5, 7 ve 9 değerlerine sahip farklı örnekler hazırlanmıştır. Parçacık miktarında 5, 10, 15, 20 ve 25 mg seçilmişir. Süre parametresi ise 5, 10, 20, 25, 30 dakika olarak belirlenmiştir. Herbir çalışmada incelenen değerler haricindeki tüm koşullar sabit tutulmuştur. Optimizasyon çalışmaları sonucunda pH değeri 9, parçacık miktarı 20 mg/25 ml çözelti ve adsorpsiyon süresi 20 dakika olarak berlirlenmiştir. Sentezlenen parçacıklar ile bakır(II) ve kadmiyum(II) giderim yüzdeleri yaklaşık %92- %97 aralığında bulunmuştur.

1. INTRODUCTION

1.1 Nanoparticle Technology

The prefix nano is used to denote one billionth. Here, nanometer defines one billionth of 1m or one millionth of 1 mm. Although there is not a specific definition of nanoparticles (NP's), generally they are called as particles from 1 nm to 100 nm. This size usually depends on the material, field or application used (Hosokawa et al, 2007; Okuyama et al, 1992). NP's exist both in the realm of quantum and Newtonian physics. Some examples of nanoparticles can be seen below as figure 1.1.



FCM : Flash Creation Method
PLGA : Poly-lactic-glycolic acid (Spherical crystallization method)
PMMA : Polymethylmethacrylate

Figure 1.1 : Examples of nanoparticles and related phenomena (Hosokawa et al, 2007).

The study of Nanotechnology is an interdisciplinary area between fundamental sciences which are physics, chemistry and biology and applied sciences which are electronics and materials. It has a wide variety of applications from electronics to cosmetics (Wen-Tso, 2006; Penn et al, 2003; West and Halas, 2000).The first study of Nanoparticles Technology starts in 19th century. Faraday was the first scientist who has prepared the colloids of relatively monodispersed gold particles. Over the past 20 years, the study of nanoparticles that have 1-20 nm diameter has become a major interdisciplinary area (O'Brien and Pickett, 2001; Berry, 1967). The great potential and easy manipulation of nanoparticles allowed scientist to develop new technologies and products (Ghosh et al, 2008; Guzman, 2006).

Nanoparticles may have different forms such as spherical, tubular and aggregated or agglomerated. The chemical and physical properties change drastically between bulk material and nanosize particles. As a result of the small surface area/volume ratio, new physical properties like melting point and dielectric constant will be occurred. (Parham and Rahbar, 2009; Hosokawa et al, 2007). This change in physical, elecronic, optical and mechanical properties called "size effect" (Hosokawa et al, 2007). In some cases the major disadvantage of nanoparticles is the aggregation which can be caused by the small size and large surface area. Aggregation makes physical handling of nanoparticles very difficult when they are liquid or dry. The preparation of nanoparticles depends on many factors such as size of particles required and surface characteristics etc. (Mohanraj and Chen, 2006; Bhadra et al, 2002; Langer, 2000).

According to Hosokawa et al. (2007) "particle size is a term to represent the three-dimensional particle in one-dimensional scalar value" (p.10). It is important to obtain the mean particle size and distribution and reduce agglomeration (Hosokawa et al, 2007). According to the type of materials they produced, nanoparticles are classified into three groups: Metallic, semiconductor and polymeric nanoparticles. Magnetic nanoparticles are produced from metallic type of nanoparticles and they can be attracted with a magnet (Wen-Tso, 2006; Ito et al, 2005; Tanaka et al, 2005).

1.2 Magnetic Nanoparticles

According to Hosokawa et al. (2007) classification of magnetism and magnetic materials are mentioned as below (p.42).

1. Feeble magnetism

-Diamagnetism

- Paramagnetism
- Super-magnetism

2. Antiferromagnetism

- Antiferromagnetism
- Herimagnetism
- Metamagnetism

3. Ferromagnetism

- Parasitic ferromagnetism
- Ferrimagnetism
- Ferromagnetism

Magnetism of metal materials

(1) Transition metals (I) Fe, Co, Ni Ferromagnetism

(2) Transition metals (II) Cr, Mn, _Fe Antiferromagnetism

(3) Transition metals (III) Others Paramagnetism

(4) Rare earth metals Ferromagnetism or Antiferromagnetism

(5) Other metals Paramagnetism or Antiferromagnetism

Basically diamagnetism occur as a result of the response of electron's orbital motion to an externally applied magnetic field. Diamagnetism is very weak and can be overpowered by any other type of magnetism. Other type of magnetisms results from the unpaired electrons, especially in 3d and 4f shells. If magnetic moment is uncoupled, this type of magnetism is called paramagnetism. In case of ferromagnetism atoms have equal magnitude and this cause direct coupling between moments. Ferromagnetism can be observed with Fe, Ni and Co. These materials have magnetic property without an external field. In ferrimagnetism magnetic moments are unequal (Faraji et al, 2010; Chen, 1986).

The size of magnetic nanoparticles allow them to be compared to the size of a virus which is 20±500 nm, a protein which is 5±50 nm or a gene which is 2 nm wide and 10±100 nm long. This results the use of magnetic nanoparticles in biotechnology very easily (Indira and Lakshmi, 2010; Tartaj et al, 2004).

Iron oxide nanoparticles have particle sizes less than 40 nm and large surface area. Although there are many applications of magnetic nanoparticles, usually their use depends on their stability. To obtain the stability particle size must be below the critical value which is between 10-20 nm. This size allows them to have single magnetic domain and superparamagnetic behaviour. In nature magnetite, Fe_3O_4, is a ferrimagnetic material but when it is nano-sized, it represent superparamagnetic property when it is attracted by an external magnetic field. This property makes Fe_3O_4 very useful for separation process (Yantasee et al, 2007; O'handley, 2000). Their low toxicity and biocompatibility also make iron oxide nanoparticles very environmental friendly and popular in biotechnology applications.

There are three advantages of using nanometer-size iron oxide particles. First one is the large surface/volume ratio, as a result of this ratio, surface properties overcome the nanostructure. Second advantage is their small size. As mentioned earlier small size changes the magnetic property and allow them to have superparamagnetic behaviour. Third one is their easy synthesis procedure which have low temperature and spend time.

There are also disadvantages of using iron oxide particles. With the large surface area iron oxide particles react with the oxygen in the air and each other, these cause oxidation and agglomeration. As a result of the oxidation they lose magnetism and dispersibility. In order to avoid these problems coating of the iron oxide surface has become a very popular application and different inorganic or organic materials have been used to do so, such as polymers, organic species, silica or carbon. This shell also help them to have different properties (Qiu et al, 2009; Chin and Yaacob, 2007; Lu et al, 2007).

Recently magnetic nanoparticles are used to produce multifunctional naoparticles. Producing multifunctional nanoparticles have advantages. First oxidation and agglomeration is being overcome and second, with every different structure attached to the core, particles have different functions. To do this there are two different routes to follow. First one is called molecular functionalization. Coating is being made with a biofunctional molecule. This allows them to interact with a biological entity. Second route is to combine them with other functional nanostructures (Gao et al, 2009; Gu et al, 2005; Kim et al, 2005).

1.3 Stability Achievement Methods for Particles

Stability of synthesized particles is very important and in order to maintain this stability its necessary to have a layer that protect the particle from oxidation. Stabilization and protection is usually considered as very close definitions (Lu et al, 2007; Lu et al, 2005; Kobayashi et al, 2003). In order to avoid oxidation and agglomeration coating of nanoparticles has been made with variety of materials such as carbon, silica, metal oxides, surfactants etc.

1.3.1 Organic coatings

Surfactants and polymers are the organic type of coating materials. These materials are used during or after the synthesis of nanoparticles to passivate the surface and avoid agglomeration. There are different ways for the synthesis of organic material coated nano particles including in situ and/or after synthesis procedures. These procedures depend on to the stabilization of particles by dispersing them.

1.3.2 Inorganic coatings

Metal oxides are an example and mostly used type of inorganic coatings. Their synthesis and coating process is very easy due to the oxidation of metal ion. Particles should be synthesized during the controllable oxidation of metal core. Precious metals like silver and gold, silica and carbon are other examples of inorganic coatings. For both of these methods Strategies for surface functionalization has been purposed as two different routes. Ligand addition method includes double layer structure on the surface of particles. Here incoming ligands are used to cover original ligands. In ligand exchange method there is the replacement of original ligand and bifunctional ligand (Faraji et al, 2010).

1.4 Composite Structures

According to Hosokawa et al. (2007) defines classification of composite structures and their images are as follows (p.23).

Table 1.1 : Classification of composite structures (Hosokawa et al, 2007).

Classification	Type of composite structure
1) The composite structure using NPs.	a) Core-shell, b) internal dispersion, e) hollow, f) porous,
2) The composite structure formed from afflomeration of NPs.	a) Core-shell, b) internal dispersion, c) agglomeration, d) coating (surface modification), e) hollow, f) porous,
3) The composite structure body fabricated from NPs.	g) nano dens body , h) nano porous body, i) nano thin film

Classification has been made according to the pore structure. Dispersibility, cohesive property, porosity and compact density are the physical properties of the composite structures. These structures can be made with two or more type of particles (Hosokawa et al, 2007). Figure 1.2 exibits the type of nanoparticles classified on table 1.1.

(a) Core shell

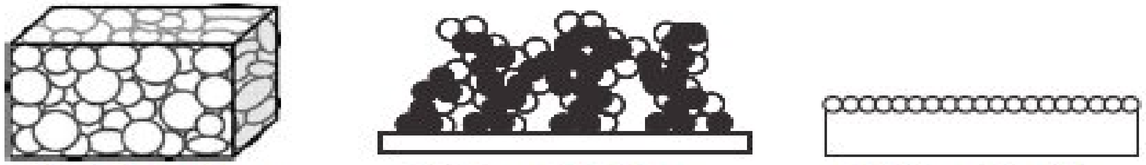
(b) Internal dispersion

(c) Agglomeration

(d) Nanoparticle coating

(e) hollow

(f) Porous



(g) Bulk body from nanograins

(h) Porous body from nanograins

(i) Nano thin film

Figure 1.2 : Images of composite structures (Hosokawa et al, 2004).

1.4.1 Core/shell structure

This structure was first used with semiconductor materials and since then it's been used widely and studied extensively. Magnetic/metallic core/shell structure formation can be made with redox transmetalation (Faraji et al, 2010).

Zeng and Sun (2008) represent the image of the mechanism of formation of core/shell nanoprticles in a poler solvent as below (p.393).

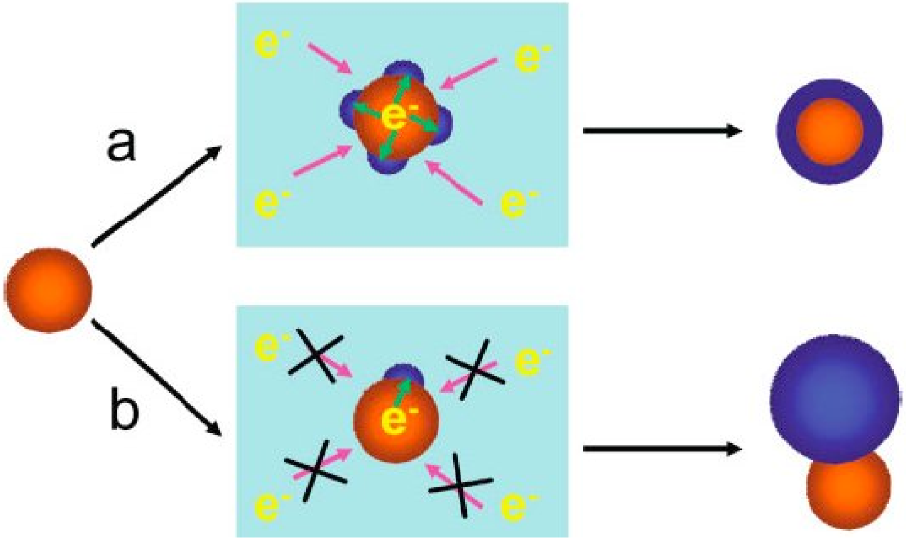


Figure 1.3 : Schematic diagram of the formation of core/shell particles (Zeng and Sun, 2008).

1.4.1.1 Methodologies for shell synthesis

There are three ways to synthesize core/shell structure. In simultaneous fabrication, core and shell form simultaneously. This fabrication especially used with carbon and silica. In sequential fabrication core is formed right after the shell. Usually metal cores have been made from iron-group metals and during the formation of shell this core is not being sacrificed. In redox (displacement) fabrication protective shell is being formed from the surface atoms of metal core. This fabrication method involves the potential difference between metal core and metal shell (Wei et al, 2011; Chen et al, 2003; Ravel et al, 2002; Lin et al, 2001). Lv et al. (2010) purpose below method for the synthesis of magnetite cored multicomponent NPs.

1.4.2 Multicomponent nanoparticles

These particles can be formed by the combination of different type of structures. According to Hosokawa et al. (2007) image of multicomponent nanoparticles is as below.

