



Magnetite Nanoparticles in Wastewater Treatment

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Abstract – Clean water is very important for health and well-being of humans and ecosystem. However, over the year, a billion tons of industrial waste, fertilizers and chemical waste were dumped untreated into water bodies, such as rivers, lake and oceans contributing towards water pollution, then threatening human health and ecosystem. Hence, the need for clean water has urged scientists to research and find solutions for improving water quality. Application of nanoparticles in wastewater treatment improves the environmental quality by elimination of harmful pollutants in wastewater. Magnetite is one of the nanoparticles used in wastewater treatment because of its specific large surface area, high reactivity in adsorption and recoverable from treated water via magnetic separation technology. Preparation method of magnetite nanoparticles is the important key to its adsorption efficiency.

Keywords: Adsorption, magnetic adsorbents, heavy metals removal, magnetite nanoparticles, review, wastewater, wastewater treatment

Introduction

Water is an important natural resources for sustaining livelihoods, human well-being and socioeconomic development. Globally, there is enough water available currently to fulfil human needs. However, according to the Food and Agriculture Organization, world population is predicted to grow from 6.9 billion in 2010 to 9.1 billion in 2050 (World Water Development Report, 2012). Drastic increase in world population has caused doubt and worry in terms of clean water source for future needs. Human being keeps demanding more clean water for their hygiene, sanitization and health. Humans use about 70% of freshwater for irrigation, 20% for industrial and 8% for domestic use. Used water is discharged as untreated wastewater into open water bodies, then leads to ultimately contamination of water, mostly into rivers, lakes and sea. Uncontrolled consumption of clean water results in large production of wastewater discharged into the water bodies. There are two types of wastewater, domestic or sanitary wastewater and industrial wastewater. Domestic wastewater is wastewater that comes from residential sources, including toilet, sinks, laundry containing intestinal disease organisms. Industrial wastewater is discharged from manufacturing and processes and commercial enterprises containing residual acid, plating metals and toxic chemicals. About 11 billion per day of wastewater is collected from homes, municipal, commercial and industrial premises, and drainage over 624 200 kilometres (Thurgod, 2004).

Effects of Wastewater Pollutants

It is essential to know that contaminants in wastewater threatened human health and environment. Wastewater discharged into water bodies may result in decreased levels of dissolved oxygen, water colour changes, release of toxic substances, increased in nutrients and bioaccumulation in aquatic life

(Environmental Canada, 1997). Excessive nutrients such as nitrogen and phosphate found in agricultural wastewater fertilized rapid growth of microscopic algae and water weeds exhibiting eutrophication phenomenon. These plant growth and decomposed consume dissolved oxygen in the water and produce algal suspension and weed mats on the surface of water smothering other aquatic life in the water. Besides, bacterial breakdown of organic solids contributes to the depletion of dissolved oxygen level in the contaminated water bodies (Borchardt and Statzner, 1990). When the dissolved oxygen level is low, it will affect the survival of the fish in the contaminated water. Either in short or long term, fish tend to get the disease, retard in growth, do not swim well and their lives endangered (Chambers and Mills, 1996). As time goes on, high concentration of toxic substances in wastewater accumulates in the tissue of plants and animals then threatened human health through the food chain (Chambers and Mills, 1996). Table 1 shows the illustrations of contaminant and possible effects of the contaminant to the human health.

