



## Synthesis of metal oxides nanopolymer composition for water treatment

تحضير متراكبات من أكاسيد المعادن مع البوليمر لاستخدامها في معالجة المياه

A graduation research project  
Submitted

to the Department of Chemistry in partial fulfillment of the requirements  
for the completion of the degree of Bachelor of Science in Chemistry

**By**

**Yaser Saad aldoosri**

**Under supervision**

**of**

**Dr. Sami Abdulaziz alhussein**

هـ 1437 /1436

## الملخص العربي

اهتمت الدراسات البحثية في مجال علوم المواد بأنتاج مواد جديدة ذات أحجام نانومترية للتحكم في التلوث الناتج من المواد العضوية والمواد غير العضوية من الماء نظرا لخطورتها علي صحة الانسان. لذا فإن البحث الحالي يهتم بتحضير بوليمرات متشابكة تحتوي علي مادة اكسيد الخارصين ذات الحجم النانومتري والمحضرة بمواد امنه بيئيا تعتمد علي بوليمرات السائل الايوني لتجميع البوليمرات المتشابكة الفعالة بعد امتصاص الصبغات العضوية والعناصر الثقيلة من الماء الملوث.

**الهدف:** تهدف الدراسة الحاليه الي تحضير بوليمرات متشابكة وادخال اكاسيد معادن ذات أحجام نانومتري بطريقة مبتكرة وذلك للحفاظ علي البيئه المائية من التلوث.

**تصميم الدراسة:** اهتمت الدراسة الحاليه بتغير التركيب الكيميائي لبوليمرات حمض الأكرليك المتشابك وتعديل تركيبه الكيميائي وادخال اكاسيد المنجنيز والحديد ذات الحجم النانومتري لزيادة فعاليتها الكيميائية لامتصاص الملوثات العضوية وغير العضوية من الماء.

**مكان ومدته العمل:** تم هذا العمل في كرسي أبحاث السيرفكتانت-قسم الكيمياء كلية العلوم جامعه الملك سعود. تمت الدراسة لمدته 3 شهور خلال التيرم الثاني من العام الجامعي

1437/1436

**فرضيه البحث:** اهتمت الدراسات السابقه علي استخدام البوليمرات المتشابكة في احجام مللي وميكرو ونانومترية للتخلص من الملوثات العضوية وغير العضوية للماء. أفترضت الدراسة الحاليه أنه يمكن تعديل تركيب تلك المواد البوليمرية عن طريق عمل متراكبات مع اكاسيد الحديد والمنجنيز ذات الحجم النانومتري وذلك لزيادة كفاءتها علي الامتصاص للملوثات.

**منهج البحث:** أعتمد البحث علي تحضير بوليمرات متشابكة من حمض الاكرليك مع 2- اكريلاميدو 2-بروبان سلفونك واستخدامها لتحضير متراكبات تحتوي على اكاسيد معادن نانومترية من المجنيتيت واكسيد المنجنيز بعمل أكسده للايونات داخل الهيدروجيل باستخدام محلول الأمونيا وذلك لزيادة كفاءة تلك المواد. تم التعرف علي التركيب الكيميائي للمواد المعدله عن طريق طيف الاشعه تحت الحمراء. تم دراسته الادمصاص والامتصاص للملوثات عن طريق ميكروسكوب الماسح الالكتروني وجهاز الاشعه فوق البنفسجية.

### **مميزات البحث الفكرية:**

1. إدخال أنواع جديدة من البوليمرات المترابطة علي مواد لها احجام نانومترية.
2. إن الهدف الأول لا ينحصر في تقييم كيمياء السطح بالتفصيل ولكن في تقييم فعالية تلك المواد كمركبات متعددة الأغراض.
3. وفي العمق فهم العلاقة بين التركيب والفعالية والخواص في أنظمة المواد البوليمرية.

### **تتمركز الميزة الفكرية للبحث المقترح في:**

1. إدخال أنواع جديدة من المواد البوليمرية متعددة الأغراض.
2. وفي العمق، فهم علاقة خاصية نشاط تركيب السطح لنظام المواد البوليمرية الحديثة.

**النتائج:** أثبتت النتائج أن المركبات قد تم تعديل تركيبها الكيميائي كما هو مخطط واضافه تركيبات جديده متشعبه ساعدت في التحكم في الملوثات المائية.

## English Summary

Environmental pollutants in water caused by the waste products of industry increased the need of novel polymeric materials with the purpose of removing and separating toxic heavy metal ions through complex and ion exchange mechanisms. Nanotechnology has found widespread use in areas in water treatment and purification that is now being widely explored. Water supports all forms of life on earth. The availability of clean water to the human population is of paramount importance. The United Nations reports that though access to improved drinking water has expanded, nearly one billion people do not have safe drinking water.

In this study, we attempted to address these problems by synthesizing new hydrogels polymeric nanocomposite based on solution polymerization method so that the prepared nanoparticles would be economically viable for up-scale, and simultaneous recovery and reuse.

Hydrogels containing amide, amine, carboxylic acid and ammonium groups, can bind metal ions and be good polychelators for water purification applications. This work focused on:

- Synthesis of crosslinked polychelator hydrogels composed of acrylic acid (AA), and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). N,N-Methylene-bisacrylamide (MBA) was used as a crosslinker agent.
- Characterization of the crosslinked polymer by FTIR and SEM.

- Preparation of polymer nanocomposite by reaction of the prepared polymers with ferric ions and manganese ions followed by oxidation reduction reaction in basic medium to prepare magnetite and manganese oxide nanocomposites.
- The influence of treatment time and the initial feed concentration on the amount of crystal violet removed from waste water was investigated.

Copolymerization of acrylic acid (AA) with AMPS was performed by different ratios of crosslinker (MBA) in aqueous medium in the presence of APS as free radical initiator. The crosslinked copolymer of AMPS/AA was determined by FT-IR. The prepared hydrogel was used to form polymer-metal oxide composites by rinsing in metal ions ( $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ ) solution to absorb its capacity of metal ions and then treatment with basic medium to form metal oxide inside the network of the hydrogel.

<b>Page</b>	<b>Title</b>
<b>7</b>	<b>Introduction</b>
<b>31</b>	<b>Experimental</b>
<b>37</b>	<b>Results and discussion</b>
<b>42</b>	<b>Conclusions</b>
<b>43</b>	<b>References</b>

## **1. Introduction:**

### **1.1. Water Purification Methods**

Water is one of the essential companions of life on earth. During the phases of creation, evolution and continuity of life on earth, water remained as its most vital component. The molecular as well as macromolecular functions of making life possible are carried out using water. It is very appropriate to say that existence of life on Earth is largely owed to the presence of water. It is vital to us, both as a universal solvent as well as being an important component of metabolic processes within the body. Clean and fresh water is essential for the existence of life.

Widely distributed toxic substances, such as heavy metals, phenolic compounds, and other non-biodegradable pollutants from some industrial wastewaters are considered to be harmful to humans and the environment [1]. Some bacteria release serious toxic chemicals and affect the overall quality of the treated water. For instance, cyanobacteria release toxins (microcystins and nodularins) while undergoing the treatment process. Finally, the chemical reactions occurring in water treatment plants produce some disinfection byproducts, and the presence of disinfection resistant microorganisms in influent waters compromise water quality standards. Very recently researchers illustrated some major threats to conventional water treatment technologies [2]. Besides in the rapid growth of the world population, industrialization, unplanned urbanization, agricultural activities as well as the excessive use of chemicals have contributed to environmental pollution [3]. Inorganic and organic wastes produced by human activities have resulted in high volumes of contaminated water which threatens human health and other living organisms [4]. Discharge of colored substances into

water bodies not only can aesthetically cause issues but also it is harmful to biological organisms and ecology [5]. Textile industries and other dyeing industries such as paper, printing, leather, food and plastic are major industrial wastewater sources. Generally, the volume of discharged wastewater from each step of a textile operation is approximately at a high rate of between 40 L/kg and 65 L/kg of the product [6].

The removal of hazardous substances from wastewater and remediation of contaminants in surface water and groundwater is a major problem in the world. In order to ensure safe drinking water for all, some membranes such as reverse osmosis (RO), forward osmosis (FO), membrane distillation, and capacitive deionization could be promising in the desalination of both sea and brackish water [7, 8]. But, other conventional water treatment technologies such as physical (boiling, distillation, filtration, sedimentation, microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), sludge storage, and removal, coagulation and flocculation); chemical degradation (ozone, chlorine, chloramine, ultraviolet, H<sub>2</sub>O oxidation, solar water disinfection or photo catalytic degradation, supercritical water oxidation, sonochemical degradation); and biological (microbial water sludge treatment) have failed because of their dependence on influent water qualities. Current drinking water treatment schemes are challenged to effectively remove ambient bromide and iodide before final disinfection, in order to produce acceptable levels of the suspected carcinogen bromate [9], when using ozone or advanced oxidation processes [10]. The presence of dyes in textile wastewater is an environmental problem due to their high visibility, resistance and toxic impact. Low concentration of dye in water is easily visible and can reduce photosynthetic activities in aquatic environments by preventing the penetration of light and oxygen [11]. Given their synthetic



origin and complex aromatic structures, dyes are non-biodegradable substances that remain stable under different conditions [12]. In addition, dyes have direct and indirect toxic effects on humans as they are associated with jaundice, tumors, skin irritation, cancer, heart diseases, allergies, and mutations. Knowing the source, composition, and process of wastewater generation, it is necessary to select an appropriate treatment method for the removal of dye from wastewater and to improve the quality of treated wastewater discharged into the environment. Different treatment methods have been applied to remove trace amounts of pollutants from wastewaters. These techniques are such as ion exchange [13], coagulation/flocculation [14], chemical precipitation [15], electrochemical reaction [16], electro-dialysis [17], reverse osmosis and membrane filtration [18]. However, each of these method exhibits several limitations such as high capital or operating costs, low efficiency and generation of excess sludge so that some of these methods are inappropriate for use by small-scale industries [19].

Dyes have a synthetic origin and complex aromatic molecular structures. These structures make them more stable and more difficult to biodegrade. During manufacturing and textile printing, the dyes may not be entirely used, and some may be released into the environment [20], causing high concentrations of dyes in wastewater. Many organic and inorganic chemical reagents are used in the textile sector, and dyes and metals can have both direct and indirect toxic effects on humans [21,22]. Consequently, the self-purification ability of streams and conventional biological treatment systems are hindered by the presence of dyes and metals [23]. The color removal process for dyes or dye wastes relies on either concentrating the color into sludge or the complete destruction of the dye molecule. The major treatment methods for dyes and dye wastes are physicochemical and biological

methods. Physicochemical methods involve physicochemical processes such as membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic mineralization, electrolysis, chemical reduction and advanced chemical oxidation [24].