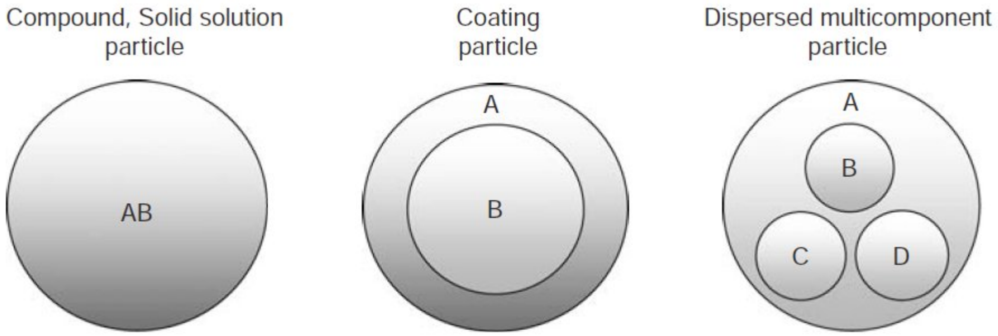


Figure 1.4 : Image of the comparison between multicomponent particles and core/shell Particles (Hosokawa et al, 2007).

There are advantages of using multicomponent nanoparticles. First one is the different functions of each component. As an example gold coated magnetite nanoparticles have been reported for their use in many different biological treatments and applications since core has the magnetite and shell has the antibacterial property. It is not possible to have the same advantage with single-component structures. In nanometer size, physical and chemical properties are all have critical length scales. When two or more structures combined and attracted with each other, strong interactions in hybrid particle allow rational modulation in physical and chemical properties. In order to have a successful synthesis, heterogeneous nucleation must be promoted while homogeneous nucleation suppressed. To do this lattice spacing should match well in two different components (Zeng and Sun, 2005).

There are different ways to form multicomponent nanoparticles. These structures usually share the same interface with two nanoparticles joined. They can be synthesized through nucleation and growth on the preformed nanoparticle. The growth is similar to the synthesis of core/shell structures. Here experimental conditions such as solution concentration and temperature play an important role on the morphology of particles. When polarity of the solvent is controlled it is easy to control core/shell or heterodimer structure as well. Another way to form these structures is to use formation of metastable core/shell particle and recrystalization. Below figure 1.8 shows the synthesis route of Ag/Fe_3O_4 nanoparticles via micellar structure and ultrasonicaton. Sonication is helping to form microemulsion (Zeng and Sun, 2008; Zu et al, 2007; Kortan et al, 1990). Below, the image of different methods to produce multifunctional nanoparticles and the synthesis route of Fe_3O4/SiO_2/Ag nanoparticles can be found.

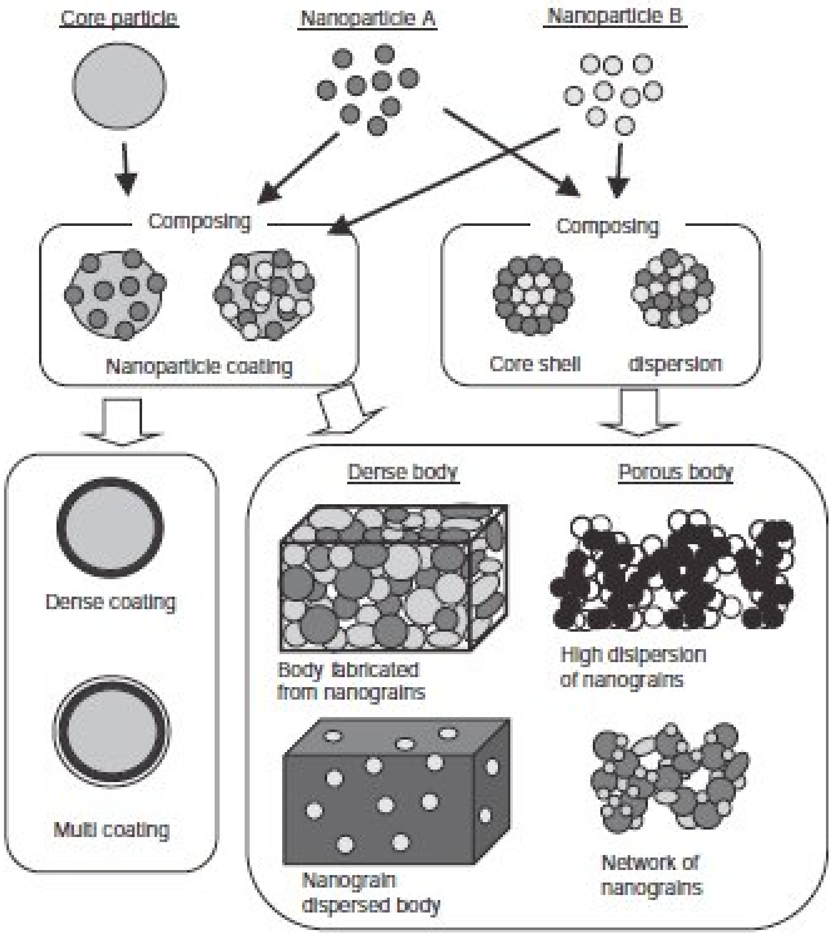


Figure 1.5 : Nanostructures fabricated from several types of nanoparticles (Hosokawa et al, 2007).

Figure 1.6 : Purposed diagram for the synthesis of magnetite multifunctional NPs (Lv et al, 2010).

1.5 Synthesis of Nanoparticles

Environmental friendly and sustainable methods for the synthesis of nanoparticles have become the major concern for scientists. Earlier many methodologies are recorded. Biomolecules have advantages in terms of being protecting agents since they are more benign materials (Philip, 2009; Mohanpuria et al, 2008; Huang et al, 2007).

1.5.1 Chemical synthesis

These methods are divided into two main groups. First one is the solution techniques or aerosol/vapour phases that produces magnetic nanoparticles, second one is dispersion in submicron sized organic or inorganic matrixes that produce composites.

1. Precipitation from solutions
- Coprecipitation
- Microemulsion
- Polyols
- High Temperature decomposition of organic precursors
- Other solution techniques
2. Aerosol/vapour techniques
- Spray Pyrolysis

In order to avoid handling problems of nanoparticles, there must be a narrow size distrubution and well controlled surface properties. Composite and hybrid nanoparticles are the type of particles overcame these problems. Nanocoating and microemulsion, heterocoagulation and nanocoating by sol-gel method are the methods to produce particles with the diameter less than 100 nm (Hosokawa et al, 2007). During the chemical synthesis control of the growing process is very important because this cause the narrow size distribution of particles. Ions present in metal salt solutions are being decomposed with a specific pH and form metal ions.Then these ions form particles. When the growth of particles is blocked, they start forming nanoparticles. This process can be made by capping agents. Capping agents may block the growth of particles or they interact with them and modify their properties. As a result not the individual property of each component but the property of entire structure is being concerned (Hernando et al, 2005; Fiorani, 2005; Sampedro et al, 2003).

1.5.1.1 Precipitation from solution

These methods include the rigorous control of size and shape during the preparation. In case of homogenous precipitation particles are obtained as uniform. This process includes the growth of nuclei and seperation of nucleation. Critical supersaturation of species starts when the nucleation occurs with a short burst, as a result nuclei starts to grow uniformly until the final size is attained. In this method monodispersion is important and in order to obtain it nucleation and growth must be separated into different periods (Faraji et al, 2010). Figure 1.9 displays the mechanism of nanoparticle formation as suggested by Tartaj et al. (2003).

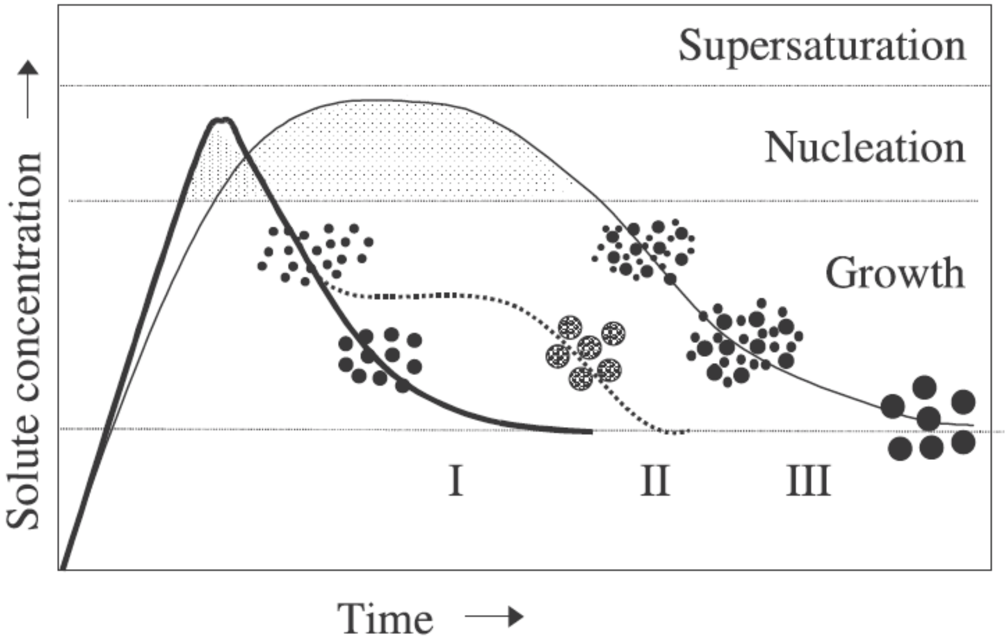


Figure 1.7 : Mechanism of nanoparticle formation (Tartaj, et al, 2003).

Co-precipitation

In this method, aqueous salt solutions are used. Particles form with the addition of a base that starts precipitation. Optimum pH level must be around 8-14. This process can be made under inert atmosphere at room temperatures or at elevated temperatures. Formation of Magnetite with this method is possible but magnetite is being oxidized very easily and it may turn into maghemite. The type of salts used affect the shape, size and composition of Magnetic nanoparticles. Large hydroxide particles are the precursor of Fe_3O_4, and the formation of these particles is promoted with the increased ratio of Fe^{+2}/Fe^{+3}. If this ratio is increases from 33 to 100%, the mean diameter of magnetite particles increases from approximate 9 to 37 nm. This method is very popular depending on its simplicity, less reaction time and temperature comparing to thermal decomposition and hydrothermal (Faraji et al, 2010; Iida et al, 2007; O'Handley, 2000).

In order to have reproducible magnetite nanoparticles synthetic conditions must be fixed. However magnetite nanoparticles are easily oxidized and turn into maghemite but the important issue on co-precipitation method is to obtain a control over particle size and narrow size distribution. As a result of the this method particles might be polydispersed. Hence the type of surfactant used in the process is very important (Lu et al, 2007; Kandori et al, 1992). Below comparison of different methods can be found as figure 1.10.

Table 1.2 : Comparison of the synthetic methods (Lu et al, 2007).

Synthetic Method	Synthesis	Reaction Temp. (^{0}C)	Reaction period	Solvent	Size distrubition	Shape control	Yield
Co-precipitation	Very simple, ambient conditions	20-90	Minutes	water	Relatively narrow	Not good	High/scalable
Thermal-decomposition	Complicated, inert atmosphere	100-320	Hours-days	Organic compound	Very narrow	Very good	High/scalable
Microemulsion	Complicated, ambient conditions	20-50	Hours	Organic compound	Relatively narrow	Good	Low
Hydrothermal synthesis	Simple, high pressure	220	Hours ca. days	Water-ethanol	Very narrow	Very good	medium

1.6 Characterization of Nanoparticles

There are numerous techniques for the characterization of nanoparticles. Some methods are used to identify the crystal structures. These methods are generally called as X-Ray techniques such as X-Ray diffraction, Small angle X-Ray scattering and Raman scattering. Some methods are used to identify the surface structure such as X-Ray photoelectron Spectroscopy or FT-IR. TEM and SEM are also considered as one of the techniques to determine the composite structure.

1.6.1 Electron microscopy

Transmission electron microscopy (TEM) is considered as one of the most powerful devices to image nanoparticles. It is possible to get data about size and shape. TEM devices have a special mode called Selected Area Electron Diffraction. This mode is making the elemental analysis of the selected part of the nanoparticle image (Hernando et al, 2005; Garcia et al, 1999; Hövel et al, 1993).

In order to obtain the particle size of the core TEM can be used and a number-weighted mean value is obtained. TEM can also give data about shape and size distribution.

Another popular technique to determine morphology and size distribution is Scanning electron microscope (SEM). In SEM, electron beam is being irradiated through the sample and then image is obtained from the generation of second beam. As a result conductivity is a crucial property for the sample. Here thickness of the sample affects the measurement too. It must be less then 100 nm. Both SEM and TEM have Energy Dispersive Spectroscopy (EDS) option which enables the elemental analysis.

SEM is not enough to detail the core/shell since it can only report the total particle size. SEM resolution is also lower than TEM and it can only give information about particles that are larger than 20 nm. There is also a device called 3D-SEM that helps to obtain 3D image of nanoparticle. This device takes pictures from different angles to obtain a 3D image. If the particles are well dispersed then 3D-SEM can obtain the height difference between particle surface and the tickness of the particle.

