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# A review on concepts useful to the synthesis of superactivated carbon-magnetite nanocomposite and its application on the adsorption of Cd, Pb, Cr, Fe ions in aqueous solutions

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*Highlights*

- *The synthesis of a super activated carbon-magnetite nanocomposite can be advantageous to both SAC and nanomagnetite in the adsorption of heavy metals from aqueous solutions*
- *Different modifications can be done on nanocomposites of superactivated carbon and magnetite to increase and enhance its functions; however,*
- *Further incorporation of more material to the nanocomposite causes a decrease in adsorptive capacity.*

## Abstract

The synthesis of nanoparticles and nanocomposites proves to show potential on different fields. In the treatment of heavy metals such as cadmium, chromium, lead, and iron from aqueous environments specifically, there have been studies on the application of such nanoparticles. Researchers developed different methods for the synthesis of superactivated carbon, magnetite nanoparticles, and their nanocomposites with other particles. KOH activation has been commonly used to synthesize superactivated carbon. For the synthesis of magnetite nanoparticles, most researches cited used ferric chloride, with the addition of different reagents. For the synthesis of a Superactivated Carbon-Magnetite nanocomposite, different methods have been employed. SAC-Mag Nanocomposite has shown higher adsorptive capacity than naked Sb AC and Magnetite. Further impregnation of other material in the nanocomposite causes a decline in its -adsorptive capacity. This review covers information useful for the synthesis of superactivated carbon-magnetite nanocomposite for the adsorption of Cd, Pb, Cr, Fe ions in aqueous solutions.

*Keywords: Activated carbon, superactivated carbon, magnetite nanoparticles, heavy metals, SAC-Mag Nanocomposite*

## Contents

## 1. Introduction

Nanoscience and nanotechnology have received increased attention in recent years. Nanoparticles are small particles of sizes ranging from 1 nanometer to 100 nanometers. Particle aggregation, photoemission, electrical and heat conductivities are only some of the unique physical characteristics of nanoparticles. These particles also have unique chemical properties like catalytic activity [1]. Throughout the years, researchers have been able to note the importance of such particles in different applications and fields. Different branches of medicine have been drawn to nanoparticle research in drug-delivery systems for their ability to overcome multiple biological barriers and release dosage in the optimal range, resulting in increased therapeutic efficacy and weakened side effects [1]. Noble metal nanoparticles, including silver and gold, have been used for chemical sensors and biological sensors [2]. In environmental applications, nanoparticle research has been mainly focused on the remediation of materials contaminated by hazardous substances [3], and sensors for environmental stages [4]. The removal of heavy metals such as cadmium, arsenic, and lead has garnered attention because of the adverse effects these metals have on the environment.

In this review, we provided an overview on the concepts that are related to the synthesis of superactivated carbon-magnetite nanocomposite for the adsorption of cadmium, lead, iron, and chromium metal ions in an aqueous environment.

### *1.1. Cd, Cr, Fe, Pb ions in the environment*

Heavy metals constitute the industrial and agricultural waste in water. Heavy metals pose hazards to living organisms. Studies have shown that heavy metals can affect the biological systems and functions and can even be carcinogenic. Sharma and Agrawal [5] cited that in plants, some heavy metals have been reported to affect photosynthetic functions, essential function in plants. These are just some of the hazards of heavy metals.

Various methods have been developed in efforts of removing these toxic heavy metals from aqueous sources. These include ion exchange, precipitation, membrane filtration, electrochemical methods, and more. These methods, however have been found to be costly and not applicable in small-scale treatments. The use of particles in nanoscale has proved its efficiency and flexibility in solving the problem. [6]

The adsorption of heavy metals in aqueous solution to activated carbon and magnetite nanocomposite is discussed further in this article.