## **1.2. Nanotechnology and water treatments**

Nanotechnology plays an important role in the water treatment, desalination and purification [25, 26]. Nowadays, nanomaterials have been used for water treatment as nano-fibers, nano-filters and adsorbents [27,28]. There are several pollutants that change the drinking and industrial waste water such as organic, inorganic pollutants and biological substances such as algae [29]. Organic dyes and heavy metals have several toxicity and hazardous problems that have serious health problems, according to US protection agency [30]. Nanomaterials based on inorganic substances such as clay minerals, titanium dioxide, silica, silver and Zinc oxide attracted great attention in the field of water purification to remove organic and inorganic pollutants [31-32]. Moreover, crosslinked organic polymers such as hydrogels, microgels and nanogels achieved good results for the removal of water pollutants [33, 34]. The combination between inorganic and organic nanomaterials succeeded to achieve high adsorption for removing of toxic pollutants. Accordingly, there is an emerging need to develop novel low cost and more economic techniques and materials that contains hybrid polymers to remove.

The advent of Nanotechnology has given many impressive nanomaterials for example, nanofibers, nanowires, fullerenes, zeolites and various nanoparticles for water purification; but carbon nanotubes (CNTs) is a

preferred technique for their remarkable waste water treatment capabilities and their suitability for organic, inorganic and biological water pollutants. Nanotechnology has given immeasurable opportunities to purify water even at ionic state. The different nanomaterials have been fabricated with features such as high aspect ratio, reactivity, and tunable pore volume, electrostatic, hydrophilic and hydrophobic interactions which are useful in adsorption, catalysis, sensing and optoelectronics. Nanoscale metals (silver, titanium, gold and iron) and their oxides have been widely used in environmental mitigation.

Recent researches use advance nanotechnology in water purification for safe drinking. Nanotechnology deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio [35]. Nanoparticles are expected to play a crucial role in water purification [36]. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. No doubt that nanotechnology is better than other technique used in water treatment but today the knowledge about the environmental fate, transport and toxicity of nanomaterials is still in infancy [37].

Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids have a

significant impact on water quality in natural environment [38]. Nanotechnology used for detection of pesticides [39] chemical and biological substances including metals (e.g. Cadmium, copper, lead, mercury, nickel, zinc), Nutrients (e.g. Phosphate, ammonia, nitrate, nitrite), Cyanide Organics, Algae, Viruses, Bacteria, Parasites, antibiotics and biological agents .

Innovations in the development of novel technologies to desalinate water are among the most exciting and seem to have promise [40]. Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Misconceptions and One of the many impressions that people have about the future of nanotechnology is the expectation that nanoparticles can be used to kill harmful organisms, repair body tissue, in water quality improvement and to cure disease. Recent applications of nanoparticulate silver have included open wound and burn treatment and preliminary studies have shown that a 20 ppm silver colloidal suspension (~30 nm diameter) in purified water has a 100% cure rate for malaria. Titanium dioxide, especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. Iron oxide and titanium dioxide are good sorbents for metal contaminants.

Silver nanoparticles are effective in disinfecting biological pollutants such as bacteria, viruses and fungi [41]. Titanium nanoparticles have been used in micro pollutants transforming redox reactions [42]. Most of the nanomaterials have increased pores and surface activity, which enhance salt repulsion and prevents macrovoid formation [43]. Nanomaterials have played important roles in degrading various recalcitrant dyes, and halogenated compounds and removal of heavy metals with disinfecting

microbes. Gold and iron nanoparticles are especially suitable for removing inorganic heavy metals from surface and waste waters [44]. Nanomaterials usually are not only successful within disintegrating various contaminants; nevertheless they are also active within bimetallic coupling having different alloys and metal oxides which synergistically enhance pollution catalysis. Many of nanomaterials can be used to make composite membranes. This enhances salt retention ability, curtails costs, land area and energy for desalination. For example, zeolite nanoparticles are mixed with polymer matrix to form thin film RO membrane [45, 46].

### **1.3. Using metal nanoparticle in water purification**

The growing use of engineered nanoparticles (NPs) and nanomaterials (NMs) for water purification has raised concerns for human exposure which stems from the absence of specific technologies aimed at the removal of heavy metal ions from the water and the safety of the new NPs and NMs that may be used by the water industry [47-48]. The results of studies on the nano-based water treatment applications are mainly divided into three categories as (i) nan materials for water filtration (e.g., nano membranes) [49, 50] (ii) nano materials for water remediation (e.g., zeolite, carbon nanotubes, and magnetic nanomaterials) [51–52] and (iii) nanomaterials for water purification. Four classes of nanoscale materials that are being evaluated as functional materials for water purification: (1) dendrimers (2) metal-containing nanoparticles, (3) zeolites and (4) carbonaceous nanomaterials. These have a broad range of physicochemical properties that make them particular attractive as separation and reactive media for water purification.

Nanoparticles have two key properties that make them particularly attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique properties of nanoparticles to develop high capacity and selective sorbents for metal ions and anions. Characterization of the interactions of the nanoparticles with the bacteria by atomic force microscopy (AFM), Transmission Electron Microscopy (TEM) and laser confocal microscopy showed considerable changes in the integrity of the cell membranes, resulting in the death of the bacteria in most cases. Photolytic nanomaterials allow ultraviolet light also used to destroy pesticides, industrial solvents and germs.

Stoimenov et al. showed that MgO nanoparticles and magnesium (Mg) nanoparticles are very effective biocides against Gram-positive and Gram-negative bacteria (*Escherichia coli* and *Bacillus megaterium*) and bacterial spores (*Bacillus subtilis*) [53]. Magnesium oxide nanoparticles or magnesia nanoparticles (MgO), nanodots or nanopowder are spinel, high surface area particles. Nanoscale magnesium oxide nanoparticles or magnesia particles are typically 5-100 nanometers (nm) with specific surface area (SSA) in the 25-50 m<sup>2</sup> g<sup>-1</sup> range and magnesium (Mg) nanoparticles, nanodots or nanopowder are spherical black high surface area particles. Nanoscale magnesium particles are typically 20-60 nanometers (nm) with specific surface area (SSA) in the 30-70 m<sup>2</sup> g<sup>-1</sup> range. Preparation of magnesium oxide (MgO) nanoparticles to absorb large amounts of halogen molecules up to 20 % by weight, making them safer to handle and measured their bactericidal activity on three representative strains of bacteria and bacterial spores [54].

Zinc oxide nanoparticles have been used to remove arsenic from water, even though bulk zinc oxide cannot absorb arsenic. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, ferrihydrite, goethite, hematite, lepidocrocite, maghemite and Zinc oxide. Adsorption of organics to the nanoparticle media was extremely rapid. More than 90% of the organics is adsorbed within 30 minutes. Other recent studies have demonstrated the magnetic enhanced removal of cobalt and iron from simulated groundwater. The magnetic field-enhanced filtration/sorption process differs significantly from magnetic separation processes used in the processing of minerals and more recently, for water treatment and environmental applications. Conventional processes use for example, fine stainless steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this reason, in order for such processes to remove metal ions and nanoparticles from solution, precipitating or flocculating agents must first be added to effect formation of large particles. In contrast, the magnetic filtration/sorption process is unique because metals are removed in most conventional wastewater treatment processes in the form of metal hydroxides since they have low solubility. As noted above, ferric hydroxide is often added to scavenge a wide variety of heavy metal contaminants. The use of iron ferrite and Zinc oxide in wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. The effect of particle size on the adsorption of

dissolved heavy metals to iron oxide and titanium dioxide nanoparticles will be studied in laboratory-scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants [55].

Zeolites are effective sorbents and ion-exchange media for metal ions. NaP1 zeolites ( $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ ) have a high density of Na ion exchange sites. They can be inexpensively synthesized by hydrothermal activation of fly ash with low Si/A ratio at 150°C in 1.0-2.0 M NaOH solutions. NaP1 zeolites have been evaluated as ion exchange media for the removal of heavy metals from acid mine wastewaters. Alvarez-Ayuso et al. reported the successful use of synthetic NaP1 zeolites to remove Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating wastewater [56]. Nonporous ceramic oxides with very large surface areas ( $1000 \text{ m}^2 \text{ g}^{-1}$ ), and high density of sorption sites can be functionalized to increase their selectivity toward target pollutants.

Carbonaceous nanomaterials can serve as high capacity and selective sorbents for organic solutes in aqueous solutions. A number of polymers that exhibit antibacterial properties were developed for this purpose including soluble and insoluble pyridinium-type polymers which are involved in surface coating, [57] azidated poly (vinyl chloride) [58] which can be used to prevent bacterial adhesion of medical devices, PEG polymers that can be modified on polyurethane surfaces and also prevent initial adhesion bacteria to the biomaterial surfaces [59] and polyethylene imine (PEI) [60] that exhibit high antibacterial and antifungal activity. High activity of polycationic agents is related to absorption of positive charged nanostructures onto negative by charged cell surfaces of the bacteria. This process is thought to be responsible for the increase of cell permeability and may disrupt the cell membranes. Cross linked polycations are prepared as



nanoparticles. These are formed from PEI by crosslinking and alkylation followed by methylation in order to increase degree of amino group substitution [61]. Because of its positive charge and hydrophobicity, PEI nanoparticles have attracted attention as possible antimicrobial agents. Studies on PEI nanostructured compounds are made to evaluate its antibacterial properties as a function of hydrophobicity, molecular weight, particle size and charge that can play a significant role in antibacterial effect of the tested compound. The antibacterial activity is evaluated against *Streptococcus mutans* cariogenic bacteria.

In another research area of nanoparticles with magnetic properties, A.S. AL-Hobaib et al. studied the using of maghemite iron oxide nanoparticles ( $\gamma\text{-Fe}_2\text{O}_3$ ) with a size of about 10 nm have been successfully incorporated in mixed matrix reverse osmosis membranes based on interfacial polymerization (IP) of thin film nanocomposite (TFNC) on porous polysulfone supports. TFNC elaborated in this study comprise iron oxide nanoparticles (NPs), with different concentrations varying from 0.1 to 0.9 wt%, dispersed in polyamide host matrix. The performances of the obtained TFNC were evaluated based on the water permeability and salt rejection. Results indicated that the NPs improved membrane performance under optimal NP concentration. By changing the content of the filler, better hydrophilicity was obtained; the contact angle was decreased from  $74^\circ$  to  $29^\circ$ . Also, with initial NaCl concentration of 2000 ppm and under pressure of 225 psi, the permeate water flux increased from 26 to 44 L/m<sup>2</sup> h at NPs concentration of 0.3% with the maintaining of high salt rejection of 98% [62].