Although SEM and TEM are used to obtain information about the morphology, they are not enough for a complete analysis. In addition elemental analysis must be combined with the image taken form electron microscopes. Before using one of the electron microscope techniques sample preparation must be made accurately. For this there are some methods to follow. 1. In Dispersion method sample is being dispersed in a solution by ultrasonic vibration and then it can be directly placed in a sampler holder. 2. In crushing method first sample is crushed with a mortar and then placed on a sampler holder. 3. In embedding method sample is embedded in an epoxy resin and analysed. 4. Ultramicrotomy is a method that sample is embedded in an epoxy resin as an ultrathin flake. 5. In Ion milling method sample is embedded in epoxy resin by using ion beam. Structure and elemental analysis can be made with Energy dispersive X-ray diffraction (EDXD). EDX analysis helps to obtain elemental ratio in the Nanoparticle structure (Faraji et al, 2010; Hosokawa et al, 2007; Arrio et al, 2005; Jaeger et al, 1991).

Below is the TEM image of synthesized magnetite particles with co-precipitation method (Tartaj et al, 2003 p. R186).

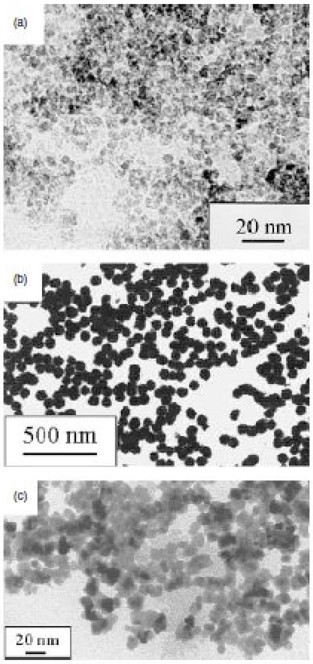


Figure 1.8 : TEM image of magnetite nanoparticles (Tartaj et al, 2003).

1.6.2 Zeta Potential

Formation of the colloidal systems occurs when two different phases disperse well in each other such as emulsions or aerosols. Sometimes aggregation occurs and particles may settle out because of the gravity. When aggregation continues and particles get denser it turns into coagulation. The stability of colloidal systems was investigated by the scientist Derjaguin, Verwey, Landau and Overbeek. Their theory called DVLO purposes that stability of a particle in colloidal systems is related with its total energy function respresented as V_T.

$$V_T = V_A + V_R + V_s \tag{1.1}$$

V_S is the potential energy of the solvent. V_A and V_R are the attractive and repulsive contributions.

$$V_A = -A/(12 \pi D^2) \tag{1.2}$$

A is the Hamaker constant and D is the particle seperation

$$V_R = 2 \pi \varepsilon a \zeta^2 \exp(-\kappa D) \tag{1.3}$$

a is the particle radius, π is the solvent permeability, κ is a function of the ionic composition and ζ is the zeta potential. According to this theory Van der Waals attractive (V_A) and double layer repulsive forces that happens between particles defines the stability of a colloidal system. Repulsive forces block particles to get closer as a result of an energy barrier. When this barrier is passed attractive forces will collide the particles (Hunter, 1988).

Zeta potential is called the potential at solid-liquid interface. This potential is used to identify the electrical double layers and their related properties. It is an easy measurement that is applied on the electrode. It helps to have the definition for electrochemical properties such as electrode capacitance. It’s a result that gives the detailed information on ion distributions between solid-liquid phases (Kirby and Hasselbrink, 2004).

There are two parts in the liquid layer. First one is called inner region (Stern Layer). In this region there is a strong bond between ions. Second is called outer (diffuse) region. In this one ions are less associated and here there is a stable entity between ions and particles. As a result of the gravity ions moves particles and these ions stay in the boundary. Zeta potential is the potential calculated in this boundary.

Zeta potential also gives the meaning of the stability of the system. When all particle have large negative or positive zeta potential there will be repulsive forces that prevent particles to come together, reverse happens in case of low zeta potential. In order to be stable particles should have +30 or -30 mV or more zeta potential (Hunter, 1988).

Normally as a result of some chemical processes such as protonation or adsorption on the surface a charge density occurs. This density also makes the electrical field which attracts counter-ions and repulse co-ions.

There are three different ways to measure zeta potential;

1. by measuring electroosmotic mobility
2. by measuring streaming current or streaming potential
3. by measuring response of a small particle in an applied electric field.

Colloidal studies usually uses the third technique (Kirby and Hasselbrink, 2004).

1.6.3 Dynamic light scattering

This technique is used to measure the size of particles. It is also called Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering.

It depends on measuring the brownian motion and realting this data to calculate the size of particles. Brownian motion occurs as a result of the interaction between solvent molecules and particles. Solvent molecules effect randomly moved particles. In this sense size of the particle changes the measurement, if they are large there will be a slower brownian motion which is observed. For DLS measurements accurately known temperature is very important since it is related with viscosity. Temperature should also stay constant because small changes may result non-random movements that spoil the the data collected.

Measured particle size in DLS actually is a mean of how effective particles can diffuse through the fluid, therefore it is called hydrodynamic diameter. This diameter depends on the same translational diffusion coefficient. This is related with the core, concantration and type of ions in the medium (Pecora, 1985).

1.6.3.1 Ionic strength of medium

As mentioned earlier total ions in the medium affect conductivity, diffusion speed of the particles and the thickness of the electrical double layer. Low conductivity results a larger double layer which causes a reduction in the diffusion speed and a large hydrodynamic diameter. High conductivity supresses the double layer and hydrodynamic diameter (Pecora, 1985).

1.6.3.2 Non-spherical particles

Generally it not easy to measure the size of non-spherical particles. Techniques used in this field are usually sensitive to different properties such as density or scattering intensity etc. Microscope images are also depends on parameter like edge or contrast. In this technique measure size is related with the translational diffusion speed of the particle therefore when size changes diffusion speed and hydrodynamic size will be affected. Because of these reasons DLS is accepted as a very sensitive technique to measure the particle size (Pecora, 1985).

1.7 Application of Nanoparticles

There are numerous applications of magnetic nanoparticles. According to Faraji et al. (2010) these applications can be classified as follows:

- Industrial Applications
- Biological Applications
- Drug Delivery
- Bioseparation
- Magnetic Resonance Imaging
- Hyperthermia
- Catalysis Applications
- Environmental applications

1.7.1 Environmental applications

Magnetic iron oxide particles are used for many applications in biomedicine, bioseperation and waste water treatment. In wastewater treatment they are used as the sorption material of ligands, dyes and metal ions. This makes them useful for the adsorption of heavy metal ions from industrial wastewater. Their magnetic property also makes the removal of these particles from the intermediate very easy (Parham and Rahbar, 2009; Uheida et al, 2006).

One of the advantages of magnetic nanoparticle technology is its cost-effective solution for the environmental problems. There are basically two types of pollutants in industrial water: Organic and Inorganic pollutants. Inorganic pollutants mostly consists of the heavy metal ions occurred from the metal coating procedures (Faraji et al, 2010; Zhang, W. 2003; Blowes et al, 2000).

For the removal of organic pollutants, heavy metals amd microcystins core/shell structures have been a popular solution. Core/shell particles should have high specific surface area and magnetic core in order to be used of this purpose. Carbon coated particles have higher stability and better biocompatibility comparing to the other shells. Another advantage of using magnetic particles for the waster water treatment is their ability to be recycled after each use. Below is the image of an application of carbon shell magnetic particles in polluted water (Wei et al, 2011; Murray et al, 2001; Khanna and Linderot, 1991).

Humic acid is used to remove heavy metal ions and organic pollutants from water. Earlier some studies suggests that Calcium humate has found very efficient to remove metals like iron, mercury, cadmium and copper (Pena-Mendez et al, 2004; Ghabbour and Davies, 1999).

Phenol removal has been made with humus based filters and also they are used for the sorption of gases. Its been found that humates can be used for the removal of hydrogen sulfide, mercaptans and sulfur dioxide as well (Green and Manahan, 1981).

1.7.1.1 Magnetic seperation techniques

Magnetic separation which has been made by using magnetic particles is very fast, compatible and it has high selectivity. For these reasons it became very popular in environmental applications, mining, food and steel industry and biotechnology.

In this technique first step includes the adsorption of analyte on the coated or modified surface of nanopartices. Then by using an external magnetic field preconcantration or removal of the analyte from the solution was made. Later it is also possible to use synthesized nanoparticles to repeat the same process (Arteaga et al, 2010; Jun et al, 2009; Gong et al, 2007).

Toxic heavy metal pollution is a global problem. New environmental regulations also bring the necessity of low level of heavy metal ions in the environment which cause the development of new technologies for the removal of these metal ions. Earlier various type of materials such as silica's, zeolites or polymers have been used for the removal processes. Current studies show that use of nanoparticles for this purpose is very fast and efficient. Magnetite nanoparticles used for the removal of Cu(II) ions. Recently it is also reported that magnetite particles acan be used to remove Arsenic ions form water with magnetic seperation technique (Jing-fu et al, 2008; Chang and Chen, 2005; Savage and Diallo, 2005).

According to Jing-Fu et al, Humic acid has high affinity to magnetite nanoparticles and its sorption prevents the agglomeration of particles. Humic acid has carboxylic and phenolica groups that have complex capacity with heavy metals. Below, the method of treatment of magnetic nanoparticles and some results of removal percentages of heavy metal ions from water can be found (Jing-fu et al, 2008; Hu et al, 2004; Ills and Tombacz, 2003) .

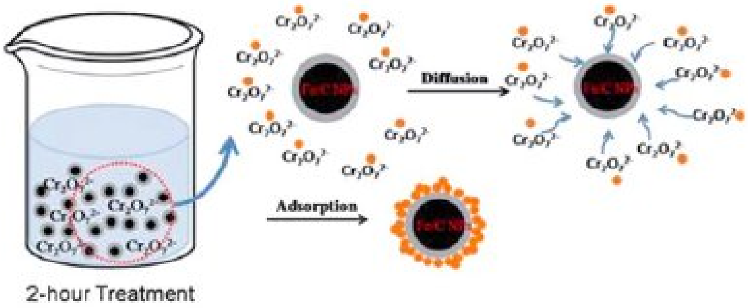


Figure 1.9 : Wastewater treatment with magnetic nanoparticles (Wei et al, 2011).

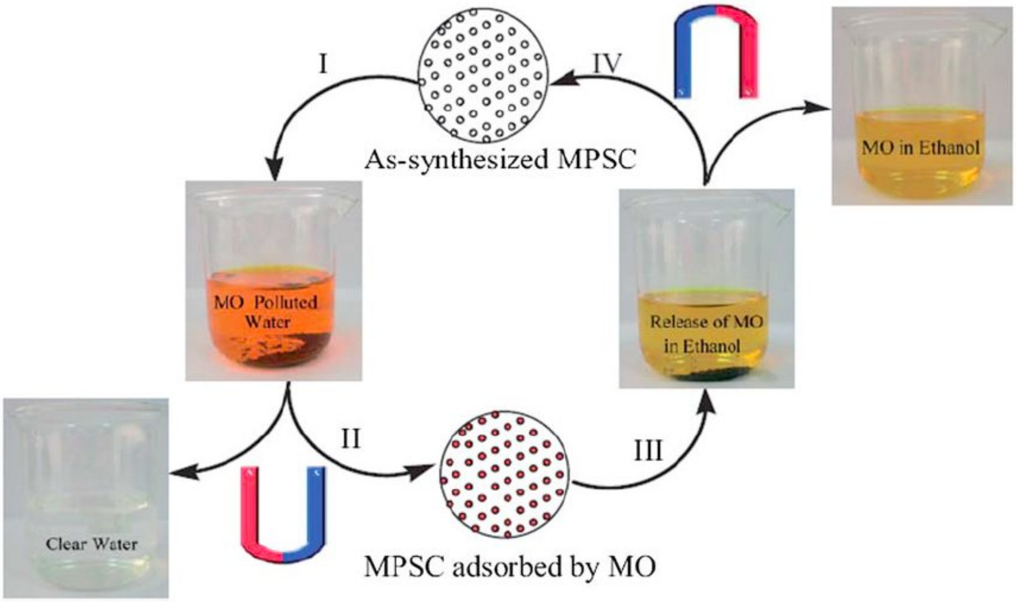


Figure 1.10 : Propesed scheme for the removal of heavy metal ions by magnetic nanoparticles (Wei et al, 2011).

1.8 Natural Organic Matter (NOM)

1.8.1 Humic Substances

Nakashima et al. (2008) defines humic substances (HS) as " Organic macromolecules with various functional groups such as carboxylic, hyroxyl, phenyl, phenolic, and quinolic groups" (p. 155). Formation of humic substances occurs as a result of the breakdown of plant and animal tissue containing proteins, cellulose and lignin. Their solubility in water classify them into three different groups (Nakashimaet al, 2008; Carter and Suffet, 1982).

1. Fulvic acid (water soluble at any pH)
2. Humic acid (water-soluble at pH > 2)
3. Humin (water soluble at any pH)

Tan (2003) suggests the extraction of soil in order to produce humic substances as below.

