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ABSTRACT

The book explores the critical role of magnetite nanoparticles coated with efficient materials as exceptional adsorbents for organic pollutants in water. This book comprehensively delves into the significance of leveraging magnetite nanoparticles in the extraction of pollutants to address the escalating concerns of water pollution worldwide. The research investigates various coating materials and their effectiveness in enhancing the adsorption capabilities of magnetite nanoparticles. The study not only assesses the extraction methods but also evaluates the potential applications of these coated nanoparticles in tackling the pressing issue of water contamination. With a focus on achieving optimal results in pollutant removal, this book provides valuable insights into developing and utilising advanced materials for sustainable water purification.

LIST OF ABBREVIATIONS

AELB	Atomic Energy Licensing Board
IAEA	International Atomic Energy Agency
UKM	Universiti Kebangsaan Malaysia

CHAPTER 1

SYNTHESIS OF MAGNETIC NANOPARTICLES FUNCTIONALIZED WITH SURFACTANT

1.1 Magnetic nanoparticles (MNPs)

Magnetic nanoparticles (MNPs) is a type of nanoparticles that can be manipulated using magnetic fields (Soloveva et al., 2016). An iron atom possesses a robust magnetic moment because of the four unpaired electrons in the 3d shell. Fe^{2+} ions have 4 unpaired electrons in their 3d shell, and Fe^{3+} ions have 5 unpaired electrons in their 3d shell. Thus, the formed crystals from iron ions of Fe^{2+} or Fe^{3+} can be in ferromagnetic or ferrimagnetic states. MNP are vulnerable to air oxidation and can be easily aggregated in aqueous systems (Teymourian et al., 2013). Among the various types of MNPs, magnetite (Fe_3O_4) is commonly studied due to its advantages, such as superior high surface area, low toxicity, small particle size, ease of dispersion in water and high magnetic properties (Bui et al., 2018)

Magnetic field-based separation using magnetic nano and microparticles has received significant attention for their superior characteristics, such as good dispersion, rapid and effective binding of targets and reversible and controllable flocculation (Su et al., 2015). Due to the large surface area, MNPs guarantee high extraction efficiency when dealing with small sample volumes (Karimi et al., 2016).

The main issue in applying MNPs in these fields is their chemical stability and level of dispersion in the solution. Due to van der Waals forces and high surface energy, these nanoparticles tend to agglomerate easily in an aqueous medium due to van der Waals forces (Laurent et al., 2008). In addition, they are highly reactive and susceptible to oxidation by air, resulting in a loss in magnetism and dispersibility (Shahriman et al., 2018).

These problems can be solved by surface modification of MNPs with appropriate organic coating. Recently, organic compounds such as silane, octadecylsilane, triphenylamine and polymers are often used to coat the surface of MNPs to maintain their chemical stability in various media.

Among these, silicone non-ionic surfactants are potential modification agents for MNPs. Using this surfactant as a coating agent aids in obtaining the desired colloidal dispersion, which also provides a large surface area, high stability, and applicability in harsh chemical media.

For many applications, surface modification of MNPs is a crucial challenge. MNP, with some surface modifications, can be used to separate and concentrate chemicals conveniently using an external magnetic field. Therefore, integrating magnetic separation and surface modification would provide a powerful analytical tool with simplicity, flexibility and selectivity (Su et al., 2015).

1.2 Surfactants

1.2.1 Properties of Surfactants

Surfactants are organic compounds of polar head and non-polar tail groups in natural and synthetic forms. They form self- assembled aggregates like micelles in the presence of water. Surfactants are added as wetting agents to lower the liquids' surface tension. They are also used to spread and lower the interfacial tension of the liquids readily.