There are several important criteria to select and design adsorbents such as fast removal, ion selectivity and reusability. Recently, adsorbents based on

nanomaterials gained much attention due to their high performance to adsorb pollutants from aqueous environments such as carbon nanotubes, Titania, silica and clay polymer composites [63-64]. Ionic polymer clay nanocomposites [65] showed high performance to remove organic and organic pollutants [66,67]. The efficiency of nano-clay polymer composites was affected by method of preparation, type of polymer composites and application technique such as membrane, nano-filters, etc...

Sodium montmorillonite (Na-MMT) has attracted great attention in recent years for its application in the field of water purification [68, 69]. The exfoliation of Na-MMT from multilayer sheets to dispersed monolayer polymer composites plays an important role in the preparation of nanocomposites to apply in water treatments [70-71]. Cationic exchanges of Na ions or crosslinking are preferred mechanisms to disperse clay sheet in the polymer composites [72, 73]. Moreover, the addition of organic molecules to solid inorganic colloidal particles enhances the material's capability to adsorb at the interface and forms an interfacial adsorption layer [74]. Thus the size and shape dependent nonlinear optical properties of NMs have shown their potential applications, especially in biological and chemical sensing as well as in the area of water purification. This leads to the fact that nanotechnology offers the possibility of an efficient removal of inorganic and organic pollutants as well as germs [75, 76]. Thus NPs and NMs have been used for detection and removal of chemical species including metals (e.g. cadmium, copper, lead, mercury, nickel, zinc, etc.), nutrients (e.g. phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites and antibiotics [77]. The rapid growth of the field is mainly due to the technological promise of the nanomaterials like NPs and nanocomposites (NCs) [78-79].

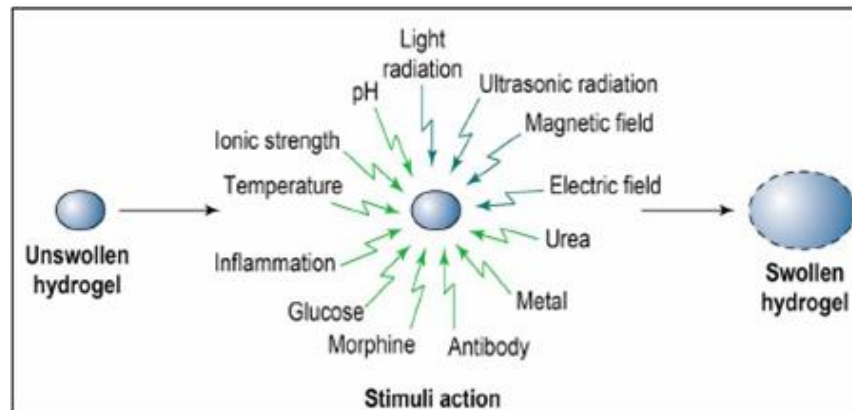
Nanoparticles can be categorized based on single/multiple materials into core-shell or nanocomposite particles. In general, it can be said that simple NPs are made from a single material but as the name indicates, composite and core-shell particles are composed of two or more materials. The core-shell type NPs can be broadly defined as comprising a core (inner material) and a shell (outer layer material).

Polymeric nanoparticles, also sometimes known as nanogel/microgel particles, have shown such prospects. Polymeric hydrogels nanoparticle (nanogels), in general, are characterized as spherical, three-dimensional covalently crosslinked polymer network in the colloidal size range (50 nm – 5  $\mu$ m). They can swell or shrink, depending on the surrounding solvent conditions. These particles have widely been studied in recent years because of their relatively low preparation cost and fast response in volume transition triggered by environmental change. A number of applications of various types of polymeric hydrogels nanoparticle have been developed, such as in controlled delivery of drugs and proteins [80, 81], for nanoreactors [82], as microlenses assembly for detection of protein [83], for heavy metal scavenging in water purification [84-85] and for enhanced oil-recovery from oil fields [86], etc. These nanoparticles are commonly synthesized via the major emulsion polymerization technique that can be classified into different methods such as conventional emulsion polymerization, surfactant-free emulsion polymerization, as well as mini (or nanoemulsions) and microemulsions polymerizations which differ from the kinetically and thermodynamically different emulsion behaviors and the products are usually in the form of colloidal dispersions. They can also be synthesized to possess specific stimuli-responsive properties (e.g., pH-sensitive or thermal responsive etc.) Such that they would swell or shrink

corresponding to changes in the environmental conditions surrounding them (e.g. change in pH, ionic strength or temperature) [87].

#### 1. 4. Application of microgels and nanogels in water treatment

Nanogels are more commonly classified in three ways. Nanogels first classification is based on the type of functional groups incorporated into their network. The second classification is based on their responsive behavior, which can be either stimuli-responsive or non-responsive. In the case of non- responsive nanogels, they simply swell as a result of absorbing water, while stimuli- responsive nanogels swell or deswell upon exposure to environmental changes such as temperature, pH, magnetic field, and ionic strength. Multi- responsive nanogels are responsive to more than one environmental stimulus **Figure 1**. In the last classification of nanogels, they are sorted by the nature of the crosslinks within their network, in which nanogels can be either physically or chemically crosslinked. As mentioned before, crosslinks play an important role to prevent dissolution of the polymer chain, mechanical strength and also to keep the network structure of the hydrogels under different environmental conditions [88].

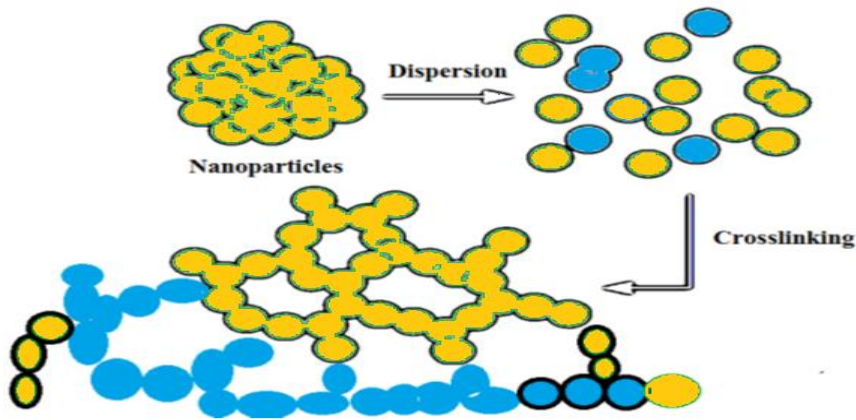


**Figure. 1.** stimuli- responsive nanogels exposure to environmental changes

The chemically crosslinked nanogels formed by covalent interactions are stable and capable of maintaining their robust structure under all environmental condition unless a labile functional group has been attached to the network. The method commonly used to synthesize chemically crosslinked nanogels is copolymerizing monomers with multifunctional crosslinker in order to obtain primary crosslinked polymer network chains in each individual particle, while the secondary network is a system of crosslinked nanoparticles. The covalent bonding contributes to the structural stability of the nanostructured gels. Epichlorohydrin (ECH) is one of the widely used crosslinker due to an ether linkage formed between ECH and most of water soluble polymers [89], and sufficient crosslinked junctions were formed to maintain a permanent structure in the nanogels; otherwise insufficient crosslinked junctions were formed, which produced unstable nanogels.

The formation of physically crosslinked nanogels is due to the non-covalent interaction such as hydrophobic interaction, ionic interaction, and hydrogen bonding. This system is vastly applied in the encapsulation of drugs delivery systems and proteins within the structural network of nanogels, because the nanogels can release incorporated agents from the interior network by the dissolution of their structure. Therefore, physically cross-linked nanogels are of great interest in the field of biodegradable systems that are able to go from the solution state to stable gel state, and vice versa [90]. The main disadvantage of this system is that they can lose their stability and disintegrate upon exposure to many factors, such as temperature, ionic strength, and polymer composition as a result of weak non-covalent Interactions. Therefore, physically crosslinked microgels are less stable compared to their chemically cross-linked counterparts [91].

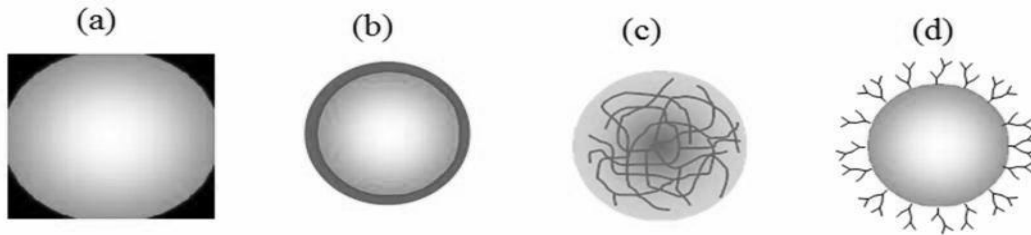
The self-assembly nanogel materials have gained much attention due primarily to the novel properties depending on their sizes and aspect ratios [92]. In the past few years, there are different methods used for synthesizing self-assembly nanogels using emulsion polymerization technique besides the conventional physical and chemical methods [93-94]. Gels are usually formed by the free radical polymerization of monomers in the presence of a functional crosslinking agent and can be prepared either in bulk or in nano- or microparticles. In previous works [95-96], we succeeded to prepare self-assembled nanogels using free surfactants technique due to complexity of emulsion prepared nanogel methods. In this respect, Ayman et al. prepared a new class of gels with two levels of structural, firstly preparing primary crosslinked polymer network chains as individual particle, while the secondary network is a system of crosslinked nanoparticles. They expected that these gels will have new and unique properties including a high surface area and high affinity to form self-assembly layer at surface of different substrates. The poly(vinyl alcohol), PVA, and poly(acrylic acid), (PAA), nanoparticles were prepared as individual particles followed by chemical crosslinking to prepare PVA-HPC nanogel [97].