Table 1: Possible Effect of Contaminants in Wastewater to Human Health

Contaminants	Sources	Effects	References
Metals	Aluminium	Organic chemicals	Memory damage, convulsion, Alzheimer diseases
		Fertilizers	
	Cadmium	Aircraft plating Finishing	Hyperglycemia, reduced immunopotency, anemia, liver and kidneys damage
		Petroleum refineries	
		Chlorine Fertilizer	
Chromium	Petroleum refineries	Convulsion, kidney and liver damage, skin ulcers, lung cancer	
	Steelworks		
	Aircraft plating Finishing		
	Pulp and paper mills		
	Organic chemicals		
	Alcalies, Chlorine		
	Fertilizers		
	Petroleum refineries		
	Steelworks		
	Aircraft plating, Finishing		
Flat glass, cement			
Textile mills			
Tanning			
Power plants			
Iron		Degenerative disease, ageing	Jordao et. al., 2002
Lead	Pulp and paper mills	Encephalopathy in children	Bond and Straub,1974; Jordao et. al., 2002
	Organic chemicals		
	Alcalies, Chlorine		
	Fertilizers		
	Petroleum refineries		
	Steelworks		
Mercury	Pulp and paper mills	Brain damage, heart,	Bond and

		Organic chemicals Alcalies, Chlorine Fertilizers Steelworks Aircraft plating Finishing	kidney and lung disease, human nervous central system damage	Straub,1974; Wang, Kim, Dionysiou, Sorial, & Timberlake, 2004; Rai and Tripathi, 2007
	Nickel	Pulp and paper mills Fertilizers Petroleum refineries Steelworks Aircraft plating Finishing	Cancer	Bond and Straub,1974; Jordao et. al., 2002; Devi et. al., 2011
	Zinc	Pulp and paper mills Organic chemicals Alcalies, Chlorine Fertilizers Petroleum refineries Steelworks	Muscular pain and intestinal haemorrhage	Bond and Straub,1974; Honda, Tsuritani, Ishizaki, & Yamada,. 1997; Jordao et al., 2002; Singh, Sharma, & Bohra, 2000;
Organic/inorganic matters	Fluoride	Scrubbing of flue gases Glass etching	Dental and skeletal fluorosis, deformation of ligaments, bending spinal cords	Bond and Straub,1974; Janardhana et al., 2009
	Nitrate	Sewage industrial Fertilizer	Methemoglobinemia in infants,cancer	Abdel-Raouf, Al-Homaidan, Ibraheem, 2012; Purushotham, Narsing Rao, Ravi Prakash, Ahmed, & Ashok Babu, 2011
	Potassium	Sewage industrial Fertilizer	Nervous and digestive disorders, kidney heart disease, coronary artery disease, hypertension, diabetes, adrenal insufficiency, pre- existing hyperkalaemia	Abdel-Raouf et. al., 2012; Purushotham et al., 2011
	Sulphate	Pulp processing Viscose film manufacturing	Laxative effect	Bond and Straub,1974; Abdel-Raouf

Textile industry
Tanneries
Gas manufacturing
Sewage industrial

et. al., 2012;
Purushotham et
al., 2011

Structural Background of Magnetite

Magnetite is a black, opaque mineral that has an inverse spinel crystal structure. It has an alternating octahedral and mixed tetrahedral-octahedral layers (Hill, Craig, & Gibbs, 1979). Half of the octahedral is filled with ferrous crystal species because of ferrous crystal stabilization energy. Meanwhile, at the other half octahedral lattice sites and all tetrahedral lattices sites is filled with ferric species. The deduced chemical formula for magnetite crystal structure can be written as $Y[XY]O_4$, where X and Y represent ferrous and ferric, while the bracket is for octahedral sites and the absence of bracket represents tetrahedral sites. Furthermore, magnetite has a face centered cubic unit cell with crystal lattice parameter, $a = 0.8396$ nm (Cornell and Schwertmann, 2003).