The surfactants' polar head and non-polar tail are always organic compounds which contain hydrophilic and hydrophobic groups, respectively. Hydrophilic molecules comprise ions like sulphate and carboxylate from polar groups such as primary amines, amine oxides, and non-polar groups, with electronegative atoms like oxygen atoms and aldehydes or amides. The hydrophilic group gives solubility characteristics in polar solvents, while the hydrophobic group enhances solubility characteristics in non-polar solvents such as oil. The hydrophilic and hydrophobic determine the size and shape of surfactants (Nkadi et al., 2009). Surfactants can be classified using charged groups in their head. Four groups in surfactants are anionic, cationic, zwitterionic and non-ionic.

1.2.2 Types of Surfactants

1.2.2.1 Anionic Surfactants

The anionic surfactant contains a negatively charged head group. The negative charge causes repelling because of the slightly negative surface. High amounts of anionic surfactant are causing foaming in the solution. An example of an anionic surfactant is sodium lauryl sulphate, which has high

solubility in water at room temperature (Johansson & Somasundaran, 2007). Their water solubility depends on the double bond of the structure. They are stable under a pH of more than 10 and sensitive to acids. Figure 1.1 shows the structure of anionic surfactant, which contains a hydrophilic head (negative charge head group) and a long hydrophobic tail.

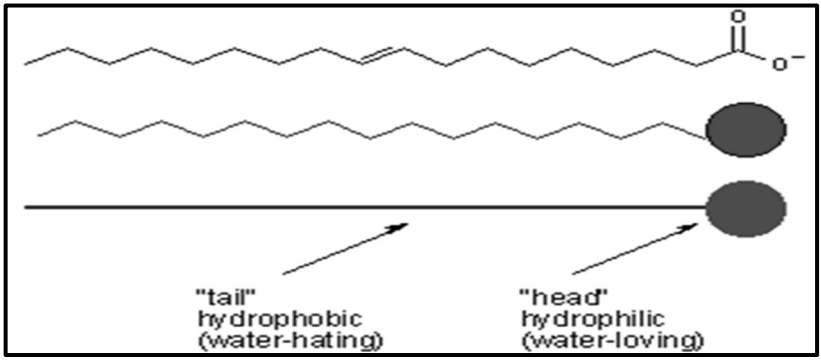

Figure 1.1 Structure of anionic surfactant
Source: Formulation of Carpet Cleaners. In Handbook for Cleaning/Decontamination of Surfaces

Anionic surfactant is widely used in pharmaceutical and cosmetic applications. They are usually used in cleaning applications. For example, they have been used to emulsify oily soils and lift soils from surfaces (Johansson & Somasundaran, 2007). In addition, they are also one of the ingredients in shampoo used for cleaning and hair conditioning. Moreover, oil removal also could be achieved by using this surfactant. Typical anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates, soaps, carboxylate, sulfate and sulfonate ions.

1.2.2.2 Cationic surfactants

Cationic surfactant is a positively charged head group surfactant (Gelardi et al., 2016). They are hydrophilic, which is water-loving and contain positively charged ions. Examples of cationic surfactants include trimethyl alkylammonium chlorides and the chlorides or bromides of benzalkonium and alkylpyridinium ions. They are quarternary ammonium compounds and good as emulsifying agents and do not form insoluble scums. Figure 1.2 shows the cationic surfactant structure with a positively charged group in its head.

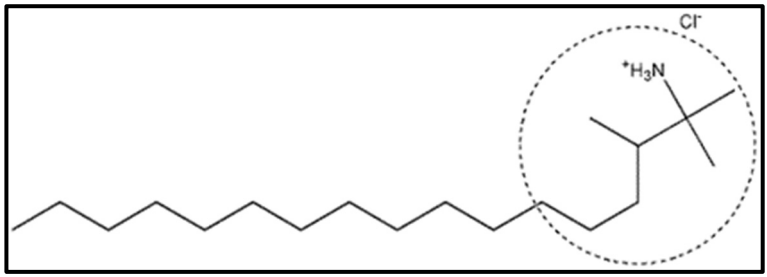

Figure 1.2 Structure of cationic surfactant

Cationic surfactants are widely used in applications involving preservation and disinfection from bacteria. They are good bactericides and can be used as antiseptics to clean wounds or burns. They have bactericidal activity against some positive or negative organisms, so they are heavily used in bathrooms and hand sanitisers. Cationic surfactants such as quaternary ammonium and pyridinium are essential for pharmaceutical use (Tadros, 2009).