### *1.2. Carbon nanoparticles, activated carbon, and superactivated carbon*

Carbon nanoparticles, and/or activated carbon, with their high surface area, microporous character, and their chemical nature, have been the subject of many research topics on the adsorption of metal ions. These are widely used in many fields. Functionalized carbon nanotubes have been used as sensors for molecular hydrogen [7], carbon nanoparticles have been used as visible-light photocatalysts [8], the importance of fluorescent carbon nanoparticles have been noted by Kumar et al [9].

Activated carbon is usually synthesized from carbon-rich materials such as bamboo, coconut husks, and more, followed by either physical activation or chemical activation, or both. In physical activation, the source is converted to activated particles through carbonization by pyrolysis at very high temperatures, followed by exposure to oxidizing atmospheres like oxygen or steam. In chemical activation, certain chemical/s (usually basic, or acidic, or a salt) is/are introduced to the source material before the process of carbonization. Chemical activation allows for carbonization at lower temperatures and shorter carbonization time, hence chemical activation is more widely preferred.

Compared to conventional activated carbon, superactivated carbon is known to be more porous, and to have extraordinarily large capacities [10]. In a review of literature done by Bernaldo et al. [11], it is stated that the particle size of superactivated carbon is 100 times smaller than the particle size of activated carbon. The iodine value of SAC is also significantly higher than that of conventional activated carbon. SAC has an internal surface area greater than 1000 $m^2/g$. The high surface area makes it “highly accessible to the passage of fluid and vapor that is potential for adsorption.” This advantage provides potential for higher efficiency in the removal of certain chemicals.

The adsorption of heavy metals such as Hg(II), Pb(II), Cd(II), Ni(II), Cu(II) in industrial wastewater onto activated carbon was shown to be evident in a study by Kadirvelu et al. [12]

### *1.3. Magnetite nanoparticles*

Magnetite, a ferrimagnetic mineral form of iron oxide ($Fe_3O_4$), is the only mineral that exhibits strong magnetism, in contrast to others, such as ilmenite and hematite [13].

Potential applications of magnetite nanoparticles, especially in the biomedical field has been evident through various researches. Water-based suspensions of nanomagnetite can be formed with proper surface coating [14]. The interaction between this suspension with an external magnetic field is what makes Magnetic Resonance Imaging (MRI) possible [15]. Lu et al. [16] cited works on the applications of nanomagnetite technology in magnetic fluids, catalysis, medicine, data storage, and environmental remediation. Research has found that magnetite nanoparticles can bind to certain heavy metals. [17] These nanoparticles can be functionalized/modified with varying enhancements depending on the application.

Activated carbon and magnetite nanoparticles have both been subjects of research on the removal of heavy metal ions. The effects of synthesizing a nanocomposite consisting of the two substances on the removal of such heavy metals (Cd. Cr, Fe, Pb) in aqueous solution is something worth noting.

## 2. Methodology

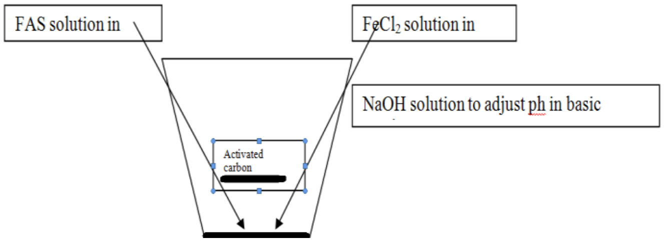

***Figure 2.1*** *Schematic diagram of SAC-MNP*

### *2.1. Superactivated carbon synthesis*

In the synthesis of superactivated carbon-magnetite nanocomposite, there are methods that are followed to attain the necessary product.