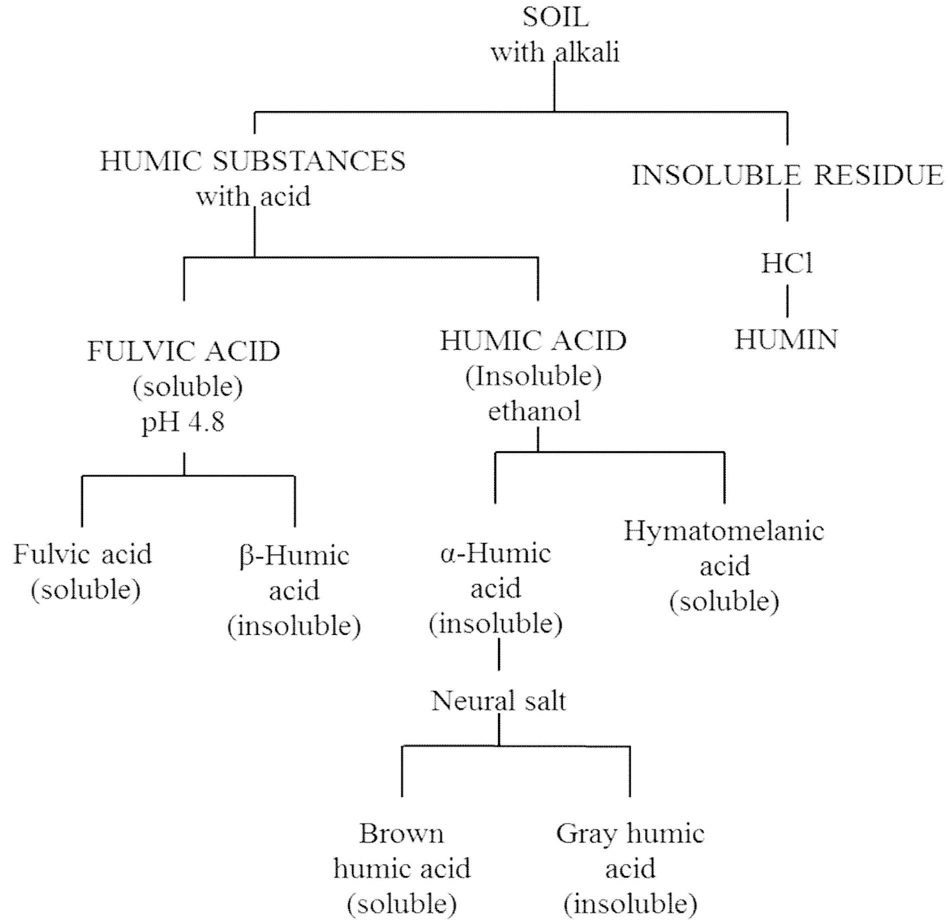


Figure 1.11 : Flow sheet for the extraction for humic substances (Tan, 2003).

For the first time it was Berzelius (1839) who extracted and isolated humic substances.

For the formation of HS various theories has been suggested such as sugar-amine condensation theory, the lignin theory or polyphenol theory. Its been suggested that humic acid has actually low molecular weight compounds but in time they agglomeration starts and structure turns into a supermolecule. This aggregation depends on the formation of dimers and trimers at low pH (Pena Mendez et al, 2004; Hosse and Wilkenson, 2001).

The origin and age of humic substances affects the size, molecular weight, elemental composition, structure, the number and position of functional groups. Dissolved organic carbon content of humic substances in surface waters differs from 0.1 to 50 ppm. In ocean waters this concentration ranges between 0.5 to 1.2 at surface and 0.1 to 10 at deep ground waters. The elemental compositon of humic materials is 40-

60% carbon, 30-50% oxygen, 4-5% hydrogen, 1-4% nitrogen, 1-2% sulfur, and 0-0.3% phosphorus (Tan, 2003). At first it has been thought that humic acid (HA) was present only in soil but then understood that it is the most widely distributed carbon containing material in Earth's crust. The color of HA changes from dark brown to black. It is a colloidal polydispersed, odorless, hydrophilic and acidic substance. It has a high molecular weight (Tan, 2003). Below is the suggested molecular formula of Humic acid by Stevensen (1982).

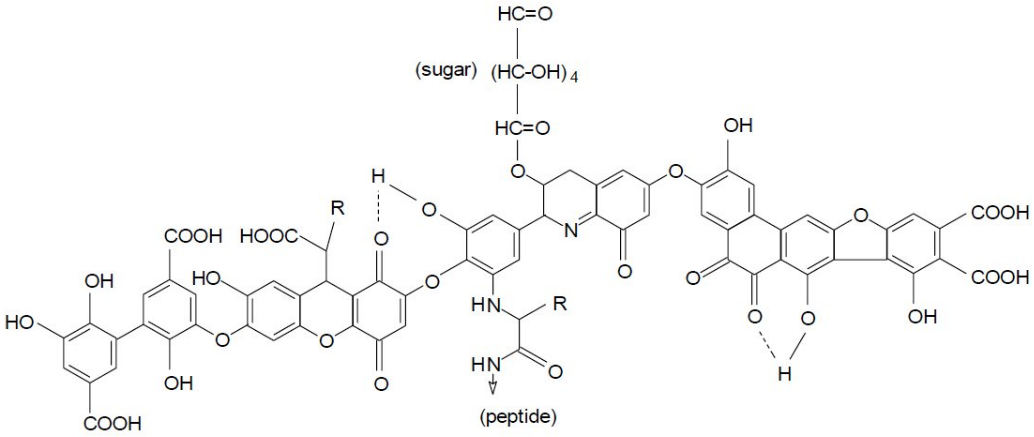


Figure 1.12 : Model structure of Humic acid purposed by Stevensen (1982) (Pena et al, 2005).

Some pollutants in water make a complex with HA through hydrophobic interaction, electrostatic interaction, hydrogen bonding and coordinate bonding (Nakashima et al, 2008; Carter and Suffet, 1982). Type and amount of functional group affect the charge of HA Although it's been many researches about the binding between metal ions and HS, actual structure is still unsolved. It has been offered that major binding sites have oxygen containing functional groups such as carboxylic or phenolic etc (Andjelkovic et al, 2006; Avena et al, 1999; Aiken et al, 1985).

1.8.1.1 Methods of characterization

There are many different methods used to identify the functional groups in HS. Mostly any type of spectroscopic techniques is found useful for the study of functional groups . Characterization methods of humic acid was suggested as below by Gaffney et al. (1996).

1.8.1.2 Metal and radionuclide transport and Binding

Binding of humic substances over heavy metal ions enriches the concentration of these metal ions in aquatic environments. When the ionization of humic of humic substance increase the metal binding increase too. This happens because intermolecular repulsion increases with increase in the ionization (Gaffney et al, 1996; Moulin et al, 1992; Purdue and Lytle, 1981).

2. EXPERIMENTAL SECTION

2.1 Instrumentation

Varian Flame Atomic Absorption Spectrometer was used to measure the absorbance values of standard metal solutions and synthetic mixture solutions in order to observe the adsorption character of nanoparticles. For an equal and homogenous sorption process Edmund Bühler 7400 Tubingen shaker was used. Shaker period is adjusted to 300 min^{-1}. SEM analyses were made with JOEL JSM-7600F Scanning Electron Microscope and FEI Quanta 250 FEG . Zeta potential analysis were made with ZetaPals Zeta potential Analyzer BIC (Brookhaven Inst. Corp.). Chiltelrn Hotplate Magnetic Stirrer was used to achieve homogenous heating during the co-precipitation of nanoparticles. A regular magnet is used to collect particles from the sample solution. At every stage of synthesis BANDELIN RK100H ultrasonic bath was used for successful coating of particles.

2.2 Chemicals and Reagents

Humic acid and silver coated magnetite particles were prepared by a thermal co-precipitation synthesis method. The chemical reagents used in this procedure were Fluka Ferrous Chloride hexahydrate (98% pure), Merck Ammonium iron(II)sulfate hexahydrate, Aldrich Humic acid sodium salt, Merck Ammonia (25%), Merck Tin(II)chloride, Merck Hydrochloric acid, Fluka Silver nitrate, Fluka Sodium Hydroxide, Merck Copper and Cadmium AAS standard solutions. All reagents and standards were of analytical grade and were used without any further purification. All dilutions have been carried out with milliQ pure deionized water.

2.3 Preperation of Fe_3O_4/HA/Ag Nanoparticles

Particles were prepared by a co-precipitation process. During the synthesis procedure, methods purposed by Lv et al, 2010 and Liu et al, 2008 have been combined and modified. Modifications such as milliQ water usage for each step during the synthesis, increasement in heating and ultrasonication time were made as distinct from the other methods. Stoichiometric mixture of $FeCl_3.6H_2O$ and $NH_4FeSO_4.6H_2O$ (molar ratio 1.5:1) were heated to 90^0C for 45 minutes on Chiltelrn hot plate magnetic stirrer. For this purpose, 6.1 g $FeCl_3.6H_2O$ and 4.2 g $NH_4FeSO_4.6H_2O$ were weighed and dissolved in 100 mL pure water separately. After the heating process 10 mL of 1000 mg l^{-1} Humic acid sodium salt solution was mixed along with ferrous and ferric chloride solutions and 10 mL 25% ammonia solution added immediately to precipitate humic acid coated magnetite nanoparticles. After reduction, heating process was carried out under 90^0C for an hour. Particles were washed with milliQ pure water twice and sonicated for 30 minutes. After sonication with the help of a simple magnet supernatant was collected with a dropper. In supernatant liquid, very small particles with very weak magnetic property were observed. These particles were discarded with the supernatant liquid.

With the aid of the redox reaction between silver and tin, silver coating of existing particles was carried out. Tin is chemically more active metal than silver (Sn/ Sn^{+2} electrode potential is – 0.136, but Ag/ Ag^{+} electrode potential is +0.799). This shows that solid tin has much more tendency to form its ions than silver. For this reason humic acid coated magnetite particles at first coated with tin particles and then tin was replaced with silver after redox reaction.

On the first step of synthesis process, Fe_3O_4/HA particles were mixed with 0.063 M acidic Tin(II)chloride solution, sonicated for 30 minutes, therefore Fe_3O_4/HA/Sn particles created and washed with milliQ water twice. On the second step, Fe_3O_4/HA/Sn particles were mixed with freshly made 0.13 M Tollen's reagent (Ammonical silver nitrate), sonicated for 30 minutes and washed with milliQ water twice. As a result Fe_3O_4/HA/Ag Magnetic particles were separated from the suspension by using a magnet and dried at 60^0C in air. Below figure 2.1 represents the synthesis of nanoparticles.

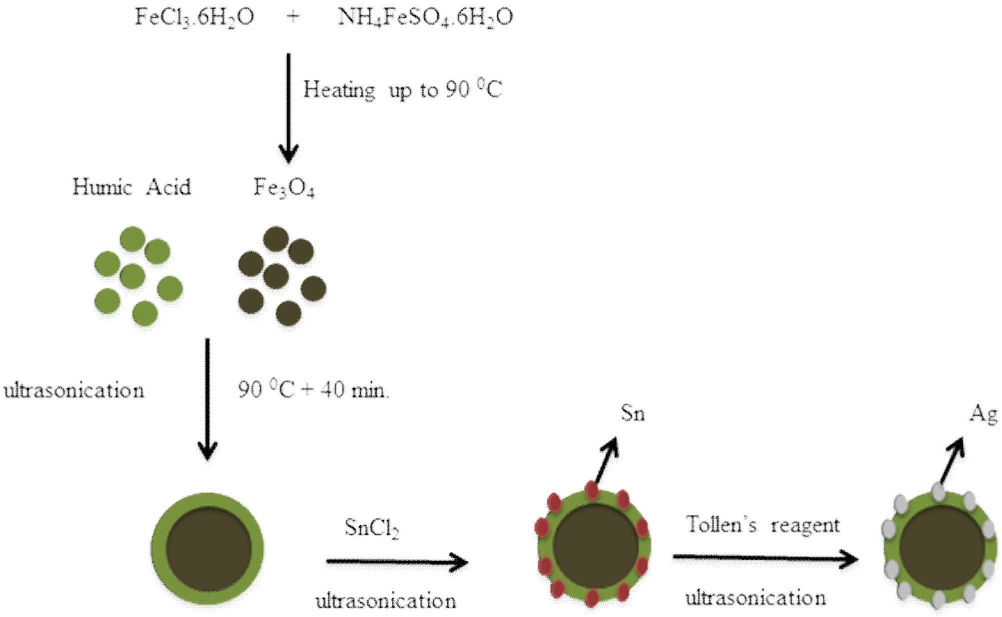


Figure 2.1 : Synthesis route of Fe_3O_4/HA/Ag multifunctional nanoparticles.

2.4 Characterization of synthesized nanoparticles

Characterization of synthesized Fe_3O_4/HA/Ag nanoparticles was made by using Scanning electron microscope and Zeta potential analysis. JOEL JSM-7600F and FEI Quanta 250 FEG Scanning Electron Microscopes were used to take images . During this stage, for each selected area EDX analyses have been made for the surface elemental analysis. This proved the existence of elements in the structure. In order to take the SEM image different dried samples (intermediates Fe_3O_4 and Fe_3O_4/HA, and final product Fe_3O_4/HA/Ag) were mechanically crushed and put on the sampler.