1.2.2.3 Zwitterionic surfactants

Zwitterionics is a mild surfactant. They can be present as anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, which depends on the pH of the water. They contain groups of two different charges. The positive charge group is ammonium, while the negative is carboxylate or sulphate. Figure 1.3 shows the zwitterionic surfactant structure containing the same group's negative charge and positive charge.

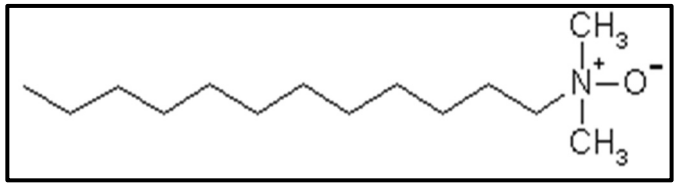

Figure 1.3 Structure of zwitterionic surfactant

This type of surfactant is widely used in personal care products for sensitive skin. This surfactant has effective dermatological properties and is commonly used in shampoos, detergents and other cosmetic products (Fernley, 1978).

1.2.2.4 Non-ionic surfactants

Non-ionic surfactants are known as derivatives of ethylene oxide and/or propylene oxide with an alcohol which contains an active hydrogen atom. Non-ionic surfactants do not have positive or negative charges on their head groups (Sonia & Sharma, 2014), preventing them from dissolving in the aqueous solution group (Figure 1.4). Examples of non-ionic surfactants are polyglycerol alkyl ethers, glucosyl dialkyl ethers, and crown ethers.

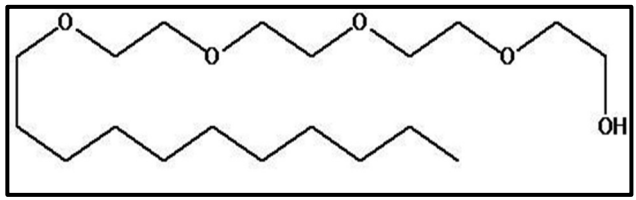

Figure 1.4 Structure of non-ionic surfactant

This non-ionic surfactant is very difficult to maintain and create the emulsion so it is known as emulsifying agent (Zhang et al., 2012). They can effectively remove oil and emulsifiers. They are widely used in industry as they are low cost, biodegradable, high chemical stability (Manosroi et al., 2003) and less irritant than other surfactant (Sonia & Sharma, 2014). These unique properties allow surfactants to be a potential coating agent for modifying MNPs' surfaces. The combination of magnetic properties of MNPs with surfactant offers the development of a new adsorbent with high chemical stability and efficiency.

1.3 Surfactant-modified magnetic nanoparticles

Recently, researchers have succeeded in developing nano-composites of MNPs and surfactants to separate organic contaminants in real matrices. Muthukumaran et al. (2016) have synthesized sodium dodecyl sulphate (SDS) coated MNPs as an effective, low-cost adsorbent for removal of cationic dye, crystal violet (CV) from aqueous solution. They found that SDS-coated MNPs are cost-effective and easily separable nano-adsorbents for efficiently removing crystal violet dye. They also studied adsorption isotherms and kinetic parameters of crystal violet dye removal from aqueous solution using this surfactant-modified magnetic nano-adsorbent.

Li et al. (2008) have introduced cetyltrimethylammonium bromide (CTAB)-coated Fe_3O_4 nano-magnets (CTAB-coated Fe_3O_4 NP) for enrichment of

selected chlorophenols in aqueous matrices before HPLC –UV determination. The fabricated CTAB-coated Fe_3O_4 NP combined with mixed hemimicelles SPE technique showed good recoveries and precision, revealing that the proposed method based on CTAB-coated Fe_3O_4 NP has potential for preconcentration of trace organic pollutants from environmental water samples. Another study by Zhao et al. (2008) also reported the preparation of cation surfactants, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) onto magnetic nanoparticles for mixed hemimicelles solid-phase extraction (SPE) method to separate several phenolic compounds including bisphenol A (BPA), 4-tert-octylphenol (4-OP), and 4-n-nonylphenol (4-NP) from real aqueous matrices. It was found that the proposed adsorbents CTAB and CPC modified on Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have strong electrostatic and hydrophobic interactions with studied analytes. The proposed method provided some advantages such as high recoveries, high breakthrough volumes and short separation times.