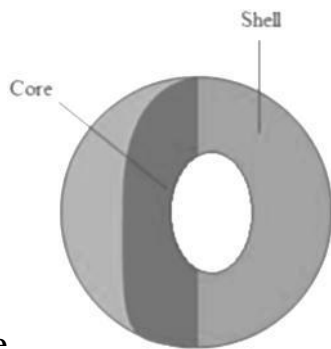
**Figure. 2.** Schematic presentation of crosslinked nanogels

Particles with core-shell structures often exhibit improved physical and chemical properties over their single-component counterparts. Among them, amphiphilic particles that consist of well-defined hydrophobic cores and hydrophilic shells or vice versa, have attracted a great deal of attention because of their applicability in modern materials science, and their technological importance in the areas of colloid and interface science [98]. For example, amphiphilic core-shell particles have been utilized in the areas of diagnostics, bioseparations, drug delivery and carrier, gene therapy, coatings, electronics, catalysis and industrial applications [99]. One important advantage of having a polymer shell on the particles is that the shell could provide a charged functional and reactive surface, and improve the stability and dispersibility of the particles. It can also protect the core from extraneous chemical and physical changes. Therefore, much interest has been devoted to the development of methodologies for the engineering of the amphiphilic core-shell particles. Considerable efforts have been made to develop new polymer supports with improved capacity, accessibility and selectivity [100,101]. This issue has tremendous implication on the environmental applications. For instance, it is well known that the chelating resins (diameter of 0.3-1.2 mm) have slow kinetics despite their high affinity towards heavy metals cations [102]. A variety of polymeric nanoparticles with different surface functional groups for instance, amine groups or epoxy groups, can be readily synthesized from scratch or through surface functionalization [103]. Besides surface chemistry, the morphology of polymeric nanoparticles can be varied as well (Fig. 3). Hence, the polymeric nanoparticles may serve as nanoscale polymer supports, for instance, nanocarrier for precious metal catalyst. In general, the synthetic processes whereby these polymeric nanoparticles are

manufactured are well-established and scalable. Despite the various advances in synthesis and functionalization of polymeric nanoparticles in recent decades, relevant environmental applications of these nanoparticles remain rare. This may be due to the misconceptions including difficulty in recovery and reuse of nanoparticles, and high synthesis/manufacturing cost. The manufacturing industry of polymer emulsions is well established world-wide, so is the associated downstream separation process. Filtration processes such as microfiltration and ultrafiltration have already been accepted by industry as major operation for separation of latex emulsions [104]. In the following section, research literatures on polymeric nanoparticles are outlined to illustrate their remediation potential.



**Fig.3.** General morphology of polymeric nanoparticles: (a) homogeneous sphere; (b) core/shell sphere; (c) microgel; (d) dendronized



sphere

Clear view of core-shell structure of hydrogels nanoparticle



To remove metal ions from aqueous solution as effective and efficient as possible, the remedial agents, i.e. the adsorbents, should optimally possess high density of binding site or chemical functional groups (e.g.  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{CONH-}$  etc.) which have selective affinity towards the metal ions, located at the solid-liquid interface [105]. In addition, these binding sites should be accessible for metal ion binding or adsorption to take place, which can be achieved by making the adsorbents as porous as possible (i.e. high specific surface area or pore volume), while the pore sizes are big enough for the metal ions to diffuse and travel to the interior binding sites located on the pore surface [106]. One of the first environmental applications of nanogels was investigated the applicability of using of poly(N-isopropylacrylamide) (pNIPAm) colloidal microgels or nanoparticles for removal of heavy metals such as Pb(II) and Cd(II). The binding sites for metal ions were derived from the thermal initiator molecules used. Hence the removal capacity for both heavy metals ions was limited as the ratio of initiator to N-isopropylacrylamide was kept small in all the synthesis. For instance, the adsorption capacity achieved for Pb(II) was only 0.4 mmole/g at solution pH 6.0. This shortcoming was overcome by copolymerizing pNIPAm nanoparticles with a co-monomer, acrylic acid [107], and an improved performance was achieved, for example, the specific adsorption capacity for Pb(II) at pH 8.0 to be 2.4 mmole/g, which they attributed to the favorable Columbic attraction between carboxylate groups and positively charged lead species. Experimentally the adsorption kinetic by the prepared nanoparticles was significantly improved [108], as compared to their bulk analogue. For instance, the former took only 100 minutes to attain adsorption equilibrium, while the latter required 100 hours at least.

Core/shell polystyrene-graft- poly(vinylamine) synthesized with average particle size 500 nm to remove  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  that the major function group is amine group and amide group, after modified the surface-aminated polystyrene nanoparticles with azo-chromophore. It was found that the ligand- modified nanoparticles remain adsorptive towards Pb(II) after 3 cycles of adsorption/desorption processes. modification of the nanoparticles and using the residual amine group and azo-chromophore the function group converted to imine group, amide group and hydroxyl group, and the Adsorption efficiency of  $\text{Pb}^{2+}$  was enhanced, but the resulting nanoparticles did not display exclusive selectivity towards Pb(II). This is because the  $\text{Cu}^{2+}$  ions have access to the amine groups buried beneath the corona [109].

Core/shell polystyrene-co- poly((2-acetoacetoxy)ethyl methacrylate) was investigated for the Hg(II), Co(II) [110], with average diameter 70 nm, the heavy metals sequestration selectivity could be altered by grafting a macrocyclic ligand. The original core/shell nanoparticles is selective towards mercury ions solely; whereas the modified nanoparticles would only adsorb Co(II) despite presence of thousand-fold excess of other heavy metals ions, such as mercury. Therefore, the polymeric nanoparticles could be conveniently engineered or tailored to display specific remedial function such as selective sequestration of heavy metals.

Poly(N-isopropylacrylamide) microgel (pNIPAm) with average 550 nm, the electrostatic interaction conferred to the microgel comes from the thermal initiators which possess sulfate group, carboxylic group and amidine group respectively responsible for adsorption of Pb(II), Cd(II), and the desorption of metal ion could be triggered by heating. Both absorption as

well as adsorption was proposed to account for the incomplete desorption [111]. Poly(N-isopropylacrylamide) microgel with metal chelating N-(4-vinyl)benzyl-ethylenediamine) (amine group) used for  $\text{Cu}^{2+}$  removal with 750 nm. The thermo sensitive microgel was incorporated metal ion chelation ability via copolymerization. [112].

Synthesis of metal-chelating nanoparticles by one-step functionalization via miniemulsion polymerization approach using Polystyrene nanoparticles for Ni(II), Co(II), Cr(II), Cu(II) and Pb(II). Polymeric nanoparticles of 13 to 19 nm were obtained successfully. The bipyridine-based metal-chelating groups are located on the surface of the nanoparticles and are accessible. It was observed that the complexation completed within minutes. In addition, the nanoparticle solution remained colloidally stable after metal ion adsorption, which indicates that the cooperative binding event occurs between every two neighboring bipyridine groups solely [113]. The application of nano-chitosan in dye removal as a new approach in adsorption technique Activated carbon from various sources such as coconut coir, jute stick, rice husk etc is the most popular of the adsorbents. The treatment of water includes adsorption methods using specific ion exchangers or extractants and combination of adsorption with catalytic treatment methods, redox processes and magnetic processes. Recently, a new technique in adsorption is reported by the application of carbon nanotube clusters.

Synthesis and application of cyclam-grafted nanoparticles as recoverable chelating agents. Due to the small size (13 – 20 nm) of the nanoparticles [114], the nanoparticle suspension was stable and transparent. The cyclam ligands binds specifically copper ions with high selectivity, in the presence of other cations. The loading of cyclam ligands of 0.73 mmole/g is one-fold

higher than those obtained by other approaches reported elsewhere [115]. Fast chelation kinetics was observed and about 85-90% utilization of the available ligands is easily achieved. The nanoparticles remain stable after dialysis or Cu(II) complexation. The binding capacity of 0.6 mmole-Cu(II)/g of the resulting nanoparticles plus its ease of preparation demonstrates its competitive edge over others, for instance PAMAM dendrimers of generation 8, which has a Cu(II) binding capacity of 0.65 mmole/g [116].

Another research area which receives considerable attention recently is the synthesis of biopolymer-based nanoparticles for environmental application [117, 118]. Chitosan is a natural polysaccharide with rich functionalities. Due to its non-toxicity and low cost, chitosan has been studied extensively in various areas such as biomedicine and water/wastewater treatment [119]. The chitosan polymer was carboxylated and later covalently bonded to Zinc oxide nanoparticles [120], whereas the chitosan nanoparticles viewed through simple ionic-gelation nucleation method, wherein tripolyphosphate (TPP) acts as ionic crosslinker, and both obtained high Cu(II) removal capacity. However, chitosan nanoparticles obtained via ionic-gelation has a critical drawback: they gradually disintegrate in aqueous media over days or aggregate in alkaline solution (pH 9.0) [121]. This is mainly due to the weak electrostatic interactions between chitosan chains and TPP molecules, as proven by the complete disintegration of spherical chitosan nanoparticles into dissolved polymer chains in solution of high ionic strength (125 mM of KNO<sub>3</sub>). Like any other adsorbents, a systematic physicochemical examination should accompany the remedial assessment of nanoparticles in order to fully understand their potentials and pitfalls.

Amphiphilic nanoparticles with poly(methyl methacrylate) (PMMA) cores and poly(ethyleneimine) (PEI) shells were successfully synthesized through a one-step emulsifier-free polymerization method. The morphologies of PMMA/PEI nanoparticles were spherical in shape with uniform size distribution and core-shell nanostructure illustrated by field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). PMMA/PEI core-shell nanoparticles were applied as novel polymeric adsorbents to remove heavy metal pollutants. Cu (II) ions were selected as the target pollutants to evaluate these nanoparticles adsorption capability. It was investigated by varying solution pH, weight ratio of nanoparticles to copper (II) ions, adsorption time and adsorption temperature, respectively. The maximum copper (II) ion adsorbed onto PMMA/PEI core-shell nanoparticles was 14 mg/g [122].

Recently, polymers prepared from N-isopropylacrylamide (NIPAm) have received considerable attention in the scientific literature because of the large volume change, which these materials undergo in response to an external stimulus such as temperature or pH. pNIPAm undergoes a transition from a swollen state to a shrunken state at 35°C. For this reason, polymers prepared from NIPA have been applied in thermo sensitive drug delivery systems and separation processes. The reversible volume phase transition that NIPA based gels undergo also makes them an attractive material for removal of pollutants from the environment [123, 124]. Polymers prepared from NIPA have been investigated as potential adsorbents for removal of metal ions in wastewater [125]. However, little is known about the adsorption of metal ions by these polymers. Ayman et al. studied and evaluated the stimuli-responsive properties and the Cu<sup>2+</sup> adsorption capacity of the cross-linked pNIPAm-co-AA hydrogels.

They studied the hydrodynamic diameter of the pNIPAm-co-AA hydrogel particles using dynamic light scattering (DLS) method. It was found that the hydrodynamic diameter of the crosslinked pNIPAm-co-AA hydrogel particles decreased with the increased of temperature from 25 C to 50 C. At temperature below the VPTT, the pNIPAm-co-AA and Cu<sup>2+</sup> loaded pNIPAm-co-AA particles exhibit nearly perfect spherical shape. The average diameters of pNIPAm-co-AA and Cu<sup>2+</sup> loaded pNIPAm-co-AA hydrogel particles are 370 nm and 440 nm, respectively. Above the VPTT, the pNIPAm-co-AA hydrogel particles undergo a volume phase transition from coil to the collapsed globule conformation. The adsorption capacity (qm) was found to be 67.25 mg/g with best fit to Langmuir isotherm and the adsorption mechanism follows the pseudo-second-order model. Gibbs free energy analysis shows that the adsorption was spontaneous and it exhibited endothermic chemisorption properties, and thermodynamically driven [126].