Activated carbon is used to increase the adsorption of the material and also to increase its magnetic potential in specific metals. Several methods are used in the synthesis of superactivated carbon. In a study dealing with a method to synthesize super-activated carbon for natural gas adsorptive storage [18],it is found that activated carbon prepared by coupling approach bears developed micropore structure, which is produced by depth activation catalyzed by chemical agent at moderate temperature and might be feasible for adsorption storage of natural gas, and considerable mesopore structure, which is formed by width activation catalyzed by chemical agent and/or steam at elevated temperature and feasible for desorption process of ANG. A sequence of activated carbon was organized from petroleum coke (Sheng lire finery, SINOPEC) using KOH as initiating agent and steam as the co-agent. The precursor was grounded and sieved to particle size range of 0.15–0.28mm, then mixed with KOH powder without sieving. In activation process, the mixture was added in a quartz boat, which is placed in a tabulated stain less steel reactor in a nitrogen flow of 40 mL/min. The samples were heated at the rate of 5 K/min to 673 K, kept for 1 hour, and then raised to 1023K and kept fora certain amount of time. Simultaneously, the saturated steam in nitrogen was introduced at the temperature 1023K. Lastly, the reactor was quickly cooled in nitrogen flow until room temperature was achieved. The products were removed, washed, and dried at 373K. Activated carbon through pure chemical activation and coupling approach were denoted as Che-AC and Cou-AC, correspondingly.

On the other hand, V. Roshni and D. Ottoor synthesized carbon nanoparticles using one step green approach [19], from coconut milk by thermal pyrolysis. It is found that during pyrolysis, coconut oil is separated from the carbon rich residue and the residue when dissolved in water showed blue fluorescence under UV light. Experimental procedure involved the thermal pyrolysis of coconut milk under a mild temperature range of 120 - 150 ºC for two to five minutes. Coconut milk was extracted from grated coconut. Moreover, while heating the sample, coconut oil was separated, leaving behind black residue. The residue obtained after the separation of coconut oil was air dried. Triply distilled water was used as a solvent throughout the experiment.

[20] Sevilla and Ferrero synthesized superactivated carbon from hydrochar. Hydrochar was chemically activated using a mixture of powdered melamine and potassium oxalate monohydrate ($K_2C_2O_4 * H_2O$). The material was added to an aqueous dispersion containing potassium oxalate monohydrate with a systematic weight ratio. Water was evaporated while stirring and the resulting mixture was heat-treated up to a certain temperature under nitrogen gas flow maintained for one hour. It is stated that highly microporous carbons with textural properties matching those of benchmark KOH activated carbons have been developed by activating hydrochar with less corrosive activating agent.

It is stated in Liu’s and Lu’s journal titled “Self-Assembled Activated Carbon Nanoparticles for Reliable Time Discretized Quantitative Surface-Enhanced Raman Spectroscopy” [21] For their procedure, to achieve the external standard method, a self-assembled film of activated carbon nanoparticles is firstly prepared by air/liquid (KCl aqueous solution) interfacethen activated carbon film was transferred onto the surface of Teflon slice (extraction film), is dipped into high concentration of analyte to achieve reliable saturated adsorption and the extraction film under saturated adsorption is called reference (external standard). The uniformity is very good in one extraction film and thus the extraction film is cut in halves (used to prepare determinant and reference) to eliminate deviation of different batches. Saturated adsorption time of extraction film is different for different concentrations of analyte and concentration can be therefore quantified by saturated adsorption time.

For steps on how activated carbon nanoparticles disintegrate in DMF, 40 mg of the activated carbon power was dispersed into DMF by ultrasonic for 20 minutes. 1mL of the carbon colloid was next added dropwise into 40 mL of 0.25 M KCl aqueous solution. The self-assembled carbon film would emerge on the surface of solution. Finally, the self-assembled carbon film was transferred onto the surface of Teflon slice (diameter: 4 mm, thickness: 0.5 mm) and the slice with carbon film was dried for use. The slice with activated carbon film was called extraction film. Before use, extraction film was dipped into ultrapure water for 10 hours to rinse.

This method is slightly far/irrelevant from the methods of other articles but it shows how important the activated carbon is in electrochemistry.