All the studies regarding the applications of the ionic surfactants modified magnetic nanoparticles towards hazardous contaminants demonstrate that the nanocomposites are effective adsorbents for treating and determining these pollutants. In this study, silicone non-ionic surfactant Sylgard 309 is used to functionalize the surface of MNPs because it has flexible polysiloxane chains without any aromatic structure, which is advantageous compared to other frequently used non-ionic surfactants, namely Triton X, Tergitol and PONPE series as none of them considered suit with HPLC-DAD, where Diode Array HPLC Detectors are most commonly used to record the ultraviolet and visible (UV-vis) absorption spectra of samples that are passing through high-performance liquid chromatography. This is due to their aromatic chromophore, which has strong UV absorbance or fluorescence signals that become obstacles for UV and fluorescent detectors. The current research focused on using silicone non-ionic surfactant Sylgard 309 modified MNPs for magnetic solid phase extraction of phenols from environmental water matrices before HPLC-DAD analysis. To our knowledge, no studies have investigated this idea yet.

1.3.1 Synthesis of MNP with ferum oxide and surfactant Slygard

MNPs were synthesized using the wet chemical coprecipitation method. A 3.1736 g of $FeCl_2.4H_2O$ and 7.5684 g of $FeCl_3.6H_2O$ were dissolved in 320 ml of deionized water, such that $Fe^{2+}/Fe^{3+} = 1/2$. The mixed solutions were

stirred under N_2 at 80 ºC for 1 hour. Then, 40 ml of NH_3H_2O was injected into the mixture rapidly, stirred under N_2 for another hour and cooled to room temperature. The precipitated particles were washed five times with hot water and separated by magnetic decantation. Finally, magnetic nanoparticles were dried under a vacuum at 70 ºC.

4.2252 g Fe_3O_4 MNPs was sonicated in 150 mL of ethanol/water (volume ratio, 1:1) solution for 30 minutes to obtain uniform dispersion. Then 16.1600 g (17 mL) of APTES was added to the solution under N_2 atmosphere at 40 ºC for 2 hours. The optimal surface modification in a molar ratio of APTES to Fe_3O_4 was found at 4:1. After that, the solutions were cooled at room temperature. The prepared APTES-modified Fe_3O_4 MNPs were separated with a magnet and washed with ethanol, followed by deionized water three times. Finally, APTES-modified Fe_3O_4 (Fe_3O_4-APTES) were dried under vacuum at 70ºC.

0.2000 g of Fe_3O_4-APTES MNPs was dispersed in 8.0000 g of 3-(3-Hydroxypropyl)–Heptanethyltrisiloxane (Sylgard 309) non-ionic surfactant solution with continuous stirring overnight at room temperature under N_2 gas. The suspension was then washed with ethanol three times. The precipitated particles were collected by magnetic decantation. Finally (Fe_3O_4-APTES-Sylgard 309) was dried under vacuum at 70ºC.

1.4 Characterization of MNP with ferum oxide and surfactant Sylgard

The magnetic nanoparticles (MNPs) combined with surfactant Slygard were firstly characterized for the functional groups by an FTIR spectrometer (Thermo Nicolet, Nexus 670) in the absorption mode with 32 scans and a resolution of ± 4 cm^{-1}, a wave-number range of 4000-400 cm^{-1}. For the KBr pellet technique, optical grade KBr was used as the background material. The MNPs were intimately mixed with dried KBr at the ratio of MNPs: KBr = 1:100, then compressed into pellets under pressure.