Importance of Magnetite Nanoparticles

There are many uses of magnetite nanoparticles in different fields. In the medical field, magnetite nanoparticles play an important role, especially in Magnetic Resonance Technology. In Magnetic Resonance Imaging (MRI), patients are scanned to observe any abnormalities in the body's tissue or organs. By using magnetite nanoparticles, the obtained image of tissues and organs is sharper and clearer (Zhang et. al., 2011). Furthermore, magnetite nanoparticles are utilized in drug delivery. Magnetite nanoparticles attached to a cancer drug through a series of method, then the magnetite nanoparticles could be delivered directly to the cancer cell in the human body area and release the drug (Lim, Jang, Lee, Haam, & Huh, 2013). In other fields, magnetite nanoparticles act as dampening and cooling agents in loudspeaker (Elmer, 1934; Raj and Moskowitz, 1990). In the environmental field, magnetite was used to remove particles and contaminations from drinking/waste water streams. Through electro-chemical interaction between magnetite nanoparticles and particles binding, magnetite can be recycled and utilized in the magnetic field recovery system. More importantly, magnetite nanoparticles are able to remove radioactive chemicals and toxins in polluted/waste water. Several scientists suggested that iron oxide is one of the best adsorbent that could be used in wastewater treatment (Schultz et. al., 1987; Edwards and Benjamin, 1989). This becomes prominent since humans are now aware of the importance of clean water for their health, sanitization and hygiene. Therefore, many organizations and scientists are working hard on protecting and restoring waterways from contamination and preserving water ecosystem from destruction.

Magnetite Nanoparticles in Wastewater Treatment

Nowadays, numerous adsorbents have been investigated for the efficiency contaminant removal from wastewater including magnetite. Magnetite has been used in precipitation/coagulation/adsorption treatment in order to remove phosphorus or copper in wastewater treatment (De Latour, 1976) and mercury (Terashima, Ozaki, & Sekine, 1986).

Lei, Hao, Zhang, & Zhou (2007) made a combination of aqueous pulsed discharged plasma (PDP) process with magnetic material nanoparticle for removal of p-chlorophenol (4-CP) contaminated wastewater. Fenton's reaction mechanisms took place on the surface of magnetic material to produce more hydroxyl radical in order to degrade more 4-CP substances. Fenton's reaction mechanism is a process where the H_2O molecule is ionized with an energized electron producing hydroxyl radical. Then two hydroxyl molecules combine together to produce hydrogen peroxide. These hydrogen peroxide reacts with ferrous ion at the surface of magnetite producing ferric ions that take the role in degrading 4-CP substances. It was found that the removal efficiency was increased as the Fe_3O_4 increased.

Meanwhile, Mann (2012) has North Saskatchewan River water tested with different concentration of combination magnetite nanoparticles, aluminium sulfate and polyacrylamide for their removal efficiency of model wastewater bacteria. Turbidity test reported that, 300 mg/L magnetite nanoparticles has the highest removal efficiency of 98% without combination of aluminium sulfate and polyacrylamide. Time taken for removing turbidity using magnetite was 10 minutes compared to 30 minutes for aluminium sulfate and polyacrylamide combination. Also, it was found that electrostatic interaction was not the dominant mechanism for the adsorption of bacteria cell. Somehow, there was some sort of chemical and colloidal interaction of O-H groups on the cell wall.

Besides, Panasiuk (2010) has studied factors affecting phosphorus removal and recovery using magnetite nanoparticles. Factors such as the ratio of Fe(II)/Fe(III), adsorption of magnetite nanoparticles in different concentration of phosphorus and efficiency of Sodium Hydroxide (NaOH) to remove phosphorus from magnetite were investigated. From the experiment, Panasiuk found that the efficiency of phosphorus removal decreased as the ratio of Fe(II)/Fe(III) increased and efficiency of magnetite nanoparticle adsorption decreased with the increased phosphorus concentration because the same amount of magnetite was used to adsorb larger amount of phosphorus in the solution. Magnetite nanoparticles was recovered from phosphorus and recycled again in 25ml of 120g/L of phosphorus solution for the second and third time. The removal efficiency of recovered magnetite was decreased after recycle for the second and third time.