There are several clay minerals such as sepiolite, kaolinite, bentonite and montmorlonite are used in the water treatments for the removal of organic and inorganic pollutants [127, 128]. The exfoliation of clay minerals using organic and inorganic nanomaterials increases the rate of adsorption of toxic substances from water [129-130]. The techniques used to exfoliate the clay minerals are based on the cationic exchange with cationic surfactants or crosslinking of monomers between clay galleries [131, 132]. Moreover, the thermosensitive polymers succeeded to exfoliate clay minerals using 20 % of clay in the polymer composites [133].

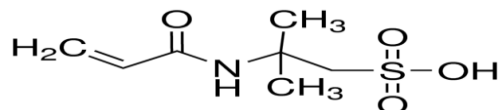
## 2. EXPERIMENTAL

### 2.1. MATERIALS AND REAGENT

#### 2.1.1. Monomers

##### a) 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS)

Chemical structure



Appearance                      White powder

Formula weight                207.52 g/mol

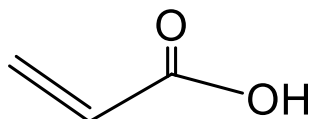
Melting point                 195 °C

Water solubility               Complete

The monomer was obtained from Sigma-Aldrich Chemical Co. and used as received without purification.

##### b) Acrylic acid

Chemical structure



Appearance                      Clear colorless liquid

Formula weight                72.06 g/mol

Melting point                 14 °C

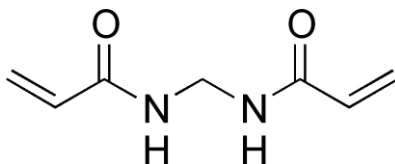
Water solubility               Miscible

The monomer was obtained from Sigma-Aldrich Chemical Co. and used as received without purification.

### 2.1.2 Crosslinker

#### N, N'-methylenebisacrylamide (MBA, 99%)

Chemical structure



Appearance white crystalline powder

Formula weight 154.17

Melting point 300 °C

Water solubility: partially soluble in cold water.

It was obtained from Sigma-Aldrich Chemical Co. and was recrystallized twice in water.

### 2.1.3. Initiator

#### Ammonium persulfate (APS) (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

Appearance White yellowish

Formula weight 228.18 g/mol

Melting point 120 °C

Boiling point 2972 °C

Water solubility 80g/100 ml (25 °C)

Density 1.98 g/cm<sup>3</sup>

The monomer was obtained from Sigma-Aldrich Chemical Co. and used as received.



## 2.1.4. metal salts

### a) Manganese nitrate

Appearance White powder

Formula weight 178.95 g/mol

Melting point 37°C

Boiling point 100 °C

Water solubility high

It was obtained from Sigma-Aldrich Chemical Co. without further purification

### b) Ferric Chloride hexahydrate

Appearance yellow solid

Formula weight 270.3 g/mol

Boiling point 280 °C

Water solubility 92g/100ml

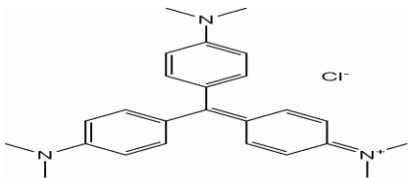
It was obtained from Sigma-Aldrich Chemical Co. without further purification

### c) Amonium solution 25%

## 2.1.5. Water Pollutants

### Crystal violet

Chemical structure



Appearance Green to dark powder

Formula weight 407.979 g/mol

Melting point 205 °C

It was obtained from Sigma-Aldrich Chemical Co. and used as received

## **2.2. SYNTHESIS PROCEDURES**

### **2.2.1 Synthesis of Copolymer Hydrogels**

Cross-linked equimolar AMPS /AA copolymers were prepared via a crosslinking solution polymerization technique using water as a solvent. The monomers were dissolved in the presence of (1 wt %) of MBA as a crosslinker (mol % based on 100 mol % of the two monomers). APS was used as initiator (0.001 mol % based on mol percentages of two monomers). The crosslinking polymerization reaction was carried out at room temperature (70\_ C) for 15 min then the reaction temperature was raised up to 60\_C until the formation of the hydrogel. The polymer rods were post cured at 105\_C in an air oven for 24 h to ensure complete polymerization and then used for dye removal.

### **2.2.2 Synthesis of polymer composite**

Composites with different metal oxides (manganese oxide and magnetite) were prepared by rinsing of AMPS-AA hydrogel in metal ions ( $\text{Fe}^{++}$  and  $\text{Mn}^{++}$ ) solutions to absorb its capacity of metal ions and then was treated with amonium solution to form metal oxide inside the network of the hydrogel . These different composites were compared for dye removal capacity and rapidity.

## **2.3. CHARACTERIZATION AND APPARATUS**

### **2.3.1 Fourier Transforms Infrared Spectroscopy (FT-IR)**

The chemical structure of the core-shell nanogels was directly analyzed by a FTIR spectrometer. Sample discs were prepared by mixing 1mg of the samples with 500 mg of KBr (Merck) in an agate mortar and scanned in a range from 4,000 to 400  $\text{cm}^{-1}$  using a (Nicolet, NEXUS-670).

### **2.3.2. Scanning Electron Microscope (SEM)**

The surface morphology of the nanogels was observed by (SEM) (JEOL JXA-840A) instrument at 20 kV. A few droplets of the diluted suspension were dropped on to a cover glass and then dried under vacuum at room temperature for 24 h. samples were coated with gold vapor prior to observation.

### **2.3.3. X-Ray Diffraction (XRD)**

The analysis was performed using a Bruker D2 Phaser X-ray powder diffractometer (30 kV, 10 mA) using Cu anode ( $k = 0.15406$  nm) at 25<sup>0</sup> C. The patterns were collected in the 2 [theta] range of 4–70<sup>0</sup> with step size of 0.02<sup>0</sup> and scan rate of 1 s.

### **2.3.4. Spectrophotometric Determination of Crystal Violet Dye**

The concentrations of CV in water were investigated before and after mixing with metal oxide-hydrogel composites using double beam UV/vis spectrophotometer (Schimadzu UV-1208 model) at  $\lambda_{\max}$  (662nm) onto PVP Macro/nanogel.

## **2.4. APPLICATIONS OF NANOCOMPOSITE**

### **2.4.1 Adsorption and Desorption Experiments**

Working aqueous solutions of CV (1, 2, 3, 4, 5 ppm) were measured spectrophotometric at a wavelength of 590 nm to establish the standard calibration curve. The absorbance of unknown sample was determined from the standard calibration curve at the same wavelength. Different concentrations of CV (500-1500 ppm) dissolved in 50 ml DW and stirred

with 0.05 g of the composite into a 100 ml conical flask at 25 °C. The filtrate samples were centrifuged and analyzed at different time intervals. The CV concentration was determined at the same wavelength (590 nm). The amount of dye adsorption at equilibrium  $Q$  (mg/g) and percent extraction (%E) was calculated from the following equation:

$$Q = [(C_o - C_e) \times V / (m)] \quad (2.1)$$

$$\%E = [(C_o - C_e) \times 100 / (C_o)] \quad (2.2)$$

Where  $C_o$  and  $C_e$  (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively,  $V$  (L) the volume of the solution and  $m$  (g) is the mass of adsorbent used.

The same procedures to determination of the amount of CV which adsorbed based on magnetite and manganese oxide composites.

### **2.4.3. Effect of Contact Time**

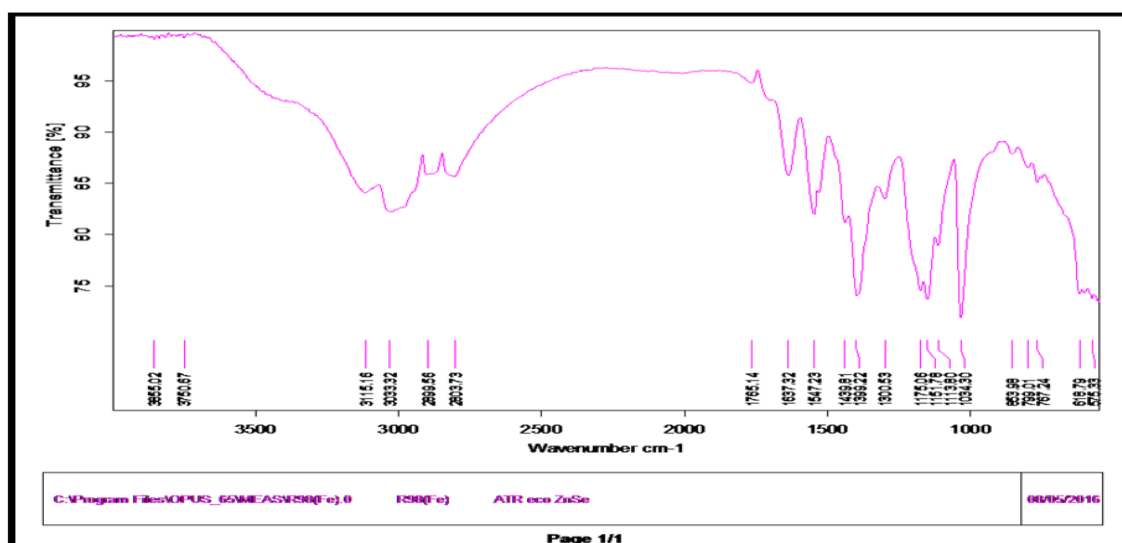
The effect of contact time on the sorption was studied in different time intervals ranging from 30 min to 80 min with the initial dye concentration of 500 ppm by agitation known wt. of adsorbent in a 10 ml dye solution at  $25 \pm 2$  °C at desired pH and at agitation speed of (150-250 rpm). After the completion of the reaction, conical flasks were taken out and the nanogels adsorbent were separated followed by the determination of the residual metal concentrations.

### 3. Results and discussion

Crosslinking copolymerization of AA and AMPS was carried out using APS as a radical initiator and MBA as a crosslinker. The persulfate initiator was decomposed under heating to produce sulfate anion radicals, which form radical on double bond of vinyl group to start radical polymerization. The vinyl groups of AA and AMPS were then reacted with the active radicals to form covalent bonds and simultaneously generate the new radicals that can process the chain propagation. In the presence of the crosslinking agent MBA, the end vinyl groups of MBA participated in the polymerization and finally formed a 3-dimensional network of poly(AA-co-AMPS).