A wide-angle X-ray diffractometer (Bruker D8 Advance) was used to study the crystalline structure of the synthesized MNPs below the nanometer scale. The CuK-alpha radiation source was operated at 40 kV/30 mA. The MNPs were placed into a sample holder, and the measurement was continuously run. The experiment was recorded by monitoring the diffraction pattern in the 2θ range from 10 to 80 with a scan speed of 1º /min and a scan step of 0.02º.

A transmitting electron microscope (FEI Talos L120C, resolution of 0.2nm@120kV) was used to examine the morphological structure and to measure the particle size of the MNPs. The samples were placed on the holder with adhesive tape and coated with a thin layer of platinum using an ion sputtering device for 1 min prior to observation under SEM. The SEM images were obtained using the acceleration voltage of 5 kV with a magnification of 100-150 kx. The average particle sizes are determined by randomly capturing SEM images from 500 nanoparticles.

Energy dispersive X-ray (EDX) was used for the elemental analysis or chemical characterization of a sample.

A vibrating sample magnetometer (VSM) Lakeshore 7404 Series was used to study the magnetic properties of the MNPs. The hysteresis loops were measured under a magnetic field strength of 10,000 Gauss at room temperature. The data were taken with 80 points/loop and a 10 s/ point scan speed.

1.4.1 Morphological analysis

The particle size of MNPs, MNP-APTES and MNP-Sylgard 309 were investigated using TEM, as shown in Figure 1.5, Figure 1.6 and Figure 1.7. The prepared nanoparticles with an approximate spherical shape and uniform nano-size distribution were observed. From the diameter distribution (Figures 1.6, 1.7, 1.8), it could be seen that the average diameters of MNPs, MNP@APTES, and MNP-Sylgard 309 are increases which can be related to encapsulation of APTES and surfactant Sylgard 309, respectively onto the surface of MNPs.

In addition, the TEM image of MNPs showed that they were agglomerated due to large specific surface area and high surface energy. After being coated with APTES, the MNP-APTES particles are well dispersed, as APTES prevent the interparticle interactions between MNPs particles. After introducing surfactant Sylgard 309, the dispersion of the MNP-Sylgard 309 nanoparticles was enhanced because surfactant Sylgard 309 provided sufficient repulsive interactions between nanoparticles, reducing the agglomeration between the MNPs particles.