The DLS experiments were conducted at 90^0 angle using 35mWsolid state laser detectors operating at 658 nm. The change in the particle size in response to pH was also determined by DLS measurements, adjusting the pH with 0.1M HCl and 0.1M NaOH in 10^{-2} M KNO_3 aqueous solution. Zeta potential analysis were made with ZetaPals Zeta potential Analyzer BIC (Brookhaven Inst. Corp.). A diluted aqueous solution of nanoparticles was used for the zeta measurements, which were carried out in triplicate, as were the DLS measurements.

First sample was diluted (portions were 1/50 and 1/100) with 10 mL KNO_3 in sonicator for 5 minutes. Second and third samples diluted in 10 mL KNO_3 and sonicated for 5 minutes. Then zeta potentials were measured.

2.5 Procedure of Heavy Metal Adsorption

Adsorption process between Copper and Cadmium metal ions and synthesized nanoparticles was investigated by using Atomic Absorption Spectrometer. Standard solutions of copper and cadmium were prepared by appropriate dilution of stock solutions in the concentration values of 1000 mg $l^{-1.}$ For Copper, calibration solutions prepared as 1, 2 and 3 mg l^{-1} and for Cadmium as 0.5, 1 and 2 mg l^{-1}. According to their absorbans value calibration graph for each metal was obtained. Merck standard solutions were diluted with milliQ pure water and then applied with synthesized particles. Adsorption process was carried out with Edmund Bühler 7400 Tubingen shaker. After the adsorption particles were collected with a magnet. Final concentration values of each sample were calculated after the absorbance values were measured with the aid of the AAS. Final and inital values were used to calculate the removal percentage and the formula can be seen below. Optimization process was carried out for each metal. pH, particle mass and sorption time were obtained. Below figure 2.2 shows the removal method of heavy methods.

$$\%\text{Adsorption} = (C_i - C_e / C_e)\ X\ 100 \tag{2.1}$$

C_i : Initial Concentration C_e : Equilibrium Concentration

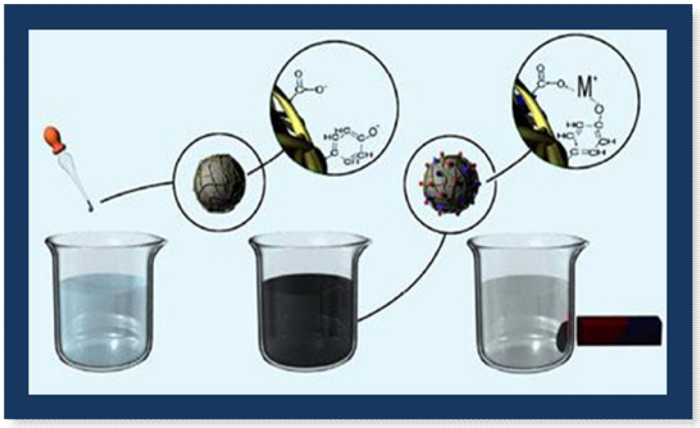


Figure 2.2 : Removal of heavy metal ions by using Fe3O4/HA magnetic NPs (Liu et al, 2008).

2.5.1 Optimization

During the optimization of adsorption, one factor at a time procedure was used. Effects of pH value, sorption time and particle mass on heavy metal removal were investigated. pH value adjustments were made with 0.01 M NaOH and 0.001 M HCl solutions. NaOH and HCl solutions were also prepared with milliQ water. To obtain the optimum pH value, solutions were adjusted to pH 3, 5, 7 and 9 values. Particle mass was 10 mg and contact time was 10 minutes. At these conditions best removal was obtained with pH 9 value. During particle mass study, pH value was set as 9 and five different particle masses applied such as 5, 10, 15, 20 and 25 mg. By using 20 mg particle mass, best removal percentages was obtained. In order to adjust the optimum contact time pH 9 value and 20 mg particle mass were used and applied to five heavy metal solution, for each solution contact time was adjusted to 5, 10, 20, 25 and 30 minutes. In the end the optimum values found as pH 9 value, 20 mg particle and 20 minutes contact time. At last three different trials were made with these optimized values and a mixture of cadmium and copper solutions were prepared to understand if there is any selectivity between different metal ions. For this study, three different solutions with different metal concentrations were prepared and adsorption process took place with optimized parameters.

3. RESULTS

3.1 Characterization of Fe_3O_4/HA/Ag Nanoparticles

3.1.1 Scanning Electron Microscope Images

JOEL JSM-7600F and FEI Quanta 250 FEG Scanning Electron Microscopes used for the characterization. EDX analyses have been made for the surface elemental analysis. Bright particles on SEM image represent Ag because silver has conductivity and conductive materials reflect light. Gray parts represent Humic acid coated magnetite particles. Black parts represent empty spaces. Images of Intermediates which are Fe_3O_4/HA and Fe_3O_4/HA/Sn and final product which is Fe_3O_4/HA/Ag was taken. The most appropriate closest image is obtained with x50000 magnification. All other closer magnification values gave blurry and bad images but according to EDX analysis, it has been proved that coating with silver was achieved. Blurry images might have happened beacuse of the grinding process of particles. By using a proper mechanical grinder, particles can be grinded to the same sizes. Figure 3.1 and 3.2 shows the SEM images of intermediates and final product.

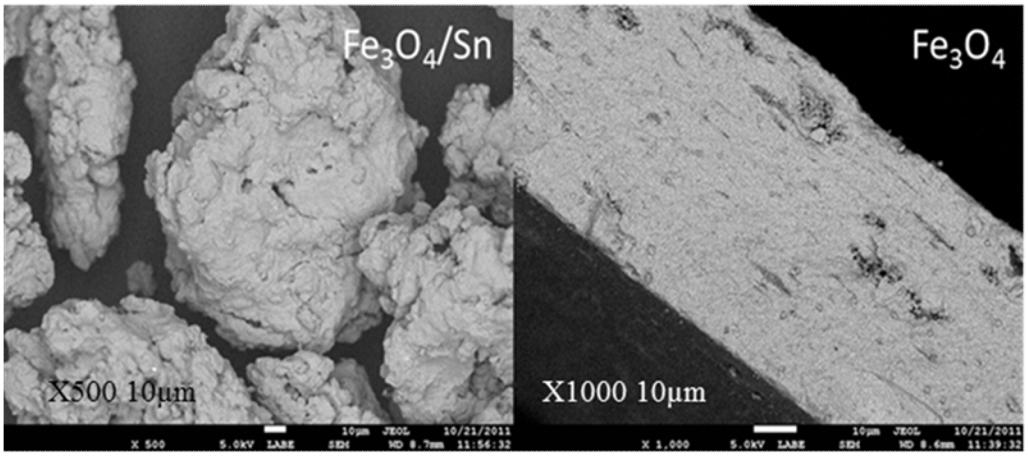


Figure 3.1 : SEM images of intermediates 1) in Fe_3O_4/HA nanoparticles after the dispersion of Sn^{+2} solution, 2) Fe_3O_4 nanoparticles.

Tin reflects light but these images show that it is not as powerful as silver. As a result of this it is not possible to recognize shiny particles on the image. Also without using tin all other silver coatings could not achieve and this situation proved by using EDX analysis. Silver existence on the final product also proves the coating of tin on intermediate.

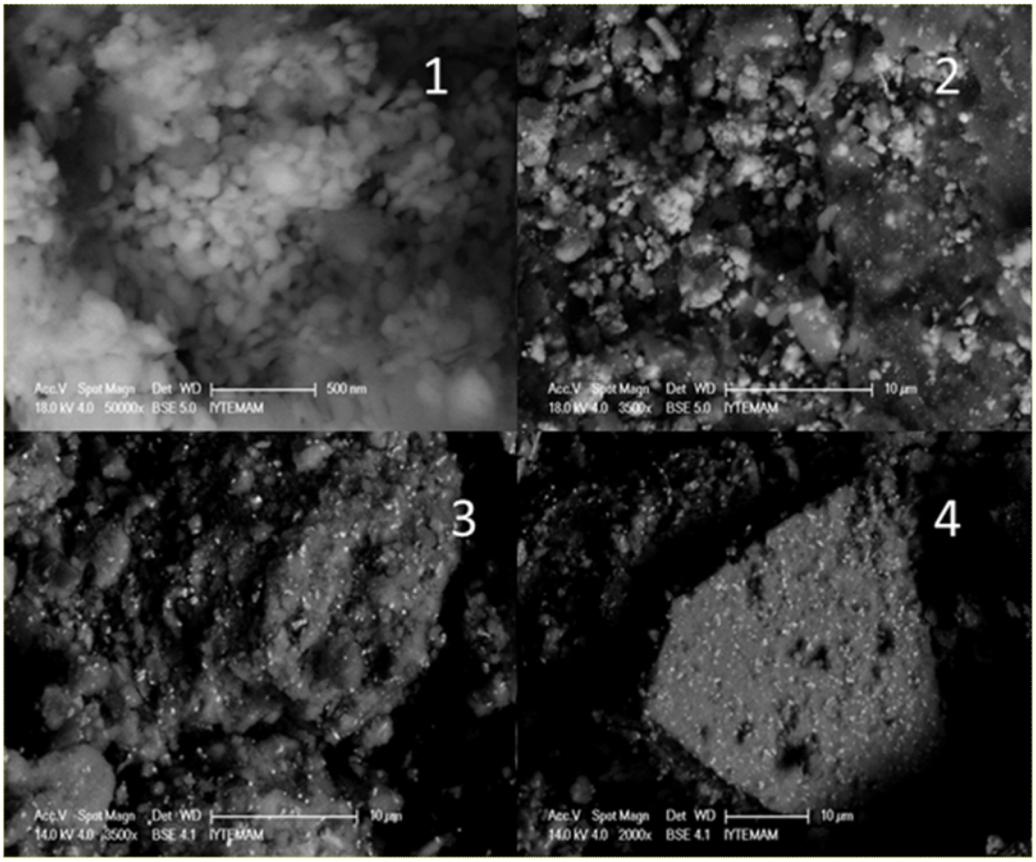


Figure 3.2 : SEM images of Fe_3O_4/HA/Ag Nanoparticles at different particle size ranges 1) x50000 2-3) x3500 4) x2000 magnification.

As it can be seen on the images closest one was taken with x50000 magnification. Although the distrubition of silver seems heterogenous on a larger view, first image and EDX analysis proves the existence of silver particles. For the removal of heavy metal ions it was also important not to synthesis another core/shell method but to have a new coated particle. Therefore the situation is applicable for heavy metal and bacterial pollution. Below is the EDX analysis of final product. Cl, O and C comes from Humic structure and Fe from magnetite structure. Figure 3.3 representes the EDX analysis of area number 2 in Figure 3.2.

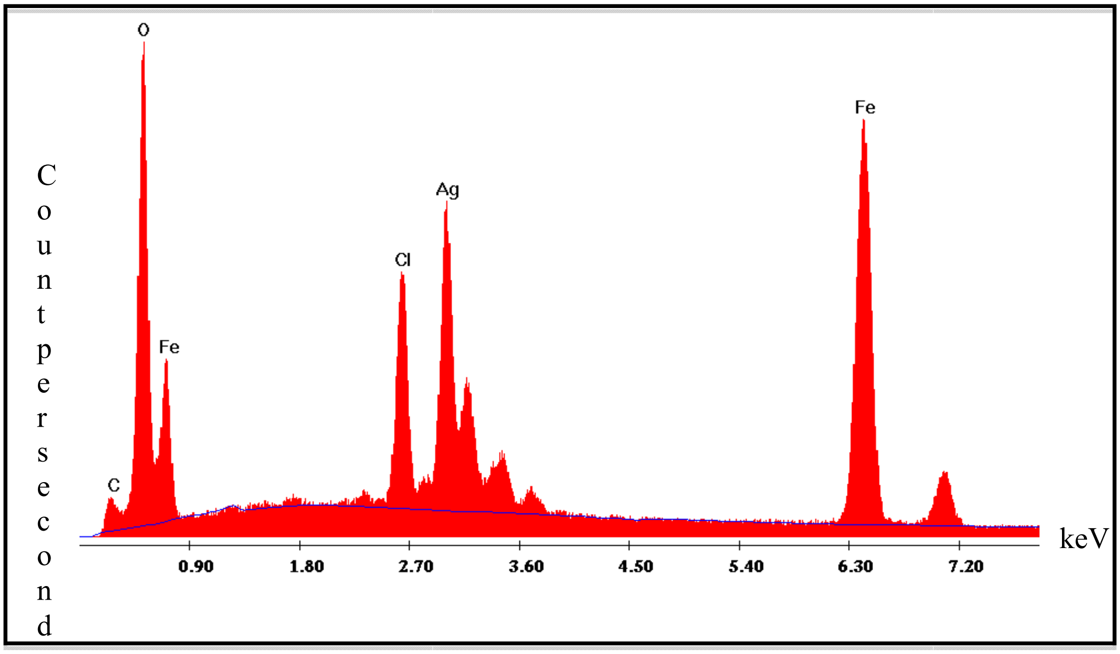


Figure 3.3 : EDX image of the surface number 2.

Liu et al. (2008) shows the TEM image of Fe_3O_4/HA nanoparticles as follows. Since it is possible to have a greater image by using TEM, Liu et al. (2008) could see the coating and size of the particles.

