

CHAPTER I

INTRODUCTION



1.1 General

Nowadays, pollution of aquatic habitats is a universal phenomenon, which is more serious in the developing countries because of discharge of mostly untreated or partially treated municipal and industrial wastewaters into them. The relatively higher toxicity of industrial wastewaters by the progress of textile, leather, surface treatment, mining, motorcar and chemical industries generate toxics such as heavy metals and dyes which are ejected into the environment, living organisms, especially plants, is of greater concern since they clean aquatic ecosystems (Sharma et al., 2007). Textile wastewater, which is a by-product of textile industry, is a mixture of colorants (dyes and pigments) and various organic compounds used as cleaning solvents, plasticizers etc. It also contains high concentrations of heavy metals, total dissolved solids, and has higher chemical as well as biological oxygen demand. Thus, textile wastewater is chemically very complex in nature. Among these compounds, heavy metals and textile dyes are the most dangerous for the environment. The heavy metals are known to be highly toxic at very low concentration in water whereas the dyes have a great influence on the photosynthetic activity in aquatic biota and exhibit a low biodegradability (Aziz et al., 2008). They also pose a problem because they may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous system. The consequence of the pollution of the water resources is an increase of the concentration of toxics in the drinking water which also increases the cost of water potabilisation (Saffaj et al., 2004).

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings. Industrial exposure accounts for a common route of exposure for adults. Ingestion is the most common route of exposure in children (Roberts 1999). Children may develop toxic levels from the normal hand-to-mouth activity of small children who come in contact with contaminated soil or by actually eating objects that are not food (dirt or paint chips). Less common routes of exposure are during a radiological procedure, from inappropriate dosing or monitoring during intravenous (parenteral) nutrition, from a broken thermometer, or from a suicide or homicide attempt.

Dyes are one of the most notorious contaminants in aquatic environments because of their huge volume of production from industries, slow biodegradation and decoloration, and toxicity. About 700 000 tons of dyes are annually produced in the world, and approximately 15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations. Biological oxidation and many physical-chemical treatments are usually inefficient in removing dye colors (Kyung et al. 2005). Spent dye baths (discontinuous dyeing), residual dye liquors and water from washing operations always contain a percentage of unfixed dye.

Dyestuffs that are poorly bio-eliminable (unless they are submitted to destructive treatment techniques) will pass through a biological wastewater treatment plant and will ultimately end up in the discharged effluent. The first noticeable effect in the receiving water is the color. High doses of color not only cause aesthetic impact, but can also interrupt photosynthesis, thus affecting aquatic life. Other effects are related to organic content of the colorants (normally expressed as COD and BOD, but could be better expressed as organic carbon, using TOC, DOC as parameters), its aquatic toxicity and the presence in the molecule of metals or halogens that can give rise to AOX emissions.

Metals can be present in dyes for two reasons. First, metals are used as catalysts during the manufacture of some dyes and can be present as impurities. Second, in some dyes the metal is chelated with the dye molecule, forming an integral structural element.

Dye manufacturers are now putting more effort into reducing the amount of metals present as impurities. This can be done by selection of starting products, removal of heavy metal and substitution of the solvent where the reaction takes place. ETAD has established limits in the content of heavy metal in dyestuffs. The values have been set to ensure that emission levels from a 2 % dyeing and a total dilution of the dye of 1:2500, will meet the known wastewater requirements. Examples of dyes containing bound metals are copper and nickel in phthalocyanine groups, copper in blue copper-azo-complex reactive dyes and chromium in metal-complex dyes used for wool silk and polyamide. The total amount of metallised dye used is decreasing, but there remain domains (certain shades such as greens, certain levels of fastness to light) where phthalocyanine dyes, for example, cannot be easily substituted.

The presence of the metal in these metallised dyes can be regarded as a less relevant problem compared to the presence of free metal impurities. Provided that high exhaustion and fixation levels are achieved and that measures are taken to minimise losses from handling, weighing, drum cleaning, etc., only a little unconsumed dye should end up in the wastewater. Moreover, since the metal is an integral part of the dye molecule, which is itself non-biodegradable, there is very little potential for it to become bio-available. It is also important to take into account that treatment methods such as filtration and adsorption on activated sludge, which remove the dye from the wastewater, also reduce nearly proportionally the amount of bound metal in the final effluent. Conversely, other methods such as advanced oxidation, may free the metal.

Magnetite is a widely used ferromagnetic material. In recent years, monodisperse magnetite nanoparticles attract more and more scientists' interests for its special transformation from ferromagnetism to paramagnetism, which is called superparamagnetism, when the diameter of magnetite particles decreases to lower than 20 nm. A characteristic of superparamagnetism is that the magnetite nanoparticles are magnetized in a magnetic field and do not retain residual magnetism after the outer magnetic field is removed. Due to this special property, magnetite nanoparticles were applied in biomedical fields such as magnetic separation process, delivery vehicle, MRI signal enhancement agent, and cancer hyperthermia treatment, and other fields such as ferrofluids in sealing, position sensing and oscillation damping (Wen et al. 2008).