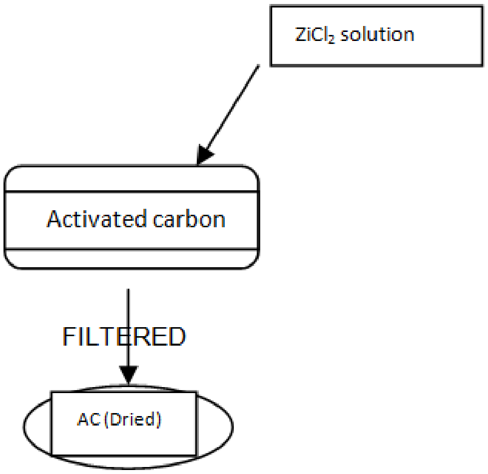

***Figure 2.3*** *Diagram of synthesis of activated carbon in rice hulls*

In a synthesis of activated carbon in rice hulls [22], 50 grams of rice hulls was prepared and readily exposed to a solution containing 500 mL of zinc chloride solution in a 100 mL of water for 24 hours. After soaking, the rice hulls were filtered and dried and was activated in a close ceramic vessel using nitrogen gas at 1023 K. Using HCl with the aid of water, the rice hulls were soaked in this solution to remove substances that contribute to the uncertainty. The rice hulls were then washed using tap water and distilled water; and were dried at 105 degrees.

### *2.2. Magnetite nanoparticle synthesis*

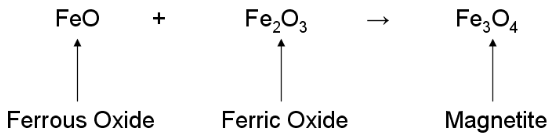
$$FeO + Fe_2O_3 \rightarrow Fe_3O_4$$

*Figure 2.2 Oversimplified magnetite synthesis reaction*

Marinescu and Neagoe synthesized magnetite nanoparticles in the presence of amino acids [23]**.** Materials made up of iron sulphate and iron chloride as magnetic nanoparticles were prepared in the presence of amino acids (L- (+)-aspartic acid, L- (+)-glutamic acid, arginine hydrochloride, L-proline, DL-tryptophan). The mixture was then prepared with its optimum molar ratio 2:1. After mixing the solution, drops of ammonia ($NH_3$) was added to adjust the pH in 3-4 of iron-amino acid solution until a compound is separated. They continued to add a certain amount of ammonium hydroxide ($NH_4OH$) to reach basic condition and to become complex ion, then the compound decomposed and black precipitate formed. This suspension was maintained for 60/30 min, under vigorous stirring. The fine magnetic powder was separated from the aqueous solution by filtration, rinsed with distilled water and alcohol and then dried on $P_4O_{10}$ at room temperature. The structure and phase purity of the nanopowders were investigated by X-ray diffractometry (XRD) in a step scanning technique in the 2h range 20–80 with a step of 2/min. For the analysis of the size of the material they used transmission electron microscopy (TEM) and for the molecular formula or the functional groups that was made by the presence of amino acids in the nanomagnetite they used Fourier transform Infrared (FTIR).

Lin and Viadero [24] synthesized nanomagnetite using Iron (II) sulfate ($FeSO_4.7H_2O$) and odium selenate ($Na_2SeO_4$). They used co-precipitation method and performed under room temperature. A solution of 2 [$Fe^{3+}$] : 1 [$Fe^{2+}$] was prepared with deionized water de-aerated by $N_2(g)$ bubbling prior to use. 25% ammonium hydroxide was slowly added dropwise in the solution then gradually black precipitate formed. Precipitation was allowed to continue at 25ºC for 30minutes, with mechanical stirring and continuous $N_2(g)$ bubbling. The synthesized nanomagnetite particles can be separated from the solution using an external magnet outside the container. The magnetite particles were strained to the bottom, and the supernatant was decanted. The particles were thoroughly washed by deionized water then followed by centrifugation around 4000rpm. Nanomagnetite was then vacuum-dried and pulverized. Particle sizes were analyzed by a transmission electron microscope (TEM) and estimated to range from 10nm to 20nm. We do have same reagent that we will be used iron sulfate and iron chloride. But they used amino acids for synthesizing the materials which is a little bit risky for us.