Most studies were focused on adsorption of magnetite nanoparticles on heavy metals from industrial wastewater since the last few decades. Oskay (2003) reported that magnetite can remove some metals in wastewater from industries and synthetic wastewater. The efficiency of using magnetite nanoparticles is affected by many factors such as amount of magnetite used, particle size of magnetite, contact time between magnetite and wastewater and pH value of the solution. Moreover, Johnson et. al. (2002) found that magnetite nanoparticles synthesized at low temperature 6 °C with pH 9 could effectively remove heavy metals from low and high concentration of initial concentration of heavy metal depending on the magnetite nanoparticles dosage. However, at low pH value, only small percentage removal of heavy metals was observed due to competition of proton and heavy metals from the oxide surface site. More importantly, by adding organic to react with magnetite, either inhibiting or enhancing the removal of heavy metal depends on the type of chelator present.

Magnetite nanoparticles give effective and specific adsorption towards contaminants in wastewater. Magnetite nanoparticles often had agglomeration problems because of its extremely small particle size. Thus, many scientist comes out with an effective approach to overcome agglomeration problem. They fabricated hybrid adsorbents by coating or copolymer with magnetite. Zhang et. al. (2015) synthesized magnetic composites of magnetite nanoparticles, graphene oxide and Mg₃Al-OH layered double hydroxide denoted as MGL composites with varying graphene oxide contents via mechano-hydrothermal method. MGL then was used for removing the heavy metal Pb(II) and hydrophobic organic pesticide 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution. They found that the MGL composites have a strong magnetic response and able to remove both Pb(II) and 2,4-D pollutants with high capacity. As the amount of graphene oxide in the composites increased, the capability of adsorption was increased. MGL gives great potential in wastewater treatment as it remains almost constant removal efficiency even after reuse over six cycles.

In addition, Muthui (2013) synthesized polypyrrole-magnetite, PPy-Fe₃O₄ nanocomposites via in-situ chemical oxidative polymerization method. PPy-Fe₃O₄ was used for removal of highly toxic hexavalent chromium, Cr (VI) in synthetic wastewater. Effect of varying mass of magnetite in PPy loading was investigated. High amount of magnetite in the nanocomposites resulting in high adsorption of Cr (VI) in a short residence time. She proved that percentage of magnetite content in nanocomposites influenced the removal efficiency rate. Other than that, Wang et al (2014) conducted an experiment of magnetic biochar

that was prepared from eucalyptus leaf residue in order to remove heavy metals such as Cr(VI), total Cr, Cu(II), and Ni(II) in electroplating wastewater. These heavy metals were effectively removed from wastewater with removal rates of 97.11%, 97.63%, 100% and 100% respectively. After 10 minutes of magnetic separation, turbidity of treated solution was reduced.

Division of Chemical Scientific and Industrial Research Organization (CSIRO) has constructed three full-scale water purification plant to treat water from anaerobic, highly colored and turbidity level. 20 g/L of magnetite with raw water was used in order to remove color and turbidity of wastewater. Contact time took about six to seven minutes only. Furthermore, treatment process and recovery process of magnetite took five times faster than normal treatment (Bolto and Spurling, 1991). Meanwhile, at Sydney, sewage treatment process plant has been constructed. In container contain partially raw sewage, 5-70 micron magnetite particle was mixed with chemical coagulant such as ferric sulfate or polyelectrolyte to gain a lower BOD level (30 – 40 mg/L). Recovery of magnetite was done by magnetic flocculation and settling then washed with dilute caustic soda solution. All process took only 10 – 15 minutes for 100 kL/day (Bolto and Spurling, 1991).

Magnetite nanoparticles were chosen as absorbents because of the following main advantages. Small size magnetite provides a large surface area and highly active surface sites, which then lead to a very high adsorption capacity. An external adsorption process by magnetite shortens the adsorption time. Also, magnetite can easily be separated from the treated water by supplying an external magnetic field (Hu et al., 2005). Table 2 shows a summary of magnetite in wastewater treatment.