At present, many methods have been developed to prepare magnetic Fe_3O_4 nanoparticles such as polyols, microemulsions, laser pyrolysis, sonochemical synthesis, and chemical coprecipitation, etc. A commonly used method to prepare magnetite particles is chemical co-precipitation. It involves co-precipitation of Fe^{3+} and Fe^{2+} by adding base, usually NaOH or $\text{NH}_3 \cdot \text{H}_2\text{O}$. Kim et al. (2006) described the preparation of nanoparticles with iron solution containing Fe^{2+} , Fe^{3+} using NaOH at room temperature. Liu et al. reported the precipitation of Fe_3O_4 with adding $\text{NH}_3 \cdot \text{H}_2\text{O}$ into $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ mixture solution at 85 °C. Reduction of Fe^{3+} or oxidation of Fe^{2+} is another way to synthesize magnetite nanoparticles. Qu. et al,(2008) introduced the preparation of magnetite nanoparticles by reduction of FeCl_3 in the presence of Na_2SO_3 . Wang et al. obtained magnetite nanoparticles with oxidation of FeCl_2 by $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$. The above methods are suitable for producing large-scale magnetite nanoparticles; while the limitation is the nanoparticles are multidisperse.

As there are more and more applications of nanomaterials in wastewater treatments, separation of nanomaterials from aqueous streams becomes an important issue. Recently, magnetic separation attracts great attentions because magnetic force is a long-range attraction; thus, separations of nanoparticles can be enhanced. Non-magnetic materials can become magnetic via magnetic seeding aggregation, which can

be easily adopted in various processes. This objective of this study is to determine the effect of surface modification on heavy metal and ionic dyes adsorption capacities and the effect of surface functional groups on selective adsorption of heavy metals and ionic dyes. In addition, study the effect of pH on selective adsorption of heavy metal and ionic dyes adsorption capacity and the effect of magnetic force for separation the superparamagnetic particles.

1.2 Hypotheses

1. Heavy metal and ionic dyes adsorption efficiency of superparamagnetic particle can be increased by surface modification with specific functional groups.
2. Selective adsorption of heavy metal and ionic dyes adsorption capacity can be affected by surface functional groups.
3. Superparamagnetic particles can be separated by magnetic force.

1.3 Objective

1. To determine the effect of surface modification on heavy metals and ionic dyes adsorption capacities.
2. To study the effect of pH on heavy metal and ionic dyes adsorption capacities.
3. To determine the effect of surface functional groups on selective adsorption of heavy metal and ionic dyes on superparamagnetic particles surface.
4. To study the effects of magnetic force on separation of superparamagnetic particles.

1.4 Scopes of study

The adsorption process formed by synthesis of silica coated superparamagnetic particle materials is utilized to remove heavy metal and ionic dye from synthesis wastewater. Silica coated superparamagnetic particle (SCP) functionalized with surface functional group is used as a adsorbent in this study. The synthesis wastewater will be obtained from the adding of heavy metal and ionic dye into water.

The scope of this thesis contains 5 parts are follow:

Part 1: The synthesis, single-functionalization with organic-ligand substitution of silica coated superparamagnetic particles (SCPs).

A chemical coprecipitation method will be performed for organic functionalization of superparamagnetic particle materials by using tetraethoxysilane (TEOS) as a silica precursor. Aminopropyltriethoxysilane (APTES), Mercaptopropyltrimethoxysilane (MPTMS) will be used for surface functionalized modification on SCP.

Part 2: Physico-chemical Characterization of synthesis Silica coated superparamagnetic particle (SCP).

The physico-chemical characteristics of adsorbents including surface area, surface charge, surface functional groups, and particles size will be investigated by measure of nitrogen adsorption-desorption measurement, acid-base titration, FT-IR spectroscopy, elemental analysis, and Scanning Electro Microscope (SEM) respectively.

Part 3: Adsorption Kinetic

The equilibrium contact time for heavy metals and ionic dyes adsorption will be performed by varying contact time from 0 to 24 h under batch conditions with a solution concentration of 5 mg/l and 50 mg/l, respectively and amount of adsorbent of 2.5 g/l. To analyze the adsorption rate of heavy metal and ionic dye onto SCP, functionalized SCPs, by using the pseudo-first-order equation of Lagergren and the pseudo-second-order kinetic model.

Part 4: Adsorption Isotherms and Mechanisms

Adsorption isotherms and mechanisms for heavy metal and ionic dye will be performed by varying concentration of heavy metal and ionic dye solution, pH under batch conditions with an amount of adsorbent of 2.5 g/l. The adsorption isotherm models consider in this experiment will be Langmuir and Freundlich types.

Part 5: Separation by magnet

Separation for SCP and functionalized SCPs will be performed by varying amount of adsorbent, pH, including effect of the presence of heavy meal and ionic dye under batch conditions. Separation efficiency by magnetic field was evaluated by Turbidity meter.