$$\mathbf{FeCl_2 + 2FeCl_3 + NaOH \rightarrow Fe_3O_{4(S)} + 4H_2O + 8NaCl}$$

*Figure 2.4 Chemical reaction of $Fe^{2+}$ and $Fe^{3+}$ with NaOH that forms Magnetite($Fe_3O_4$), water and salt.*

Statistical optimization of effective parameters on saturation magnetization of nanomagnetite particles by Ramimoghadam. So first of all, the superparamagnetic nanoparticles were prepared by the coprecipitation of $Fe^{2+}$ and $Fe^{3+}$ in an aqueous solution using base solution [24-25]. The starting materials were ferrous chloride tetrahydrate and ferric chloride hexahydrate for the magnetic core. 120mL aqueous solution of Fe2+ and Fe3+ salts (total 1.25 M) and 120mL of 5 M NaOH solution were added into the reactor containing 160 mL distilled water at 80ºCelsius under $N_2$ atmosphere, in constant mixing. A black precipitate was formed at the early phase, and the medium was continuously stirred for 2 h at 3000 rpm stirring rate and 80º C. Magnetite particles were stabilized by slow addition of 10mL 25% (w/w) TMAOH. The chemical structure of the material was characterized by FTIR and NMR. The magnetite nanoparticles produced in the previous work with an average particle size of 50 nm and particle size distribution of 0.317 was used in this step [26-27]. For polymer coating, 1.25 mL St, 0.1 mL PEG-MA or PEGEEM,0.1 mL cationic comonomerDMAPM and 0.03g cationic initiator V-50 were added into the reaction medium (distilled water). Reactions were conducted in an oil-in-water (o/w) system by an emulsifier-free emulsion polymerization technique at 65º C, under nitrogen atmosphere for 24 hours. Magnetic nanoparticles were collected by using a magnet and washed with methanol and distilled water for several times. Then, these nanospheres were immersed in 0.1 M of $H_2SO_4$ solution for 48 hours to remove naked magnetite [28]. In order to remove acidic residuals, polymer coated nanoparticles were further washed with distilled water. Average particle size, particle size distribution and magnetic properties of these nanoparticles were determined by using techniques described in previous step. The important procedure that is worth noting is the collection of magnetic nanoparticles using an external magnet. This helps ideas and provides as evidence for procedures that can be made in future studies. Definitely, this is the closest procedure that we will be doing in our experiment. But in our procedure, we will be using $N_2$ for deoxygenating the distilled water so that it can absorb air.

$$\mathbf{FeCl_2 + 2FeCl_3 + NaOH \rightarrow Fe_3O_{4(S)} + 4H_2O + 8NaCl}$$

In a different method [29]. 12 grams $FeC_{12}{\cdot}4H_2O$ and 24 grams $FeCl_3{\cdot}6H_2O$ were separately dissolved in 50 mL of deionized water. The solutions were mixed in a 500-mL beaker, and then 50 mL of ammonium hydroxide (28% $NH_4OH$) was gradually added while the solution was vigorously stirred. The clear solution was decanted (5 minutes after sedimentation of the precipitate), and the precipitate was washed using a solution of 5% ammonium hydroxide in deionized water.