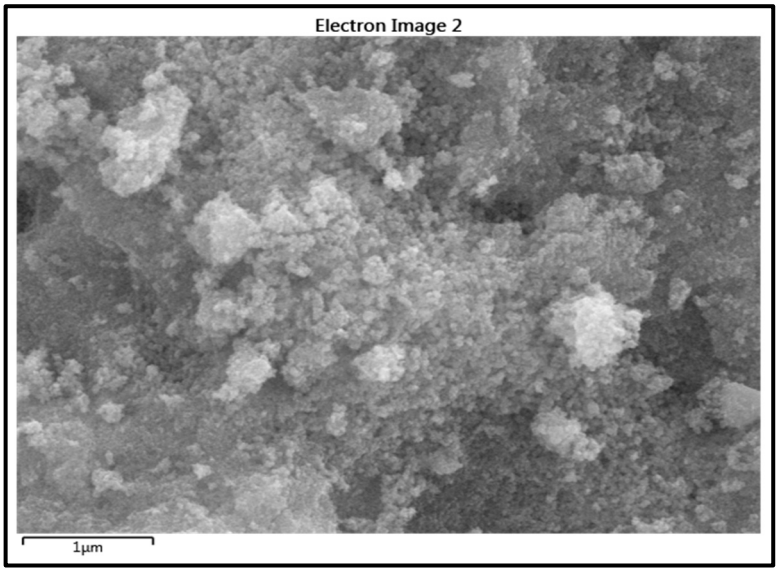

Figure 1.5 TEM image of MNPs

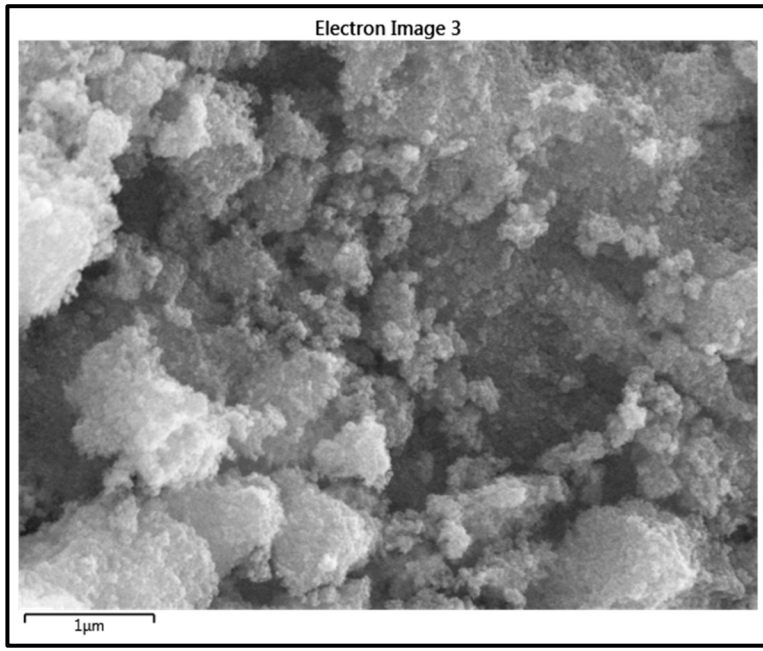

Figure 1.6 TEM image of MNP-APTES

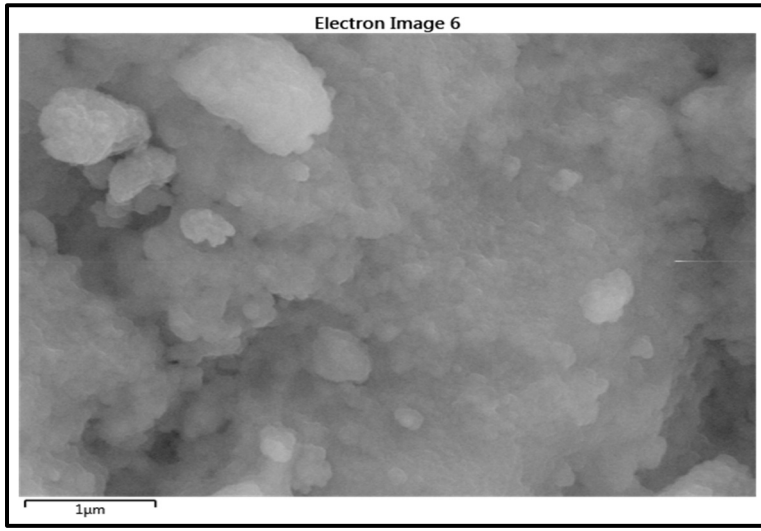

Figure 1.7 TEM image for MNP-Sylgard 309

1.4.2 Elemental analysis

EDX analysis was performed to provide elemental identification and quantitative compositional information elements such as N, O, Fe, Si, and C in the prepared MNPs, MNP-APTES and MNP-Sylgard 309 (Figure 1.8, Figure 1.9 and Figure 1.10). The elemental analysis of the MNPs sample showed that MNPs only contain 71.2% Fe and 25.6% O. After the modification with APTES, the presence of new elements, such as 4.0% C and 1.2% Si, confirmed the APTES was successfully anchored to the surface of MNPs. Finally, as evident from the spectrum of MNP-Sylgard 309, the high percentage of C (17.1%), Si (3.1%) and O (26.1%) in MNP-Sylgard 309 revealed that the surfactant Sylgard 309 was successfully introduced onto the surface of MNP-APTES.