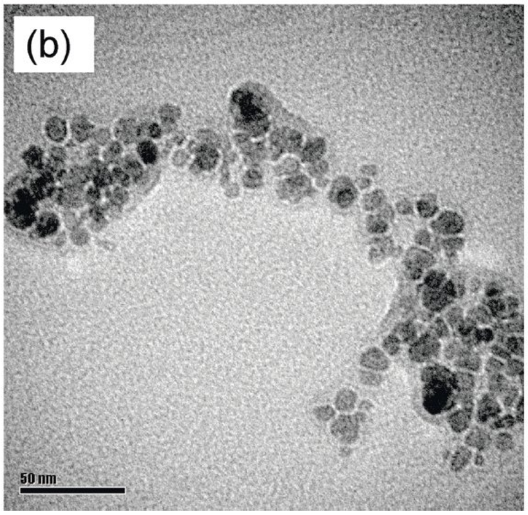
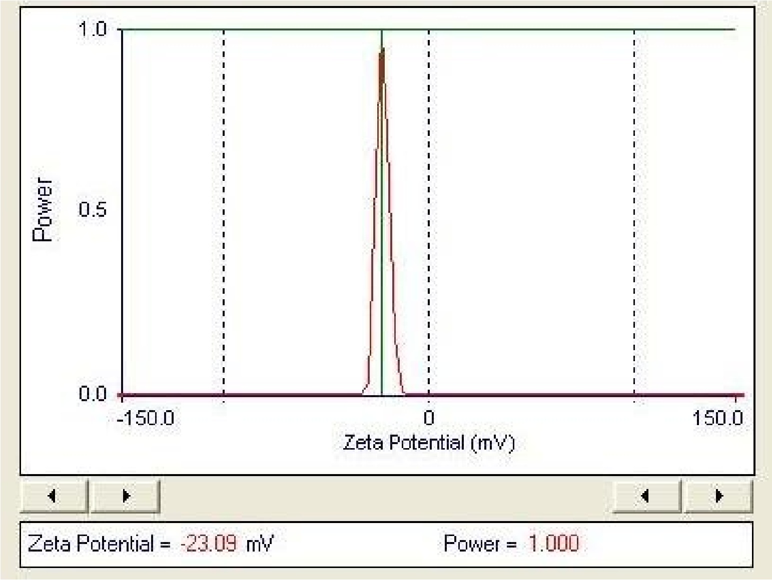


Figure 3.4 : TEM image of Fe_3O_4/HA nanoparticles, Liu et al. (2008).

3.1.2 Zeta Potential and DLS Analysis

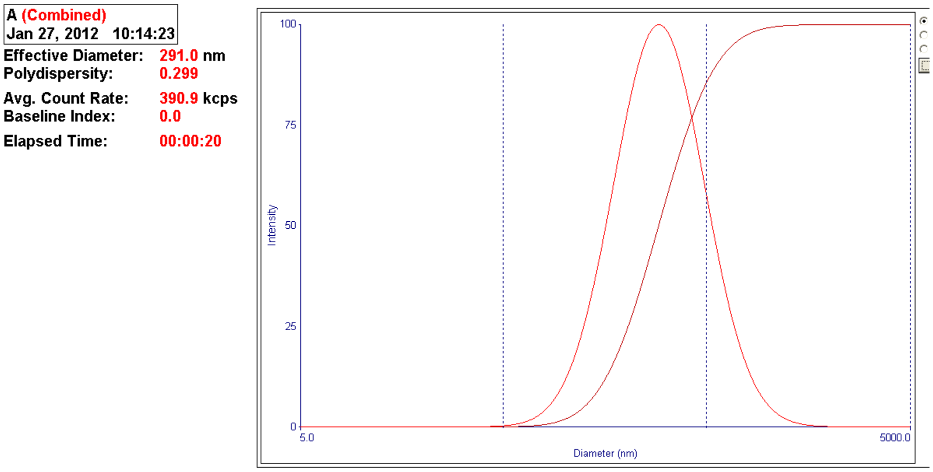
Zeta potential was used to prove negative charge of double layer and DLS analysis was used to have particles mean diameter size. Before having the results it can be assumed that particles should be more negatively charged because they are synthesized in a basic medium. Results form the analysis was also proved the same. Figure 3.5 shows the Zeta potential value which was obtained as -23.09 mV.



Zeta Potential = -23.09 mV Power = 1.000

Figure 3.5 : Zeta potential results of Fe_3O_4/HA/Ag NPs.

Normally accepted value in terms of stability should be between -30 and +30 mV. But values between 10 and 30 mV are accepted as having incipient stability too. More than that, this result also shows that synthesized particles can be used to remove metal ions since they are negatively charged. DLS analysis showed that in given conditions mean diameter of the particles was as 291.0 nm. DLS analysis result can be seen below as figure 3.6.



A (Combined)
Jan 27, 2012 10:14:23
Effective Diameter: 291.0 nm
Polydispersity: 0.299
Avg. Count Rate: 390.9 kcps
Baseline Index: 0.0
Elapsed Time: 00:00:20

Figure 3.6 : Result of DLS analysis of Fe_3O_4/HA/Ag NPs.

3.2 Optimization of Heavy Metal Sorption

3.2.1 Effect of pH on the removal of copper and cadmium

Investigation has been made with four different pH values of solutions which are 3, 5, 7 and 9. For each pH value 10 mg particle and 10 minutes of sorption time is used. Results were obtained from three different trials. As a result pH value 9 were found as the optimum value. Table 3.1 and 3.2 gives results of pH optimization study. Figure 3.7 shows these results on a scattered graph.

Table 3.1 : The effect of pH on the removal of Copper at 300 K and N = 4.

pH value	**C_i (ppm)**	**C_f (ppm)**	**Removal %**
3	1.481 ± 0.039	1.940 ± 0.616	-31.03
5	1.614 ± 0.116	0.886 ± 0.007	45.15
7	1.137 ± 0.160	0.524 ± 0.201	53.87
9	1.424 ± 0.006	0.144 ± 0.421	89.92

Table 3.2 : The effect of pH on the removal of Cadmium at 300 K and N = 4.

pH value	C_i (ppm)	C_f (ppm)	Removal %
3	1.522 ± 0.428	1.244 ± 0.239	18.27
5	3.304 ± 0.601	1.482 ± 0.376	55.14
7	2.880 ± 0.356	0.518 ± 0.180	82.01
9	1.348 ± 0.529	0.077 ± 0.435	94.27

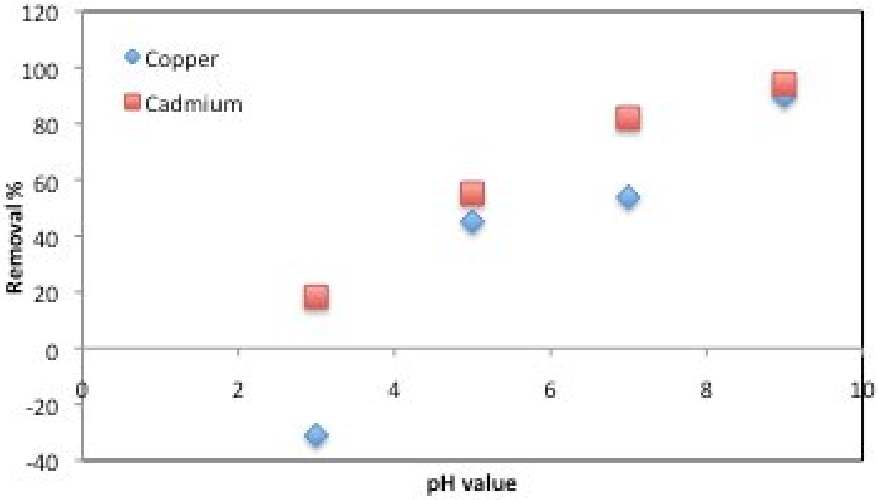


Figure 3.7 : The Effect of pH on the removal of Copper and Cadmium.

3.2.2 Effect of particle mass on the removal of copper and cadmium

Investigation has been made with four different mass values which are 5, 10, 15 and 20. For each value solutions were adjusted to pH 9 and sorption time was determined as 10 minutes. Results were obtained from three different trials. As a result 20 mg particle has been found as the optimum value. Table 3.3 and 3.4 gives results of particle mass optimization study. Figure 3.8 shows these results on a scattered graph.

Table 3.3 : The effect of particle mass on the removal of Copper at 300 K and N = 5.

Particle mass (mg)	**C_i (ppm)**	**C_f (ppm)**	**Removal %**
5	1.064 ± 0.110	0.677 ± 0.210	33.35
10	1.334 ± 0.025	0.272 ± 0.510	79.61
15	1.610 ± 0.1600	0.210 ± 0.028	86.96
20	1.090 ± 0.096	0.077 ± 0.090	92.95
25	1.319 ± 0.018	0.09 ± 0.088	93.20

Table 3.4 : The effect of particle mass on the removal of Cadmium at 300 K and N = 5.

Particle mass (mg)	**C_i (ppm)**	**C_f (ppm)**	**Removal %**
5	0.674 ± 0.120	0.518 ± 0.154	22.40
10	0.988 ± 0.030	0.298 ± 0.044	69.83
15	0.917 ± 0.002	0.159 ± 0.025	82.66
20	0.996 ± 0.037	0.034 ± 0.088	96.59
25	1.036 ± 0.057	0.036 ± 0.087	96.52

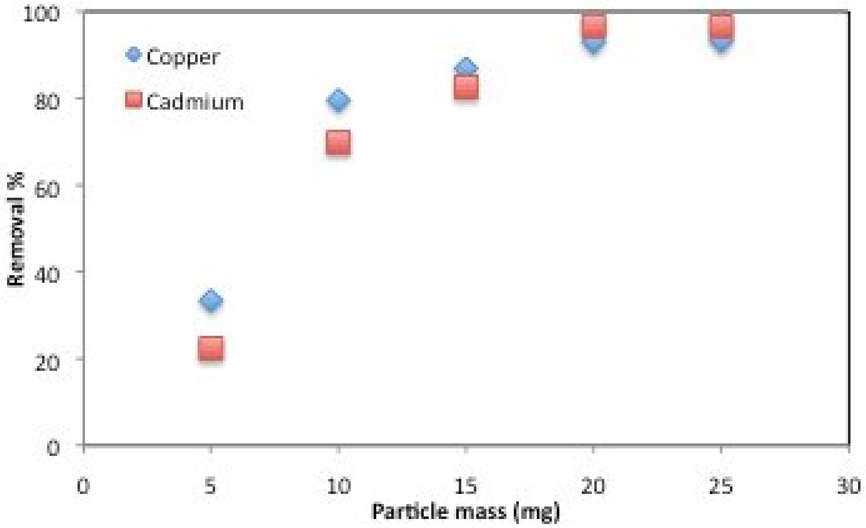


Figure 3.8 : The effect of particle mass on the removal of Copper and Cadmium.

3.2.3 Effect of contact time on the removal of copper and cadmium

Investigation has been made with four different time values which are 5, 10, 20 and 30 minutes. For each value solutions were adjusted to pH 9 and 20 mg particle used for the sorption. Results were obtained from three different trials. As a result 20 minutes has been found as the optimum value. Table 3.5 and 3.6 gives results of contact time optimization study. Figure 3.9 shows these results on a scattered graph.

Table 3.5 : The effect of contact time on the removal of Copper at 300 K and N = 5.

Time (min)	**C_i (ppm)**	**C_f (ppm)**	**Removal %**
5	1.414 ± 0.065	0.350 ± 0.074	75.59
10	1.626 ± 0.041	0.222 ± 0.009	86.47
20	1.633 ± 0.044	0.161 ± 0.021	90.25
25	1.375 ± 0.085	0.115 ± 0.085	91.64
30	1.672 ± 0.063	0.164 ± 0.063	90.27

Table 3.6 : The effect of contact time on the removal of Cadmium at 300 K and N = 5.

Time (min)	**C_i (ppm)**	**C_f (ppm)**	**Removal %**
5	0.437 ± 0.17	0.215 ± 0.059	50.72
10	0.551 ± 0.11	0.122 ± 0.081	77.92
20	0.914 ± 0.069	0.053 ± 0.021	94.37
25	0.937 ± 0.081	0.057 ± 0.019	93.95
30	1.042 ±0.130	0.032 ±0.032	96.93

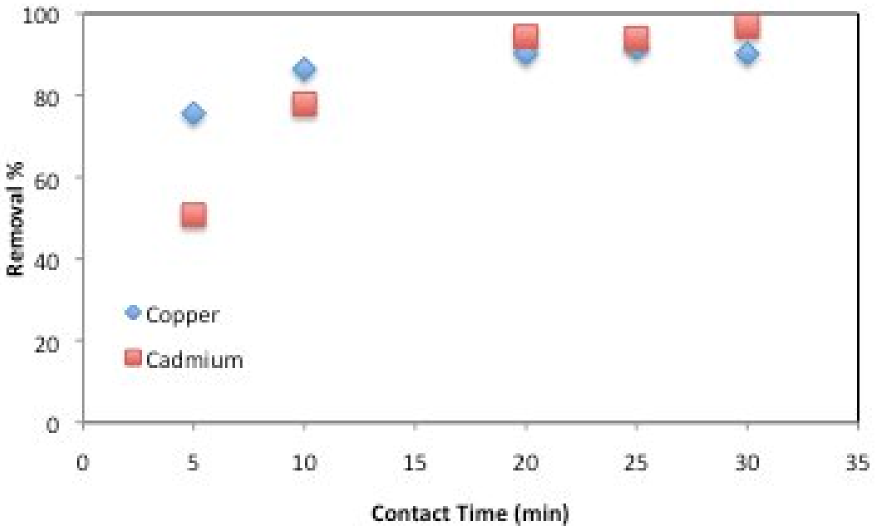


Figure 3.9 : The effect of sorption time on the removal Copper and Cadmium.