#### 3.1. FTIR spectra analysis

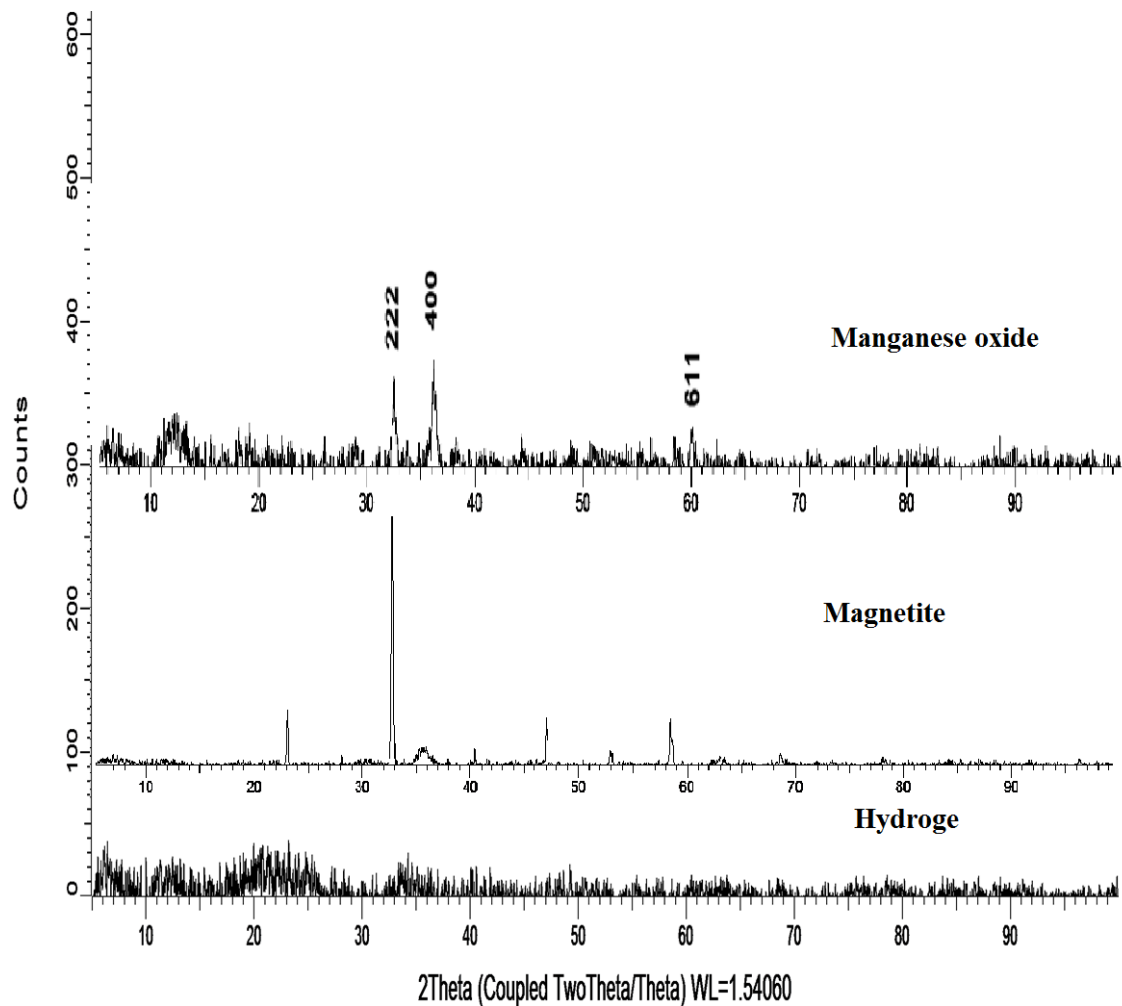
The cross-linked polymer was confirmed by the FTIR spectra of poly(AA-co-AMPS). As shown in **Figure 4**, the characteristic absorption band at  $1778\text{ cm}^{-1}$  (C=O stretching vibration of -COOH groups),  $1633\text{ cm}^{-1}$  (COO asymmetrical stretching vibration of -COO groups), and  $1149\text{ cm}^{-1}$  (stretching vibration of -SO<sub>3</sub>H groups) can be observed in the spectrum of, which strongly suggests the existence of AMPS. Consequently, it is concluded that the AA and AMPS monomers were successfully polymerized to form AMPS-AA hydrogel.



**Figure 4: FTIR of AMPS-AA hydrogel**

### 3.2. XRD spectra analysis

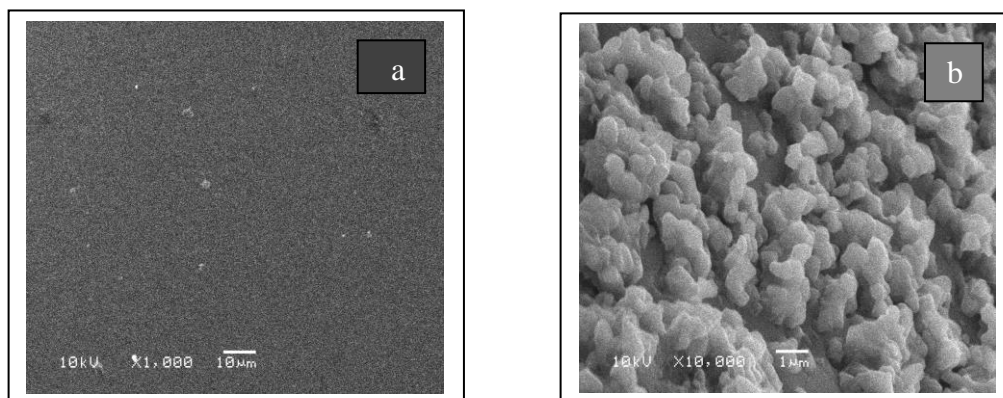
When comparing XRD of hydrogel and composites containing magnetite and manganese oxide **Figure 5** it was found that hydrogel has amorphous structure while the composites give crystalline structures of metal oxides incorporated with hydrogel.



**Figure 5: XRD of hydrogel and composites containing magnetite and manganese oxide**

### 3.3. Morphological analysis

Figure 3 shows the SEM images of composite containing magnetite and manganese oxide. It can be seen that the composite containing magnetite (**Figure 6a**) exhibits a smooth and tight surface whereas the composite containing manganese oxide (**Figure 6b**) shows an uneven and coarse surface.



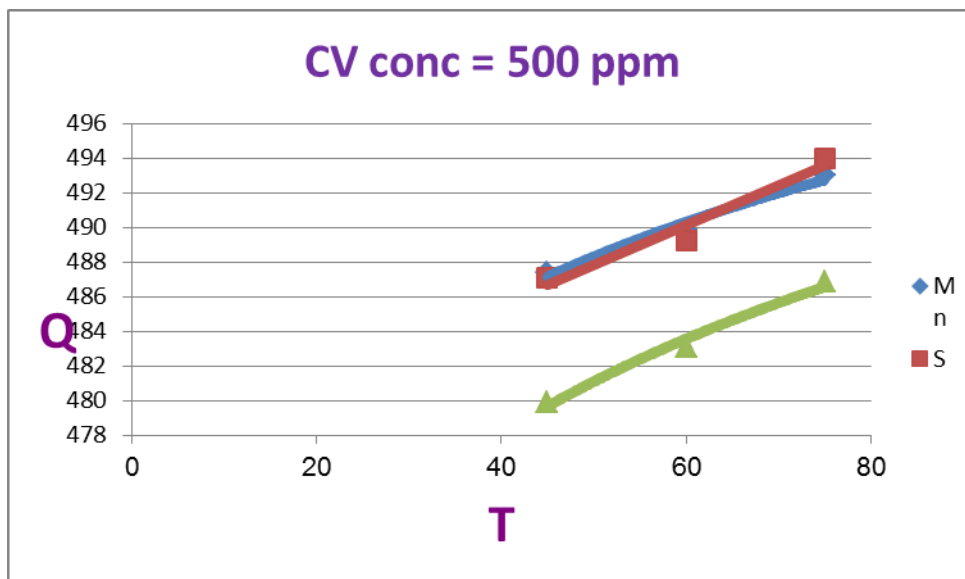
**Figure 6: SEM of a) composites containing magnetite and b) manganese oxide**

### 3.4. Adsorption characteristics of metal oxides nanocomposites

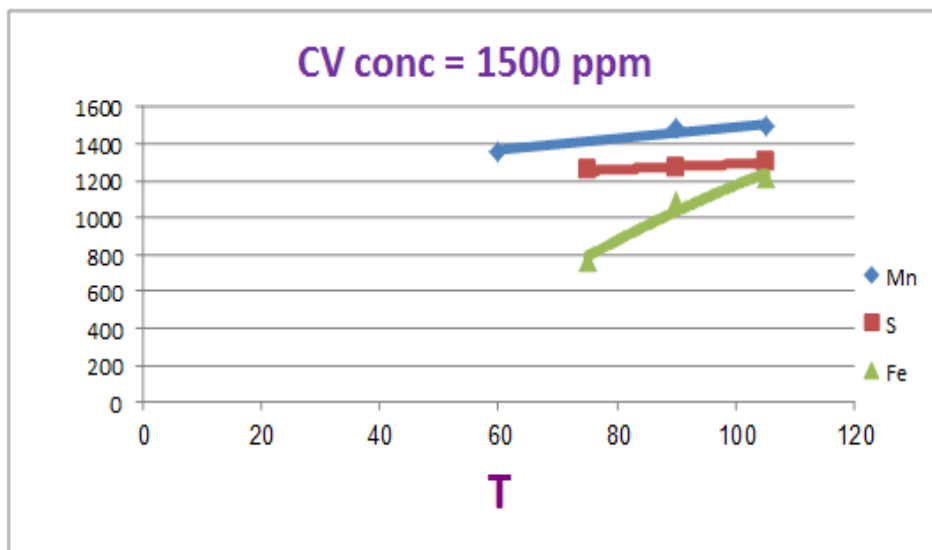
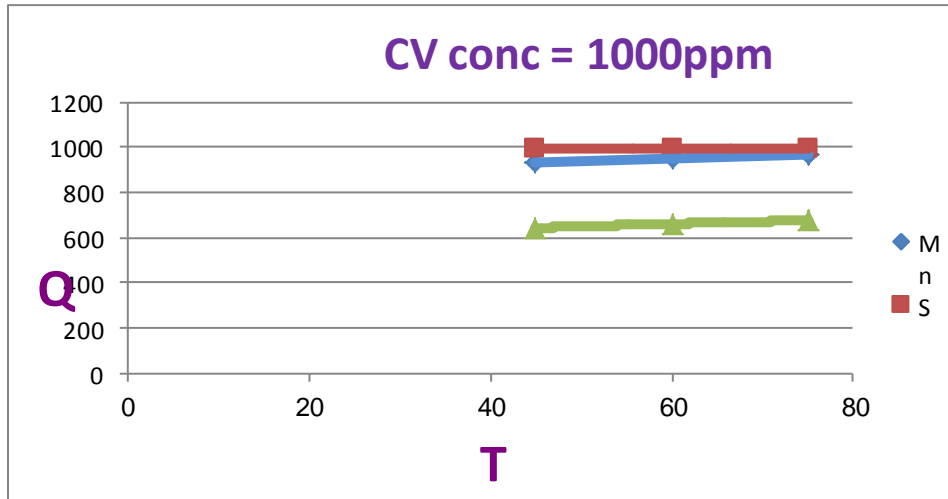
CV as cationic dye has hazard effects on the environment. It is well known that CV contains highly electronegative heteroatoms such as nitrogen that can form hydrogen bonds with water to affect on the diffusion of CV into adsorbents. Manganese oxide and magnetite nanocomposites can be used as adsorbent to remove toxic materials. The interactions between organic cations and nanocomposites are carried out using three different modes [138] such as formation of electrostatic interaction or neutral complexes between negative sites of composites and positive cations of organic dye or inorganic cations. It can be produced from the formation of non-coulombic interaction or formation of positive charges single complex between two positive charges of organic dyes and one negative charge of polymer composite. Accordingly, it is expected that the formation of electrostatic interactions between negative sites of metal Oxides nanocomposite

(produced from sulfonate and carboxylic groups of AA/AMPS and CV cation. It indicates that the presence of both negative charges on AA/AMPS surfaces are responsible for fast diffusion of large amount of CV dye into the AA/AMPS.