Preparation of Magnetite Nanoparticles

In the last decades, a variety methods of magnetite nanoparticles preparation have been developed and studied, reporting on efficient methods to produce the controlled shape, stable and monodispersed magnetite. Synthesis method is important in determining morphology, particle sizes and shape. The magnetite nanoparticles synthesis method including, co-precipitation of ferrous and ferric ions in alkaline medium (Almasy et al., 2015; Giraldo, Erto, & Moreno-Piraján, 2013; Hong, Li, Qu, Chen, & Li, 2009; Panasiuk, 2010; Petcharoen and Sirivat, 2012; Rajendran, Balakrishnan, & Kalirajan, 2015; Santoyo-Salazar, Castellanos-Roman, & Beatriz Gómez, 2007; Sun et al., 2006), electrochemical (Cabrera et al., 2008; Karami and Chidar, 2012), reverse micelle (Lee et al., 2005; Lee et al., 2008; Uskoković and Drogenik, 2007; Yao, Jiang, Wu, Gu, & Shen (2012), thermal decomposition (Zhang et al., 2006), hydrothermal synthesis (Xuan et al., 2007; Zhang et al., 2015) and high energy ball milling (Almasy et al., 2015; De Calvarho et al., 2013; Goya, 2004; Osterle et al., 2013). Most methods used are co-precipitation, thermal decomposition and hydrothermal synthesis because they could produce high quality of nanoparticles (Wu, He, & Jiang, 2008).

Co-precipitation method is a method that mixes ferric and ferrous ions in a 1:2 molar ratio in highly basic solutions at room temperature or elevated temperature. Surfactants such as dextran or polyvinyl alcohol can be added into reaction media to gain a very well disperse nanoparticle magnetite. This is because surfactant can be a protector for controlling size and stabilize colloidal dispersions (Novakova et al., 2003; Lee et al., 1996). Unfortunately, co-precipitation method results in a wide distribution of particles that needs further steps in size selection. Now, even though there is improvement in aqueous synthetic routes for magnetite nanoparticles preparation, still it cannot control particle sizes and polydispersity size. Also, due to aggregation problem, it is difficult to have single particle behavior and advantages of nanometer size. Hong et al. (2009) carried out a research on a biocompatible water-based magnetic fluid. Co-precipitation was employed using different dextran molecular weight and resulted in wide particle distribution size. Particle size gradually increased as the dextran molecular weight increased. Diameter size of magnetite nanoparticles was around 20 nm with highly aggregation problems due to large specific area surface and high surface energy. In addition, a chemical reaction between $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, deionized water and 1 M of NaOH under an air blown at a certain fixed temperature with 8 to 9 pH value producing

a black magnetite precipitation. Morphology, particle size and size distribution of magnetite nanoparticles were affected by modifying their reaction condition with dissolved oxygen, pH and temperature during preparation (Kahani and Yagini, 2014). Kahani and Yagini (2014) has made a comparison between chemical synthesis magnetite and biosynthesis magnetite. Crystallite sizes of chemical synthesis magnetite were not generally the same in sizes because of the aggregation of polycrystalline. Mean diameters of crystallites size chemically synthesis magnetite were 35.14 nm, 23.23 nm, 17.57 nm and 16.51 nm at temperature 273 K, 283 K, 293 K and 303 K respectively compared to 17.6nm crystallites size of biosynthesis magnetite. However, both chemical synthesis magnetite and biosynthesis magnetite has similar magnetic response due to their perfect crystallinity. Chemical synthesis of magnetite nanoparticles has saturation magnetization (M_s) of 78.2 emu/g, remanence of 12.9 emu/g and coercivity (H_c) of 98 Oe. Meanwhile biosynthesis magnetite nanoparticles have saturation magnetization of 60 emu/g, remanence of 10 emu/g and coercivity of 75 Oe.