3.3 Removal of Copper and Cadmium by Using Optimum Parameters

Cadmium and Copper solutions prepared by using Merck standards and adjusted to pH 9 with milliQ water. Sorption process carried out for 20 minutes with 20 mg particle. Table 3.7 represents removal percentages of copper and cadmium by using optimum parameters.

Table 3.7 : The Removal of Copper and Cadmium at 300 K and N = 4

	Mean C_i	**Mean C_f**	**% Removal**
Cu	1.180 ± 0.116	0.088 ± 0.041	92.54
Cd	0.644 ± 0.244	0.027 ± 0.024	95.81
Cu in Cd solution	1.606 ± 0.857	-0.085 ± 0.110	105.30
Cd in Cu solution	1.908 ± 1.230	0.037 ± 0.035	98.10

4. CONCLUSION

The aim of this work was to synthesize nanoparticles that can be a solution for the heavy metal and bacterial pollution in water. For this purpose multifunctional Fe_3O_4/HA/Ag magnetic nanoparticles were synthesized. In order to find a synthesis route for Fe_3O_4/HA/Ag multifunctional nanoparticles two different articles from the literature were combined and modified. Differences were made with temperature and heating time values. Co-precipitation method was used for the synthesis of nanoparticles. This route consists of two stages. First stage includes the synthesis of Fe_3O_4/HA core/shell structure. Coating of magnetite core with humic acid shell was made by using the pure ammonia continued with a heating process. Second stage consists of the coating of synthesized core/shell structure with silver followed by the redox reaction between Sn^{+2} and Ag^{+}. The reason to use Sn^{+2} is to enable the reduction of Ag^{+} on core/shell structure. Many attempts showed that without using tin it was not possible to achieve the coating with silver. For this first purpose particles dispersed in acidic tin(II)chloride solution and then in Tollen's reagent. For each trial Tollen's reagent was prepared freshly. After every stage particles ultrasonicated and washed with milliQ water twice. By using a simple magnet, particles were precipitated to the bottom of the container and supernatant was collected easily. They are dried at 60 ^{0}C in air.

Characterization of the synthesized particles made with SEM, Zeta potential and DLS. SEM images supported with EDX analysis showed that particles were succesfully coated with silver. Highest magnification was x50000. Further than this value, the image was getting blurry and it was not possible to obtain the image of coating with the size of particles. In order to obtain the size of nanoparticles DLS analysis was made. As a result of this analysis mean particle size was found as 291 nm. Zeta potential result was found as -23.09 mV. This shows that surface of the particles was negatively charged which enables to the binding of positively charged heavy metal ions. Heavy metal removal study was carried out with Varian Atomic Absorption Spectrometer. With the aid of atomic absorption spectrometer, initial and final concentration of metal solutions were found and from these values removal percentages were calculated by using the formula below.

$$\%\text{adsorption} = (C_i - C_e / C_e) \text{ X } 100 \qquad \mathbf{(4.1)}$$

In each study daily prepared copper and cadmium standard solutions were used. For linear calibration studies, copper standard solutions were prepared as 1, 2 and 3 mg L^{-1} and for cadmium as 0.5, 1 and 2 mg L^{-1}. Optimization of the conditions was made by using one factor at a time procedure. First pH value was determined by adjusting particle mass to 10 mg and contact time to 10 minutes. Four different pH values were used (pH 3, 5, 7 and 9). pH value adjustments were made with 0.01M HCl and NaOH solutions. With these values highest removal percentage was obtained with pH value 9 as 89.92% for copper and 94.27% for cadmium. Comparing to the other resources in literature pH value 9 is not neutral but removal percentages were as the highest among others. In previous studies Fe_3O_4/HA magnetic nanoparticles used for the removal of various heavy metal ions and for this study optimum pH was found as 6, Liu et al. (2008). Liu et al. (2008) have found the increase in the removal of metal ions when pH value was increased as well. In their study, for the removal of copper pH value 3 obtained 20%, pH value 5 obtained 40%, pH value 7 obtained 80% and pH value 9 obtained 90% metal ion removal. Activated biocarbon used for the removal of lead and Cadmium as well. In this study pH value was adjusted to 4.5 for lead and 4.8 for cadmium and removal percentages were 95% and 98% respectively, Singanan (2011). Daifullah et al. (2004) used rice husk for the removal of heavy metal ions. They prepared two type of sorbents with different pH values. First one had pH value 3.51 and the other had pH value 11. They found the removal percentage as 99%. Erdem et al. (2004), used natural zeolites. Their pH values were ranged between 6-7. Copper removal at this value was around 65%. Results show that the study range for nanoparticles although more basic the removal percentage reaches the highest value.

Second factor was particle mass. Particles with different mass values (5, 10, 15, 20 and 25 mg) were tested in metal ion solutions with a pH value of 9 for 10 minutes of contact time. 20 mg particles had the highest removal percentage value as 93.2% and 95.52% for copper and cadmium, respectively. Comparing to the most of the studies in literature the amount of particle used was very little with a higher removal percentage. Liu et al. (2008) was found optimum particle mass as 10 mg. Singanan

(2011) found the optimum mass value of activated biocarbon as 2.5 g. The mass of rice husk used for the removal was between 0.010 – 0.150 g, Daifullah et al. (2004). and Erdem et al. (2004) used 10 g of zeolite for the heavy metal removal. These results show that, comparing to the work of Liu et al. (2008) although the removal percentage of metal ions was the same, particle mass of nanoparticles was two times bigger. In comparison with the work of other scientist using nanoparticles requires less mass of the sorbent.

The last study was made with 20 mg particles in pH value 9 for five different contact time (5, 10, 20, 25 and 30 min.). Although it has been some little increases or decreases between 20 and 30 minutes contact time for copper and cadmium, highest removal percentage can be accepted with 20 min contact time. This result again showed that comparing to the other studies in literature using nanoparticles makes a great difference in terms of contact time. Because most of the time by using zeolites or other sorbent materials removal of the heavy metal ions takes couple of hours. Liu et (2008) were found the contact time as 15 minutes. Daifullah et al (2003) arranged the contact time as 24 hours to obtain removal values closer to 90%. Erdem et al (2004) used the natural zeolites and obtained the optimum contact time as 5.5 hours. Singanan et al. (2011) found the contact time as 180 min by using activated biocarbon. These results show that using nanoparticles is much faster than other common techniques. Adjusting the particle size can make this value even less.

At last a mixed solution of copper and cadmium metal ions was used to understand if there was any selectivity on one of these metal ions in terms of the sorption on humic acid. It was understood that it was possible to adsorb both of these metal ions with humic acid at the same time. By using the optimized values (pH:9, 20 mg particle and 20 min contact time) mean removal percentage of Copper was found as 92.54% and of Cadmium 95.81%. Percentage removal of heavy metal ions by using Fe_3O_4/HA particles was found as 86% for Copper and 96.8% for Cadmium, Liu et al. (2008). Singanan (2011) obtained the highest percentage for Cadmium as 98% by using activated biocarbon. Erdem et al. (2004) were found the highest value as 65% for the removal of Copper. Daifullah et al. (2003) were found 99% removal for Cadmium and Copper. Results show that in terms of particle mass and time Fe_3O_4/HA/Ag nanoparticles were more usefull. Because to obtain the same removal percentages very short contact time and very little amount of particles were used. For further studies these particles can be used to remove the bacterial pollution in water. In order to increase the stability property of synthesized particles, during the synthesis procedure particles will be modified using antioxidants.

REFERENCES

Aguilar-Artega, K., Rodriguez, J. A., Barroda, E. (2010). Magnetic Solids in Analytical Chemistry: A Review, Analytica Chimica Acta.

Andjelkovic, T., Perovic, J., Purenovic, M., Blagojevic, S., Nikolic, R., Andjelkovic, D., Bojic, A. (2006). A direct potentiometric titration study of the dissociation of humic acid with selectively blocked functional groups, *Ecletica quimica*, **31**, 3.

Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (1985). Humic substances in Soil and Sediment, Water Wiley, New York, 1985, 13.

Aiken, G. R., McKnight, D. M., Wershaw, R. L., MacCarthy, P. (1985). Humic substances in Soil and Sediment, Water Wiley, New York, 1985, 493.

Ashtari, P.,Wang, K., Yang, X., Huang, S., Yamini, Y. (2005). Novel seperation and preconcetration of trace amounts of Copper(II) in water samples based on neocuproine modified magnetic nanoparticles, *Anal. Chim. Acta*, **550,** 18-23.

Avena, M. J., Koopal, L. K., van Riemsdijk, W. H. (1999). Proton bindings to Humic acids: Electrostatic and intrinsic interactions, *J. Colloid Interface Sci.*, 217, 37.

Batlle, X. and Labarta, A. (2002). Finite size effects in fine particles: magnetic and transport properties, *J. Phys. D. Apply. Phys.*, **35**, R15.

Berry, C. R. (1967). Structure and optical absorption of AgI microcrystals, *Phys. Rev.*, **161,** 848**.**

Bhadra, D., Bhadra, S., Jain, P. and Jain. N.K. (2002). Pegnology: a review of PEG-ylated systems. Pharmazie, **57**, 5-29.

Brice-Profeta, S., Arrio, M. A., Tronc, E., Menguy, N., Letard, I., Cartier dit Moulin, C., Nogues, M., Chaneac, C., Jolivet, J. P., Saintctavit, P. H. (2005). Magnetic order in g-Fe_2O_3 nanoparticles: a XMCD study. *J. Magn. Magn. Mater.*, **288**, 354.

Buffle, J. (2006). The key role of environmental colloids/nanoparticles for the sustainability of life. *Environ. Chem.* **3**, 155**e**158.

Carter, W. C. and Suffet, I. H. (1982). Binding of DDT to dissolved humic materials, *Environ. Sci. Technol.,***16**, 735.

Chang, Y. C. and Chen, D. H. (2005). Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu(II) ions., *J. Colloid Interface Sci.*, **283**, 446–451.

Chekanova, A., Sorkina, T. A., Dubov, A., Nikiforov, V. N., Davydova G. A., Selezneva, I. I., Goodilin, E. A., Trusov, L. A., Korolev, V. V., Arefev, I. M., Perminova, I.V. , Tretyakov, Y. D. (2009). New environmental nontoxic agents for the preparation of core-shell magnetic nanoparticles, *Mendeleev Commun.*, **19**, 72–74

Chen, C. (1986) Magnetism and Metallurgy of Soft Magnetic Materials, Dover Publications, Inc., New York.

Chen, M., Yamamuro, S., Farrell, D. and Majetich, S. A. (2003). Gold coated Iron nanoparticles for Biomedical applications, *J. Appl. Phys.*, **93**, 7551–7553.

Chin, A.B. and Yaacob, I.I. (2007). Synthesis and characterization of magnetic iron oxide nanoparticles via w/o microemulsion and Massart's procedure, *Journal of Materials Processing Technology*, **191**, 235–237.

Daifullah, A.A.M, Girgis, B. M., Gad, H. M. H. (2003). Utilization of agroresidues (rice husk) in small waste water treatment plans, *Materials Letters* , 57, 1723– 1731

De Jaeger, N., Demeye, H., Findy, R., Sneyer, R., Vanderdeelen, J., Van der Meeren, P., Laethem, M. (1991). *Part. Syst., Charact.*, **8**,179.

Erdem, E., Karapınar, N., Donat, R. (2004). The removal of heavy metal cations by natural zeolites, *Journal of Colloid and Interface Science*, 280, 309–314

Faraji, M., Yamini, Y. and Razaee, M. (2010). Magnetic Nanoparticles: Synthesis, Stabilization, Functionalization, Characterization and Applications, *J. Iran. Chem. Soc.*,**7(1),** 1-37.

Fiorani, D. (2005) Surface Effects in Magnetic Nanoparticle, Nanostructure Science and Technology Series, Springer, chap. 6,7,8.

Gaffney, J. S., Marley, N. A. and Clark, S. B. (1996). Humic and Fulvic Acids and Organic Colloidal Materials in the Environment, ACS Symposium Series; American Chemical Society, Washington, DC, 1996.

Garcia, M. A., Paje, S. E. and Llopis, J. (1999). A simple model for evaluating the optical absorption spectrum from small Au colloids in sol-gel, Chem. *Phys. Lett.*, **315**, 313-320.

Gao, J., Gu, H. and Xu, B. (2009). Multifunctional Magnetic Nanoparticles: Design, Synthesis, and Biomedical Applications, Accounts of chemical research, **42(8)**, 1097-1107.