The adsorption behavior of CV onto modified Manganese oxide and magnetite AA/AMPS composites is investigated at different concentrations ( ppm ) of CV aqueous solution as described in the experimental section. The comparison between the hydrogel, manganese oxide –hydrogel composite and magnetite –hydrogel composite are illustrated in (**Scheme 1**) which give an indication to the high adsorption of composite contain manganese oxide, the lowest to that containing magnetite and hydrogel in between .







**Scheme 1: Metal Oxides nanocomposite kinetics of adsorption of CV at different concentrations**

## 4. Conclusions

- The present work prepared AMPS-AA hydrogel and its corresponding magnetite and manganese oxide nanocomposites.
- The composites have good metal oxide dispersion in it and possess negative charges.
- The prepared composites was compared for removal of water pollutants from water and showed fast removal of CV.

## REFERENCES

- [1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A. M. Mayes, *Nature* 452 (2008) 301–310
- [2] R. Das, M.E. Ali, S.B. Abd Hamid, S. Ramakrishna, Z.Z. Chowdhury, *Desalination* 336 (2014) 97–109.
- [3] V. Gupta, *Journal of Environmental Management*, 90(8) (2009). 2313–2342.
- [4] O. Ceyhan, D. Baybas. *Turkish Journal of Chemistry*, 25(2) (2001), 193–200.
- [5] A. L. Prasad, T. Santhi. *Sustainable Environment Research*, 22(2012), 113–122.
- [6] G. Mezohegyi, F. P. Van der Zee, , J. Font, A. Fortuny, A. Fabregat, *Journal of Environmental Management*, 102(2012) 148–164.
- [7] P. Goh, A. Ismail, B. Ng, *Desalination* 308 (2013) 2–14.
- [8] V. K. K. Upadhyayula, S.G. Deng, M.C. Mitchell, G. B. Smith, *Sci. Total Environ.* 408 (2009) 1–13.
- [9] Y. Kurokawa, A. Maekawa, M. Takahashi, Y. Hayashi, *Environmental Health Perspectives* 87 (1990) 309-335.
- [10] U. Von Gunten, J. Hoigne, A. Bruchet,. *Water Supply* 13(1995) 45-50.
- [11] G. Crini, *Bioresource Technology*, 97(2006) 1061–1085.
- [12] S. P Buthelezi, A. O. Olaniran, B. Pillay,. *Molecules*, 17(2012) 14260–14274.
- [13] X. Xing Chen, D. Wang, *Environmental Science & Technology*, 41(2007) 1439–1443.
- [14] M. Chafi, B. Gourich, A. H. Essadki, C.Vial, A. Fabregat, *Desalination*, 281(2011) 285–292.

- [15] T. A. Kurniawan, G. Chan, W.-H. Lo, S. Babel, *Chemical Engineering Journal*, 118(2006) 83–98.
- [16] M. García-Gabaldón, V. Pérez-Herranz, J. García-Antón, J. Guinon, *Separation and Purification Technology*, 51(2006)143–149.
- [17] T. Mohammadi, A. Razmi, M. Sadrzadeh, *Desalination*, 167 (2004) 379–385.
- [18] A. Z. Abdullah, B.Salamatinia, A. H. Kamaruddin, *Desalination*, 244(2009) 227–238.
- [19] M. Kobya, E. Demirbas, E. Senturk, M. Ince, *Bioresource Technology*, 96 (2005)1518–1521.
- [20] F. He, W. Hu, Y. Li, *Chemosphere* 57 (2004) 293–301.
- [21] D.K. Bakshi, P. Sharma, *J. Environ. Pathol. Toxicol. Oncol.* 22 (2003) 101–109.
- [22] H. Moawad, W.M. El-Rahim, M. Khalafallah, *J. Basic Microbiol.* 43 (2003) 218–229.
- [23] M.A. Ademoroti, D.O. Ukponmwan, A.A. Omode, *Environ. Stud.* 39 (1992) 291–296.
- [24] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 553–597.
- [25] J. Zhang, C. Cheng, Y. Huang, L. Qian, B. Zheng, H. Yuan, Y. Guo, D. Xiao, *Analyst*138 (2013) 2073–2079.
- [26] J.M. J. Frechet, D.A. Tomalia, 2001. *Dendrimers and other dendritic polymers*. New York: Wiley and Sons.
- [27] P.K. Stoimenov, R.L. Klinger, G.L. Marchin and K.J. Klabunde, *Langmuir*, 18( 2002) 6679-6686.
- [28] K. T. Dhermend, J. Behari P. Sen, *World Appl. Sci.* 3(2008) 417-433.

- [29] L. Brittany, V. Carino, J. Kuo, L. Leong and R. Ganesh, 2006. Adsorption of organic Compounds to metal oxide nanoparticles ( part of conference general environmental).
- [30] A. E. Alvarez, A.G. Sanchez and X. Querol, *Water Res.*, 37(2003) 4855-4862.
- [31] G. Li, *J. App. Pol. Sci.*, 78(2000) 676-684.
- [32] S. Lakshmi, S.S.P. Kumar , A. Jayakrishnan, *J. Biome. Mat. Res.*, 61(2002) 26-32.
- [33] J. Lin, *Biotec. Prog.*, 18 (2002) 1082-1086.
- [34] K. D. Park, *Biomaterials*, 19 (1998) 851-859.
- [35] B.J.F. Graveland, C.G. Kruif, *Trends Food Sci. Technol.*, 17(2006) 196-203.
- [36] A.S. AL-Hobaib, Kh.M. AL-Sheetan, L. El Mir, *Materials Sci. Semiconductor Process.* 40 (2015)15-19.
- [37] H. Zhao, H. Mitomo, *Journal of Applied Polymer Science* 110 (2008)1388–1395.
- [38] X. Liu, Q. Hu, Z. Fang, X. Zhang, B. Zhang, *Langmuir* 25(2009)3–8.
- [39] N. Pekel, N. Sahiner, O. Guven, *Journal of Applied Polymer Science* 81(2001) 2324–2329.
- [40] H. Kasxgoz A. Durmusx, A. Kasxgoz, *Polymers for Advanced Technologies* 19 (2008) 213–220.
- [41] N. Sahiner, *Colloid and Polymer Science* 285 (2006) 283–292.
- [42] Z. Qingsong, Z. Liusheng, M. Jinghong, L. Borun, *Macromol. Rapid Commun.* 28 (2007)116–120.
- [43] J. Zhang, A. Wang, *Reactive & Functional Polymers* 67 (2007) 737–745

- [44] K. Kabiri, H. Mirzadeh, M. J. Zohuriaan-Mehra, and M. Daliric, *Polym. Int.* 58(2009) 1252–1259.
- [45] Q. Zhang, X. Li, Y. Zhao, L. Chen, *Applied Clay Science* 46 (2009) 346–350.
- [46] L. F. Chen, H.W. Liang, Y. Lu, C. H. Cui, and S.H. Yu, *Langmuir*, 27 (2011) 8998–9004.
- [47] Y. Rao, J. M. Pochan, *Macromolecules*, 40 (2007) 290-296
- [48] P. Podsiadlo, B. S. Shima, N. A. Kotova, *Coordination Chemistry Reviews* 253 (2009) 2835–2851
- [49] E. Huttunen-Saarivirtaa, G.V. Vaganovb, V.E. Yudinb, J. Vuorinena, *Progress in Organic Coatings* 76 (2013) 757– 767.
- [50] J. K. Kim, P. A. Ruhs, P. Fischer, J. S. Hong, *Rheol Acta*, 52 (2013) 327–335.
- [51] I. Mohmood, C.B. Lopes, I. Lopes, I. Ahmad, A.C. Duarte, E. Pereira, *Environ. Sci. Pollut. Res.* 20 (2013) 1239–1260.
- [52] P.C. Ray, *Chem. Rev.* 110 (2010) 5332–5365.
- [53] D.K. Tiwari, J. Behari, P. Sen, *World Appl. Sci. J.* 3 (2008) 417–433.
- [54] S. Patnaik, A. K. Sharma, B. S. Garg, R.P. Gandhi, K. C. Gupta, *Int. Pharm.*342 (2007) 184–193.
- [55] N.A. Peppas, P. Bures, W. Leobandung, Ichikawa H, *Eur. J. Pharm. Biopharm.* 50(2000) 27–46.
- [56] M. Antonietti, F. Gröhn, J. Hartmann, L. Bronstein, *Angew. Chem. Int. Ed. Engl.*, 36(1997) 2080-2083.
- [57] J. Kim, S. Nayak, L. A. Lyon, *Journal of the American Chemical Society*, 127 (2005) 9588-9592.
- [58] Q. Qishu, G. Qian, G. Zuli, S. Yuqi, W. Chengyin, H. Xiaoya, *Colloids and Surfaces A: Physicochem. Eng.*, 415 (2012) 41–46

- [59] A. H. Wu, J. Jia, S. J. Luan, *Colloids and Surfaces A: Phys. Eng. Aspects*, 384 (2011) 180-185.
- [60] H. H. Sokker, M. E. Naeem, M.A. Hassan, E. E. Bahgat, *Journal of Hazardous Materials*, 190 (2011) 359–365.
- [61] R. Pelton, *Advanced Colloid Interface Science*, 85 (2000) 1-33.
- [62] Y. Sasaki, K. Akiyoshi, *Nanogel engineering for new nanobiomaterials: from chaperoning engineering to biomedical applications*, Chemical record (New York, N.Y.) (2010).
- [63] Y. Shaoping, F. Shiyu, L. Hao, Z. Yiming, L. Xueyun, *Journal of Applied Polymer Science*, 119 (2011) 1204–1210.
- [64] N. Morimoto, T. Endo, M. Ohtomi, Y. Iwasaki, K. Akiyoshi, *Macromolecular bioscience*, 5 (2005) 710-716.
- [65] M. Motornov, Y. Roiter, I. Tokarev, S. Minko, *Prog. Poly. Sci.* 35 (2010) 174.
- [66] S.Y. Zhao, S.H. Chen, S.Y. Wang, D.G. Li, H.Y. Ma, *Langmuir* 18 (2002) 3315.
- [67] W. L. Cheng, S.J. Dong, E.K. Wang, *Electrochem. Comm.* 4 (2002) 412–416.
- [68] A. M Atta, G. A. El-Mahdy, H. A. Al-Lohedan, A. O. Ezzat, *Molecules*; 19 (2014)10410-10426
- [69] G. A. El-Mahdy, A. M. Attaa, H. A. Al-Lohedana, *J. Tai. Inst. Chem. Eng.*, 45 (2014) 1947.
- [70] A. M. Atta, A.K. F. Dyaba, and H. A. Allohedan, *Poly.Adv. Technol.*, 24, (2013) 986.
- [71] A. M. Atta , G. A. El-Mahdy, H. A. Al-Lohedan1, A. M. El-saeed, A. M. Tawfeek, *Int. J. Electrochem. Sci.*, 10 (2015) 3584 - 3599