For electrochemical method, magnetite nanoparticles obtained through electro-oxidation of Fe in the presence of amine surfactant as supporting electrolyte and coating agent, particle size and aggregation controller. Advantages of electrochemical technique are nonhazardous, inexpensive and simple method. (Karami and Chidar., 2012). However, Cabrera at al., 2007 found that the particle size of magnetite was constant at 20 nm as the current density increased from 10 to 200 mAcm⁻². Unfortunately, the particle sizes decreased from 30 nm to 20 nm after potential were over 6 V and metallic iron appeared as an impurity. These results showed that the electrochemical method was not ideal for preparing magnetite nanoparticles in large scale manufacturing. Also, magnetite behaved as ferromagnetic with 70 emu/g saturation magnetization which was slightly lower than reported value, 92 emu/g due to lack of crystallinity (Cullity, 1972).

A water-in-oil emulsion that generates reverse micelles, which acts as nano-reactors for various physico-chemical processes called reverse micelle method. Nanoparticle diameter is controlled by the relative amount of surfactant and solvent and the ratio of polar solvent to the surfactant (Blaney, 2007). Iron oxide nanoparticles were synthesized by a reduction-oxidation reverse micelle system with presence of sodium bis(2-ethylexyl) sulfosuccinate (Aerosol OT; AOT) and heptane as surfactants. Through Transmission Electron Microscopy (TEM), 4 nm diameter of iron oxide nanoparticle with high crystallinity and narrow size distribution was produced (Iida, Nakanishi, Takada, & Osaka, 2006) Using reverse micelle as nanoscale reactor, it is possible to produce iron oxide with narrow size distributions. Unfortunately, this method needs a large amount of organic solvent and surfactant as the reverse micelle stabilizer is expensive and low yield. Thus, reverse micelle is impossible to be used in a large scale production of iron oxide nanoparticle (Ye, Daraio, Wang, Talbot, & Jin, 2006).

High quality monodispersed magnetite nanoparticle can be obtained through thermal decomposition method; somehow, it requires relatively high temperature and complicated operation (Wu et. al., 2008). Zhang et. al. (2006) reported monodispersed magnetite nanoparticle of 7 nm and 19 nm coated with Oleic acid were prepared by the seed-mediated high temperature thermal decomposition of iron(III) acetylacetonate ($Fe(acac)_3$). They found that the total adsorption amount and cover density of oleic acid molecular on the magnetite nanosurface decreased as the particle size of magnetite increased. Also, interactions among the particles was reduced because of magnetite nanoparticles surface coating..

Selection synthesis method of magnetite nanoparticle is important as controlled shape and size are correlated with their magnetic properties. Due to difficulty in decomposition method to control size and shape, hydrothermal method has been developed. In hydrothermal method, a crystalline substance was synthesised in sealed containers from high temperature (range from 130 °C to 250 °C) at high vapor pressure (range 0.3 MPa to 4MPa). Hydrothermal synthesis produced a better and high purity crystalline magnetite nanoparticles (Wu et al., 2008). Xuan et al. (2007) reported magnetite nanoparticles with average particle size of 5.2 nm produced by the reduction reaction between $FeCl_3$ and ascorbic acid in a

hydrothermal system. Unfortunately, the excessive amount of ascorbic acid as surfactant leads to the formation of FeCO_3 . Also, only a small saturation magnetization which is 5.2 emu/g was obtained due to the smaller size and the existence of the surfactant.

Milling is a simple and efficient method that involves high mechanical energy applied on a powder loaded with several heavy balls in a container. The powder inside the container is crushed into a very fine powder depending on the milling time, milling speed and weight of ball to weight of powder ratio (Goya, 2004). Almasry et al. (2015) has carried out research on the benefits and disadvantages of producing magnetite nanoparticle using wet milling and chemical co-precipitate from iron salt precursor. They demonstrated that both synthesis methods gave similar sized magnetite nanoparticle which was around 10 to 15 nm. However, their magnetic response is different. Magnetite nanoparticles synthesized via wet milling has higher saturation magnetization 14 emu/g as compared to chemical co-precipitate method 3 emu/g. In another study, Priyadarshana et al. (2015) attempted to synthesis magnetite nanoparticle from a high purity ore found in Sri Lanka using a high energy ball mill. They found that the particle size of the magnetite nanoparticles after grinding was about 20 – 50 nm with uniform particle size distribution. However, milling requires high energy and long period of milling time to produce magnetite nanoparticles. Furthermore, milling results in highly strained grains and defect particles. More important, powder is easily contaminated due to high collision between the steel balls inside the container (Tavakoli et. al., 2007). Table 3 shows a summary method of preparation, coating, phase analysis, particle size analysis and magnetic analysis of magnetite.