Ghabbour, E.A., Davies G., Ghali, N.K., Mulligan, M.D. (2001). The effect of temperature on tight metal binding by peat and soil derived solid humic acids., *Canad. J. Soil. Sci.*, **81**, 331-336.

Ghosh, S., Mashayekhi, H., Pan, B. and Bhowmik, P. (2008). Colloidal Behavior of Aluminum Oxide Nanoparticles As Affected by pH and Natural Organic Matter, *Langmuir*, **24**, 12385-12391.

Gong, J. L., Liang, Y., Huang, Y., Chen, J. W., Jiang, J. H., Shen, G. L.,Yu, R. Q. (2007). Ag/SiO_2 core-shell nanoparticle-based surface-enhanced Raman probes for immunoassay of cancer marker using silica-coated magnetic nanoparticles as separation tools, Biosens. *Bioelectron.* **22**, 1501-1507.

Green, J.B. and Manahan, S.E. (1981).Absorption of sulphur dioxide by sodium humates, *Fuel*, **60**, 488-494.

Gu, H. W.,Yang, Z. M., Gao, J. H., Chang, C. K., and Xu, B. (2005) Heterodimers of nanoparticles: Formation at a liquid-liquid interface and particle-specific surface modification by functional molecules, *J. Am. Chem. Soc.*, **127**, 34–35.

Guzman, K. A. D., Finnegan, M. P. and Banfield, J. F. (2006). Influence of Surface Potential on Aggregation and Transport of Titania Nanoparticles, *Environ. Sci. Technol.*, **40(24),** 7688–7693.

Hernando, A., Crespo, P. and Garcia, M.A. (2005). Metallica Magnetic Nanoparticles, *The Scientific World Journal*, **5**, 972-1001

Hosokawa, M., Nogi, K., Naito, M. and Yokoyama, T. (2007). Nanoparticle Technology Handbook, Elsevier.

Hosse M. and K.J. Wilkinson (2001). Determination of electrophoretic mobilities and hydrodynamic radii of three humic substances as a function of pH and ionic strength, *Environ. Sci. Technol.*, **35**,4301- 4306.

Hövel, H., Fritz, S., Hilger, A., Kreibig, U. and Völlmer, M. (1993). Width of cluster plsmon resonances: bulk dielectric functions and chemical interface damping, *Phys. Rev.*, **B48**, 18178 – 18188.

Hu, J. and Lo, M. C. (2004). Chen, G. H. Removal of Cr(VI) by magnetite Nanoparticles, *Water Sci. Technol.*, **50**, 139–146.

Huang, J., Li, Q., Sun, D., Lu, Y., Su, Y., Yang, X., Wang, H., Wang, Y., Shao, W., He, N., Hong, J., Chen, C. (2007). Biosynthesis of silver and gold nanoparticles by novel sundried *Cinnamomum camphora* leaf, *Nanotechnology*, **18**, 105104.

Hunter, R. J. (1988). Zeta Potential in Colloid Science: Principles and Applications, Academic press, UK.

Iida, H., Takayanagi, K., Nakanishi, T. and Osaka, T. (2007). Synthesis of Fe_3O_4 Nanoparticles with various sizes and magnetic properties by controlled hydrolysis, *J.Colloid Interface Sci.*, **314**, 274.

Ills, E. and Tombacz, E. (2003).The role of variable surface charge and surface complexation in the absorption of humic acid on magnetite, *Colloids Surf.*, **230**, 99–109.

Ito, A., Shinkai, M., Honda H., and Kobayashi, T. (2005). Medical application offunctionalized magnetic nanoparticles. *J. Biosci. Bioeng.*, **100**, 1–11.

Jun, B. H., Noh, M. S., Kim, G., Kang, H., Kim, J. H., Chung, W. J., Kim, M. S., Kim, Y. K., Cho, M. H., Jeong, D. H., Lee, Y. S. (2009). Protein seperation and identification using magnetic beads encoded with surface enhanced Raman spectroscopy, *Anal. Biochem.*, **391**, 24 30.

Kandori, K., Kawashima, Y., Ishikawa, T. (1992). Efects of citrate ions on the formation of monodispersed cubic hematite particles, *J. Colloid Interface Sci.*, 1**52**, 284.

Khanna, S. N. and Linderoth, S. (1991). Magnetic behavior of clusters of ferromagnetic transition metals, *Phys. Rev. Lett.*, **67**, 742.

Kim, H., Achermann, M., Balet, L. P., Hollingsworth, J. A., Klimov, V. I. (2005) Synthesis and characterization of Co/CdSe core/shell nanocomposites: Bifunctional magnetic-optical nanocrystals, *J. Am. Chem. Soc.*, **127**, 544–546.

Kirby, B., **Hasselbrink, E. F.** (2004) *Electrophoresis*, **2s**, 187-202

Kobayashi, Y., Horie, M., Konno, M., Rodriguez-Gonzalez, B. Liz-Marzan, L. M. (2003). Preperation and properties of silica coated cobalt nanoparticles, *J. Phys. Chem.***, 107,** 7420.

Kortan, A. R., Hull, R., Opila, R. L., Bawendi, M. G., Steigerwald, M. L., Carroll, P. J., Brus, L. E. (1990). Nucleation and growth of cadmium selendie on zinc sulfide quantum crystallite seeds, and vice versa, in inverse micelle media, *J. Am. Chem. Soc.*, **112**, 1327.

Langer, R. (2000). Biomaterials in drug delivery and tissue engineering: one laboratory's experience. *Acc. Chem Res.*, **33**, 94-101.

Lin, J., Zhou, W., Kumbhar, A., Wiemann,J., Fang, J., Carpenter, E.E. and C. J. O'Connor (2001). Gold-Coated Iron (Fe@Au) Nanoparticles: Synthesis, Characterization, and Magnetic Field-Induced Self-Assembly, *J. Solid State Chem.*, **159**, 26.

Liu, X., Guan, Y., Shen, R., Liu, H. (2005). Immobilization of lipase onto micron size magnetic beads, *J. Chromatogr. B*, **822**, 91-97.

Liu, J. , Zhao, Z. and Binjiang, G. (2008). Coating Fe3O4 Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water, *Environ. Sci. Technol.*, **42**, 6949–6954

Lu, J., Li, Y., Yan, X., Shi, B., Wang, D., Tang, H. (2009). Sorption of atrazine onto humic acids (HAs) coated nanoparticles, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **347**, 90–96

Mandal, S., Phadtare, S. and Sastry, M. (2005). Interfacing biology with nanoparticles, *Curr. Appl. Phys.*, **5**, 118.

Mohanpuria, P., Rana, N.K. and Yadav, S.K. (2008). Biosynthesis of nanoparticles: technological concepts and future applications, *J. Nanopart. Res.*, **10**, 507.

Mohanraj, V. and Chen, Y. (2006). Nanoparticles – A Review, Trop J Pharm Res, **5**, 1.

Morales, M. P., Veintemillas-Verdaguer, S., Montero, M. I., Serna, C. J., Roig, A., Casas, L.l., Martinez, B. and Sandiumenge, F. (1999). Surface and Internal Spin Canting in γ-Fe_2O_3 Nanoparticles, *Chem. Mater.*, **11**, 3058.

Moulin, V. and Ouzounian, G. (1992). Role of colloids and humic substances in the transport of radioelements through the geosphere, *Appl. Geochem.*, **1**, 179-186.

Murray, C. B., Sun, S., Doyle, H. and Betley, T. (2001). Monodisperse 3d transition-metal (Co, Ni, Fe) nanoparticles and their assembly into nanoparticle superlattices, *MRS Bull.*, **26**, 985.

Nakashima, K., Shaoyong, X., Yongkuan, G.,Miyajima, T. (2008). Characterization of humic acids by two-dimensional correlation fluorescence spectroscopy, *Journal of Molecular Structure*, **883–884**,155–159

Nowack, B. and Bucheli, T.D. (2007). Occurrence, behavior and effects of nanoparticles in the environment, *Environmental Pollution*, **150**, 5e22.

O'Brien, P., Pickett and N. L. (2001). Nanocrystalline Semiconductors: Synthesis, Properties and Perspectives, *Chem. Mater.*, **13**, 3843-3858.

O'Handley, R. C. (2000). Modern Magnetic Materials. Principles and Applications; John Wiley and Sons: New York.

Okuyama, K., Masuda, H. and Morooka, S. (1992). Fine particle technology, Ohmsha, Tokyo, p.3.

Parham, H. and Rahbar, N. (2009). Solid phase extraction–spectrophotometric determination of fluoride in water samples using magnetic iron oxide nanoparticles, *Talanta*, **80**, 664–669.

Pena-Mendezi, E., Havel, J., Patocka, J. (2004). Humic substances . compounds of still unknown structure: applications in agriculture, industry, environment, and biomedicine, *J. Appl. Biomed.*, **3**, 13-24

Pecora, R. (1985) Dynamic Light Scattering : Applications of Photon Correlation Spectroscopy, Plenum Press. p. 59-81.

Penn, S. G., He, L., and Natan, M. J. (2003). Nanoparticles for bioanalysis. *Curr. Opin. Chem. Biol.*, **7**, 609–615.

Philip, D. (2009). Biosynthesis of Au, Ag and Au–Ag nanoparticles using edible mushroom extract, *Spectrochimica Acta*, Part A 73, 374–381.

Purdue, E. M. and Lytle, C. R. (1983). A distribution model for binding of protons and metal ions by humic substances, *Environ. Sci. Technol.*, **17**, 654-660.

Qiu, J., Xiong, M., Liang, R., Peng, H. and Liu, F. (2009). Synthesis and characterization of ferrocene modified Fe3O4@Au magnetic nanoparticles and its application, *Biosensors and Bioelectronics*, **24**, 2649–2653.

Ravel, B., Carpenter, E. E. and Harris, V. G. (2002). Oxidation of iron in iron/gold core/shell nanoparticles, *J. Appl. Phys.*, **91**, 8195–8197.

Safarikova, M. and Safarik, I. (1999). Magnetic solid phase extraction, *J. Magn. Magn. Mater.*, **194**, 108-112.

Sampedro, B., Crespo, P., Hernando, A., Litran, R., Sanchez Lopez, J.C., Lopez Cartes, C., Fernandez, A., Ramirez, J., Gonzalez Calbet, J.M. and Vallet, M. (2003) Ferromagnetism in fcc twinned 2.4 nm size Pd nanoparticles, *Phys. Rev. Lett.*, **91**, 237203.

Savage, N. and Diallo, M. S. (2005). Nanomaterials and water purification: Opportunities and challenges. *J. Nanopart. Res.*, **7**, 331– 342.

Singanan, M. (2011). Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon, *ScienceAsia*, 37, 115–119.

Tan, K. H. (2003). Humic matter in soil and the environment, principles and controversies, Marcel Dekker inc, 2003.

Tartaji, P., Moralesi, M., Veintemillas – Verdaguer, S., Serna, C., Gonzalez, T. (2003). The preparation of magnetic nanoparticles for applications in biomedicine, *J. Phys. D: Appl. Phys.*, **36**, R182–R197.

Tanaka, K., to, T., Kobayashi, T., Kawamura, T., Shimada, S., Matsumoto, K., Saida, T., and Honda, H. (2005). Heat immunotherapy using magnetic nanoparticles and dendritic cells for T-lymphoma. *J. Biosci. Bioeng.,* **100**, 112–115.

Uheida, A., Salazar-Alvarez, G., Björkman, E., Yu, Z., Muhammed, M. (2006). Fe_3O_4 and gamma Fe_2O_3 nanoparticles for the adsorption of Co^{+2} from aqueous solution, *J. Colloid Interface Sci.*, **298**, 501.

Xu, Z. C., Hou, Y. L. and Sun, S. H. (2007). Magnetic Core/Shell Fe_3O_4/Au and Fe_3O_4/Au/Ag Nanoparticles with Tunable Plasmonic Properties, *J. Am. Chem. Soc.*, **129,** 8698.

Yantasee, W., Warner, C., Sangvanich, T., Addleman, R.S., Carter, T., Wiacek, R.J., Fryxell, G., Chalk, C.T. and Warner, M. (2007). Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles, *Environ. Sci. and Tech.*,**41**, 14.

Wei, S., Wang, Q., Zhu, J., Sun, L., Lin, H. and Guo, Z. (2011). Multifunctional composite core–shell nanoparticles, *Nanoscale*, **3**, 4474

Wen-Tso, L., (2006). Nanoparticles and Their Biological and Environmental Applications, *Journal of Bioscience and Engineering*, **102**, 1-7.

West, J. L. and Halas, N. J. (2000). Applications of nanotechnology to biotechnology commentary. *Curr. Opin. Biotechnol.*, **11**, 215–217.

Wikström, P., Flygare, S., Gröndalen, A., Larsson, P. O. (1987). *Anal. Biochem.,***167**, 331-339.

Zeng, H. and Sun, S. (2008). Syntheses, Properties, and Potential Applications of Multicomponent Magnetic Nanoparticles, *Adv. Funct. Mater.*, **18**, 391–400

Zhang, W. Z. (2003). Nanoscale iron particles for environmental remedia- tion: An overview, *J. Nanopart Res.* **5**, 323.

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