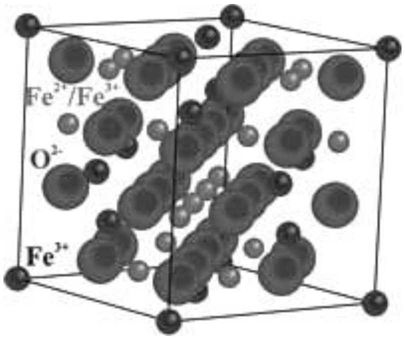

***Figure 2.5*** *Unit cell of magnetite*

Nanoparticle diameter is determined by the relative amounts of surfactant and solvent; and also, the ratio of polar solvent to the surfactant [30]. The surfactant ordodecylbenzenesulfonate is added to the xylene solution to create an opaque solution. The solution underwent sonication process that bombarded the sample in its highly intensive ultrasonic waves that homogenized the emulsion. In combination of ferrous chloride and ferric nitrate, the iron must have a molar ratio of 1:2 for ferrous and ferric, respectively. These compounds were mixed in ethanol solution and simultaneously stirred up to its homogenized emulsion solution. Afterwards, the opaque became transparent. After 12 hours of stirring, the water in oil phase equilibrated. The solution was gradually heated in a specific temperature of 90º C under anoxic conditions to prevent the oxidation of $Fe^{2+}$. To oxidize the reaction, hydrazine which is a strong reducing agent was needed. The solution in its transparent color changed to black. For the magnetite nanoparticle recovery, centrifugation of the solution was applied. After the centrifugation, the nanoparticles were ready to be separated from its solvent.

In a “Reverse Micelle” method [30], Hydrophobic compounds and subsequent precipitation are separated by utilizing micellar solutions. This process is always applied in removal of colloidal particles of substance in water treatment, so reverse micellar could treat aqueous solutions. Direct utilization of this physico-chemical reaction can be generated in hydrophilic cores by nanoreactors in aqueous compounds. Insoluble metals like iron were divided into aqueous phase (water in oil emulsions) within the reverse micelle cores. For a nanoscale reactor that contains species of interest, this set up allows the different chemical reactions in understanding if it is alterable and if there are dimensionally restricted spaces. The simultaneous nanoparticle production and steric stabilization can be denoted through adsorption of surfactant monomers.

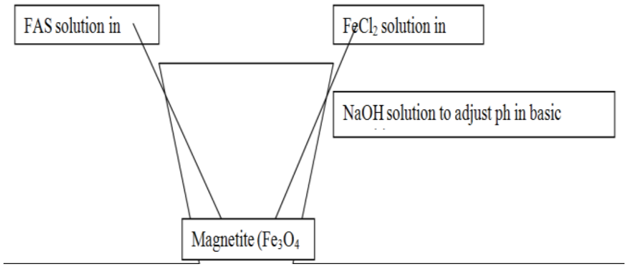

***Figure 2.6*** *Diagram of magnetite synthesis*

Kim et al. synthesized magnetite nanoparticles by preparing a stock solution of ferrous chloride and ferric chloride with the molar ratio of 1:2. Then gradually poured in a NaOH solution, the solution was under nitrogen sparging and stirred to make the mixture homogeneous. The precipitate of magnetite crystals formed was removed using magnet or an external magnetic field. The magnetite crystals had been collected using the magnet then washed by deionized water and separated using centrifuge. After that, XDS analysis determined mechanically the particle diameters at 6nm. Magnetite nanoparticles were stabilized using sodium oleate solution at 90-degree Celsius. Sodium hydroxide solution was used to control the nanoparticles diameter and make the solution in basic condition. Nanoparticle sizing is directly proportional to sodium hydroxide concentration and pH.. On the other hand, nanoparticles ‘diameter is inversely proportional if the sodium hydroxide concentration is constant. Thus, the diameter will be less than 3 nm if the pH is higher making the sodium hydroxide concentration lower.

### *2.3. Binding of activated carbon-magnetite nanocomposite*

Pratiwi and Saprudin [31] synthesized and characterized nanomagnetite (NM), activated carbon-magnetite nanocomposite (AC-NM), and activated carbon-magnetite-pyrazolone nanocomposite (AC-NM-PZ). For the synthesis of NM and AC-NM was done using hydrothermal method. So they prepare 0.2 M $FeCl_3.\cdot 6H_2O$ 0.2 M and it was added to 0.4 M sodium citrate and 0.6 M urea dissolved in 100 ml of distilled water. They weigh 5 grams of activated carbon and was added to the mixture for the synthesis of AC-NM. The solution was stirred for 30 minutes and then put in teflon hydrothermal and heated in oven at 200 ºC for 12 hours. Black residue that formed were washed with distilled water and ethanol. The sample was dried at 60º C for 12 hours then were characterized with FTIR and XRD.