Table 2: Summary of magnetite in wastewater treatment.

Sample	Method of preparation	Host removal	Factors affecting adsorption	Effectiveness	References
Magnetite	Co-precipitate	Phosphorus	<ul style="list-style-type: none"> • Ratio of Fe(II)/Fe(III) on magnetite • Adsorption time • Concentration of Phosphorus 	<ul style="list-style-type: none"> • 1:5 and 1:2 ratio of Fe(II)/Fe(III) use short time to sediment the magnetite and clear the upper liquid layer • Rapidly in 10 min, slowly after 10min until 60 min • 90% Phosphorus removal in low concentration., 19% in high concentration 	(Panasiuk, 2010)
Magnetite	Co-precipitation	Cadmium(II), cobalt(II) and lead(II)	<ul style="list-style-type: none"> • concentration of host solution • addition of organic material in magnetite 	<ul style="list-style-type: none"> • Concentration increases lead to large amount of magnetite needed to remove host • When acetic acid or malonic acid was present, decreases in removal efficiency, however oxalic acid enhances the removal of lead from solution. 	(Johnson et. al., 2002)
Magnetite	Pulsed discharge plasma	P-Chlorophenol (4-CP)	<ul style="list-style-type: none"> • Magnetite doses 	<ul style="list-style-type: none"> • Removal efficiency increases with increasing Fe₃O₄ dose 	(Lei et. al., 2007)
Ppy-Fe ₃ O ₄ nanocomposite	Copolymer template	Cr(VI)	<ul style="list-style-type: none"> • Mass of Fe₃O₄ in Ppy-Fe₃O₄ • Effect of adsorbent mass • Cr(VI) concentration 	<ul style="list-style-type: none"> • Higher amount of magnetite in nanocomposite, higher removal efficiency • Higher amount of adsorbent mass, higher removal efficiency, but it can approach its limit when no adsorption take place anymore • Higher concentration of Cr(VI) lead exhibit low removal efficiency 	(Muliwa, 2013)
Magnetite, aluminium sulfate and Polyacrylamide	-	Model bacteria Escherichia coli ATCC® 25922™, Pseudomonas putida ATCC®	<ul style="list-style-type: none"> • Magnetite ratio • Mixing time 	<ul style="list-style-type: none"> • Ratio cell:magnetite 1:50 removes 96.8% for E. coli, 94.8% for P. putida and 99.7% for M luteus. • Optimal time 10 to 20min with 200rpm 	(Mann and Mann, 2012)

Biochar-Fe3O4	Copolymer template	17453 TM and Micrococcus luteus ATCC® 4698 TM Cr(VI), Cr ions, Cu, Ni	<ul style="list-style-type: none"> • Initial pH value of Cr solution • Contact time • Temperature of Cr solution 	<ul style="list-style-type: none"> • pH from 1 to 4, removal efficiencies of Cr (VI) decreased rapidly, pH 4-6, no change • rapid removal in 30 min • increase in the temperature leads to an increase in removal efficiency 	(Wang et. al., 2014)
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Table 3: Summary of method preparation, coating, phase analysis, particle size analysis and magnetic analysis of magnetite.