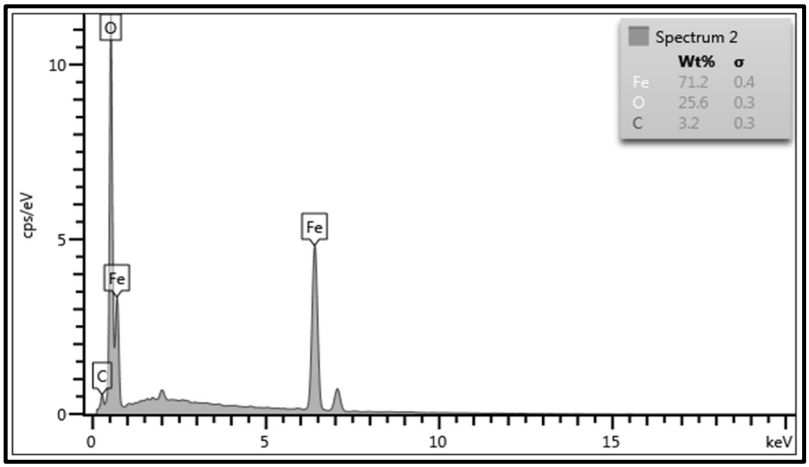

Figure 1.8 EDX spectra MNP

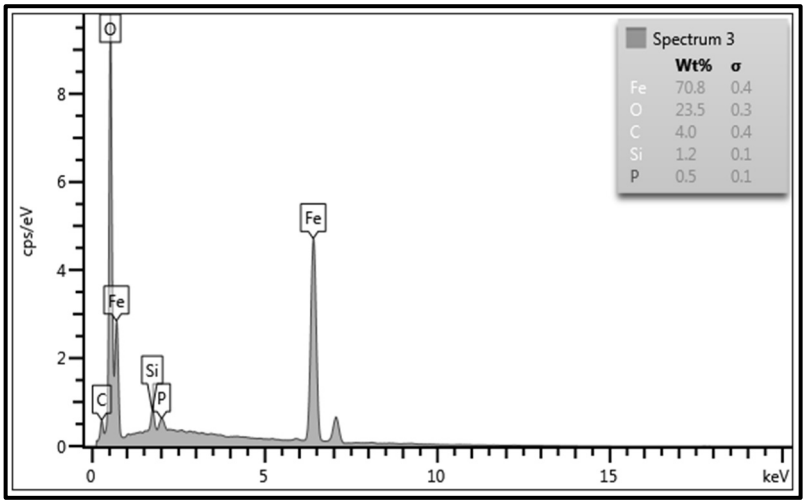

Figure 1.9 EDX spectra of MNP-APTES

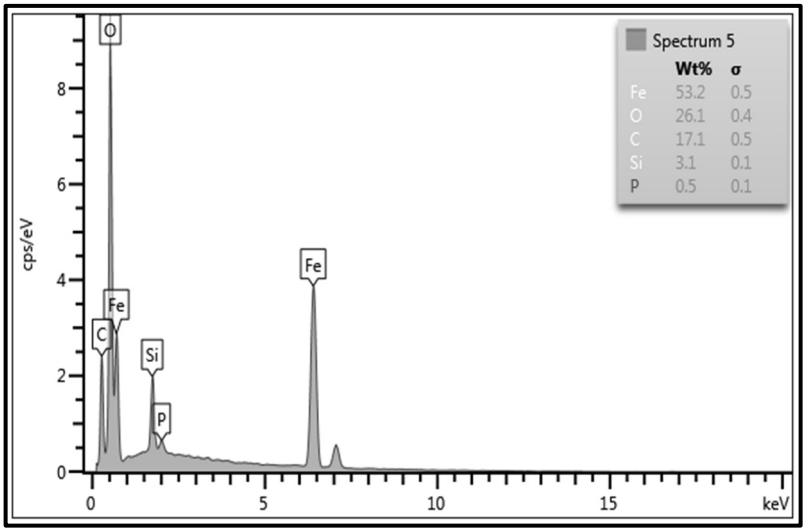

Figure 1.10 EDX spectra of MNP-Sylgard 309