- [72] F. Caruso, *Nano Surface Chemistry* (2002) 505-525.
- [73] H. Kawaguchi, *Science*, 25(2000)1171-1210.
- [74] O. Okay, *Prog. Polym. Sci.*, 25 (2000) 711-779.
- [75] D. C. Sherrington, *Journal of Polymer Science Part A: Polymer Chemistry*, 39 (2001) 2364-2377.
- [76] S. Sengupta, A.K. SenGupta, Lewis Publishers, Boca Raton, (2002) 45-96.
- [77] C. Wang, W. Yang, S. Fu, *Functionalization of colloidal particles. Colloidal polymers: synthesis and characterization*, Elaissari, A., Ed., Marcel Dekker, New York, (2003) 93-116.
- [78] M. Cheryan, *Ultrafiltration and Microfiltration Handbook*, CRC Press, Boca Raton, (1998) 345-483.
- [79] A. A. Zagorodni, *Ion Exchange Materials Properties and Application*.(1st ed.) oxford : Elsevier (2007).
- [80] M. D. LeVan, G. Carta, *Adsorption and Ion Exchange*, in *Perry's Chemical Engineer's Handbook* ed. Green D.W, Perry R.H, New York: McGraw-Hill (2008).
- [81] Morris G.E, Vincent B., Snowden M.J, *J. Colloid Interface Sci*, 190 (1997)198–205.
- [82] R. Kanazawa, K. Mori, H. Tokuyama, S. Sakohara, *J. Chem. Eng. Japan*, 37 (2004) 804-807.
- [83] Chen M. Q, Chen Y, Kaneko T, Liu X.Y, Cheng Y, Akashi M, *Polym .J*, 35 (2003) 688-690.
- [84] C. A. Bell, S. V. Smith, M. R. Whittaker, A. K. Whittaker, L. R. Gahan, M. J. Monteiro, *Adv. Mater*, 18 (2006) 582-586.
- [85] M. J. Snowden, D. Thomas, B. Vincent, *Analyst*,118(1993)1367 - 1369.
- [86] A. Markus, L. Sabine, D. E. Claus, S. S. Ulrich , *Macromolecular Rapid Communications*, 16 (1995) 283–289.



- [87] S. Amigoni-Gerbier , C. Larpent, *Macromolecules*, 32 (1999) 9071-9073
- [88] S. Amigoni-Gerbier , S. desert, T. Gulik, C. Larpent, *Macromolecules*, 35 (2002) 1644-1650.
- [89] M.S. Diallo, L. Balogh, A. Shafagati, J.H. Johnson, W.A. Goddard. *Environ. Sci. Technol*, 33 (1999) 820–824.
- [90] M. Monier, D. M. Ayad, Y. Wei, A.A. Sarhan, *Journal of Hazardous Materials*, 177 (2010) 962-970.
- [91] M. Monier, D. A. Abdel-Latif, *Journal of Hazardous Materials* , 209 (2012) 240-249.
- [92] N. Li, R. Bai, *Water Sci Technol*, 54 (2006)103-113.
- [93] Y.C. Chang, D.H. Chen, *Journal of Colloid and Interface Science*, 283(2005) 446–451.
- [94] T. López-León, E. L. S. Carvalho , Seijo B, Ortega-Vinuesa J.L, Bastos-González D, *J. Colloid Interface Sci*,283 (2005) 344-351.
- [95] Wu A.H, Jia J, Luan S.J, *Colloids and Surfaces A: Phys. Eng. Aspects*, 384 (2011) 180-185.
- [96] Tokuyama H, Yanagawa K, Sakohara S, *Separations and Purification Technology*, 50 (2006) 8-14.
- [97] Yamashita K, Nishimura T, Nango M, *Polym. Adv. Technol*, 14 (2003) 189-194.
- [98] Zhao W, Li H, Teasdale P. R, John R, Zhang S, *Reactive & Functional Polymers*, 52 (2002) 31- 41.
- [99] Chen J.J, Ahmad A.L, Ooi B.S, *Journal of Environmental Chemical Engineering*, 1 (2013) 339–348
- [100] E. González-Pradas, M. Villafranca-Sánchez, A. Gallego-Campo, D. Ureña-Amate , M. Fernández-Pérez, *J. Chem. Technol. Biotechnol.* 74 (1999) 49-54.

- [101] R. Bhattacharyya, S. K. Ray, *Chemical Engineering Journal*, 260 (2015) 269-283.
- [102] Y. Zhao, E. Abdullayev, A. Vasiliev, Y. Lvov, *Journal of Colloid and Interface Science*, 406 (2013) 121-129.
- [103] X. Nie, A. Adalati, J. Du, H. Liu, S. Xu, J. Wang, *Applied clay Science*, 97–98 (2014) 132-137.
- [104] C.W. Chiu, C.C. Chu, W.T. Cheng, J.J. Lin, *European Polymer Journal*, 44 (2008) 628-636.
- [105] L. Liang, J. Liu, X. Gong, *Langmuir*, 16 (2000) 9895-9899.
- [106] Y. Rao, J. M. Pochan, *Mechanics of Polymer-Clay Nanocomposites, Macromolecules*, 40 (2007) 290-296
- [107] A. M. Atta, G. A. El-Mahdy, H. A. Al-Lohedan, A. M. Tawfeek, A. A. Abdel-Khalek, *Digest Journal of Nanomaterials and Biostructures* 9 (2014) 531 – 541.
- [108] M. Shabani-Nooshabadi, S. M. Ghoreishi, M. Behpour, *Corrosion Science* 53 (2011) 3035–3042.
- [109] J. K. Kim, P. A. Ruhs, P. Fischer, J. S. Hong, *Rheol Acta*, 52 (2013) 327–335
- [110] D. Dupin, A. Schmid, J. A. Balmer, S. P. Armes, *Langmuir* 23, (2007)11812.
- [111] A. Schmid and P. A. Steven, *Langmuir* 25, (2009) 2486-2494.
- [112] A. Slistan-Grijalva, R. Herrera-Urbina, J. F. Rivas-Silva, M. Avalos-Borja, F. F. Castell´on-Barraza, A. Posada-Amarillas, *Materials Research Bulletin*, 43, (2008) 90–96 .
- [113] A. E. Blum and D. D. Eberl, *Clays and Clay Minerals*, 52, (2004). 589–602
- [114] K. A. Carrado and L. Xu, *Microporous and Mesoporous Materials*, 27, (1999) 87–94
- [115] Q. Zhang, L. Zha, J. Ma, B. Liang, *Macromol. Rapid Commun.* 28, (2007)116–120.
- [116] M. Xu, Y. S. Choi, Y. K. Kim, K. H. Wang, I. J. Chung, *Polymer* 44 (2003) 6387–6395.
- [117] Y. Deng, J.B. Dixon, G.N. White, *Soil Sci. Soc.* 70, 297–304 (2006).

- [118] A. J. Paine, *Macromolecules*, 23, 3109-3117 (1990).
- [119] K. Haraguchi, H. J. Li, K. Matsuda, S. Okabe, T. Takehisa, E. Elliot, *Macromolecules*, 38, 3482 (2005).
- [120] Z. Hu, G. He, Y. Liu, C. Dong, X. Wu, W. Zhao, *Applied Clay Science*, 75-76, 134-140 (2013).
- [121] Y. Xi, R. L. Frost, H. He, *Journal of Colloid and Interface Science*, 305 (2007) 150-158.
- [122] S. D.A.S. Ramôa, G. M.O. Barra, C. Merlini, W.H. Schreiner, S. Livi, B.G. Soares, *Applied Clay Science*, 104 (2015) 160-167.
- [123] N. Sahine, S. Demir, S. Yildiz, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 449 (2014) 87–95.
- [124] R. M. Guillermic, A. S. Jalmes, *Soft Matter*, 9(2013) 1344–1353.
- [125] W. Xiong, X. Gaob, Y. Zhao, H. Xub, X. Yang, *Colloids and Surfaces B: Biointerfaces* 84 (2011) 103–110.
- [126] Y. Xi, W. Martens, H. He, R.L. Frost, *J. Therm. Anal. Calorim.* 81 (2005) 91–97.
- [127] H. Zheng, Y. Zhang, Z. Peng, *J. Appl. Polym. Sci.* 92 (2004) 638–646.
- [128] Y.S. Choi, H.T. Ham, I.J. Chung, *Polymer* 44 (2003) 8147–8154.
- [129] B.K.G. Theng *The Chemistry of Clay–Organic Reactions*, Adam Hilger, London, 1974.
- [130] G.W. Beall, M. Goss, *Appl. Clay Sci.* 27 (2004) 179–186.
- [131] J.H. Park, S.C. Jana, *Macromolecules* 36(2003) 2758-2768.
- [132] A.B. Morgan, J.W. Gilman, *J Appl. Polym. Sci.* 87(2003)1329–1338.
- [133] S.A. Boyd, G. Sheng, B.J. Teppen, C.T. Johnston, *Environ. Sci. Technol.* 35 (2001) 4227–4234.
- [134] D.W. Rutherford, C.T. Chiou, *Environ. Sci. Technol.* 26 (1992) 965–970.
- [135] W. Xie, R.C. Xie, W.P. Pan, D. Hunter, B. Koene, L.S. Tan, R. Vaia, *Chem. Mater.* 14 (2002) 4837–4845.
- [136] N. Greesh, P. C. Hartmann, V. Cloete, R. D. Sanderson, *Journal of Colloid and Interface Science* 319 (2008) 2–11.
- [137] K. Kabiri, H. Mirzadeh, M. J Zohuriaan-Mehra, M. Daliri, *Polym Int* 58 (2009) 1252–1259.
- [138] G. Rytwo, D. Tropp, C. Serban, *Applied Clay Science*, 20 (2002) 273-282.