Methods	Coating	Phase analysis	Particle size analysis	Magnetic analysis	References
Co precipitation	Aldehyde dextran	Cubic inverse spinel structure	20nm	Superparamagnetic, Ms >20emu/g	Hong et. al., 2009
Co precipitation	Oleic acid, Hexanoic acid	Cubic spinel structure 8 ferric ion at tetrahedral sites, 8 ferric ion and 8 ferrous ion at octahedral sites	10-40nm	Superparamagnetic, Ms with oleic acid 33.29emu/g, Ms with hexanoic acid 58.72emu/g, bare magnetite 57.2 emu/g.	Petcharoen and Sirivat, 2012
Co precipitation	Oleic acid	Cubic spinel structure	Average size 9.1nm	Superparamagnetic, Ms 3.6emu/g	Almasy et.al., 2015
Co precipitation	-	-	Average size 26.78nm	Superparamagnetic, Ms 90 emu/g	Rajendran et. al., 2015
Co precipitation	-	Cubic spinel structure	8nm	-	Giraldo et al., 2013
Co precipitation	-	Cubic structure	20nm	-	Santoyo – Salazar et. al., 2007
Co precipitation	sodium oleate, polyethylene glycol	Cubic structure	Spherical, 8.0nm,8.5nm	Superparamagnetic, Ms 41.60 – 49.42 emu/g	Sun et al., 2006
Electrochemical	Amine	Spinel structure	20 – 30nm	Ferromagnetic,	Cabrera et. al.,

Microemulsion	Iron salts	Spinel structure	2 – 10 nm	Ms 70emu/g Superparamagnetic, Ms decreases as the size decreases, 135-173 emu/g	2008 Y. Lee et al., 2005
Reverse micelle	Sodium bis(2-ethylhexyl) sulfosuccinate (AerosolOT;	Cubic spinel structure	4nm	0.41emu/g at 0K temperature	Hironori Iida et al., 2006
Reverse micelle	Silica	Cubic structure	5-20nm	Superparamagnetic at 300K temperature with 20emu/g Ms, Ferromagnetic at 2K temperature with 30 emu/g Ms	Lee et. al., 2008
Reverse micelle	Polyaniline (PANI)	Cubic structure	10nm	Superparamagnetic 30 emu/g	Yao et. al., 2012
Hydrothermal	-	Cubic structure	10nm	Superparamagnetic, 60 emu/g	Yao et. al., 2012
Hydrothermal	Ascorbic acid	Face centered cubic structure	5.2nm	Superparamagnetic, Ms 5.2emu/g	Xuan et. al., 2007
Thermal decomposition	Oleic acid	Cubic structure	7nm, 9nm	Ferromagnetic	Zhang et. al., 2006
High Energy Ball Milling	Graphite molybdenum disulphide	-	Cubic Structure	2 μ m	- Osterle et. al., 2013
High Energy Ball Milling	-	Cubic spinel structure	12-20nm	Superparamagnetic, Ms 217 emu/g	De Carvalho et. al., 2013
Milling	3%, 10%, 50% Methyl-alcohol	Cubic spinel structure	6-10nm	Ferrimagnetic, Ms 0.7emu/g, 15emu/g, 35 emu/g Coercivity 100 Oe	Goya, 2014
Milling	Oleic acid	Cubic spinel structure	Average size 8.7nm	Superparamagnetic Ms 13.9emu/g	Almasy et.al., 2015

Conclusions

Wastewater contains dangerous contaminants that threaten human health and the environment. The wastewater discharged into water bodies pollutes water, is harmful to fauna, and more specifically to aquatic life and human. Hence, wastewater should be treated, for example, using wastewater treatment. Nowadays, numerous studies on wastewater treatment using adsorbent including magnetite have been employed. Magnetite nanoparticles have specific large surface area and highly active sites provide high removal efficiency of contaminants in wastewater. Preparation of magnetite is the key to determining morphology, particle sizes and shape of magnetite. Thus the best preparation method of magnetite must be selected to produce a very good adsorbent in order to treat the wastewater.

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