A specific amount of PZ was added to five grams of AC-NM and then dissolved in 10% $NaHCO_3$. The solution was stored then the sample was then separated from the solution with centrifugation and washed with distilled water; acetone plus distilled water in the ratio1:1; and distilled water to reach neutral pH. The resulting AC-NM-PZ nanocomposite was dried at 60ºC for 12 hours and then characterized with FTIR. UnadsorbedCd(II) ion concentration in the solution was determined with FAAS. Adsorption isotherm of adsorbent was analyzed by using Langmuir and Freundlich isotherm models.To investigate the selectivity of AC, AC-NM, and the AC-NM-PZ adsorbent in this study, 0.5 g of adsorbent was shaken with a mixture of metal ions (Cd, Pb, and Cu) under optimum condition using a shaker batch. Concentration of unadsorbed Cd, Pb, and Cu metal ions in the solution were evaluated by FAAS.

For this procedure in this article, we can say that it supports our procedure for binding process of nanomagnetite and activated carbon.

### *2.4. Characterization of complex compound*

There are many instruments that can be used to characterize unknown complex compounds. Several of the methods above use XRD, DLS, and other nano-based detection instrument. XRD characterization is aimed to determine nano-sized formation of the sample, the degree of crystallinity, crystal size and synthesized crystalline form. [32-33]. Synthesis of powders and composites of magnetite with AC also do not change the crystal structure of magnetite. The difference is in the background of AC-NM, it was greater than the NM because AC is amorphous. The XRD pattern of AC amorphous appears at 2θ values of 20-30 [34]. The amorphous nature of the air conditioner can also reduce the degree of crystallinity of samples that has been synthesized from 64.07% to 38.42%. Crystal size of synthesized NM and AC-NM was determined by using the Scherrer equation and was determined to be 39.6 nm and 30.3 nm, respectively. While the crystal form follows the pattern face centered cubic crystalline form.

FTIR tests were performed on AC, NM, PZ, and AC-NM-PZ nanocomposite. AC did not functionalize well, indicated by no functional group present. The FTIR spectrum for synthesized NM indicated by a sharp peak at wave number 565 $cm^{-1}$. It is a sharp peak absorption area bond Fe-O which lies in the area absorption wave numbers <570 $cm^{-1}$[34-35]. The FTIR spectrum for AC-NM composite showed no significant difference with the results of the analysis of functional groups AC. It was concluded that the composite does not indicate the formation of a new bond. But there is a change in the regional OH absorption wave numbers 3650-3200 $cm^{-1}$ [36] and Fe-O with a weak peak, which indicates NM. Pyrazolone (PZ) has several particular peaks such as carbonyl and phenyl group. The band at 1805 $cm^{-1}$ indicates C=O (carbonyl) group of pyrazolone ring. C=C group of phenyls is shown by an absorption at 1601 cm$^{-1}$. Absorption at 1151 cm$^{-1}$ shows the vibration of the C-N. Vibration at 1027 cm$^{-1}$ shows the C-H of ethyl group ($CH_2$). The band at 3056 and 3029 cm$^{-1}$ shows the vibration of C-H group (methyl). Absorption at 3128 cm$^{-1}$ shows the vibration of C-H aromatic groups. While vibration O-H is seen at 3422 cm$^{-1}$. Pavia stated that the vibration of carbonyl group located at 1820-1660 cm$^{-1}$, C=C aromatic vibration at 1600-1475 cm-1 and CN at 1350000 cm$^{-1}$, CH vibration of the aromatic hydrocarbon group at about 3000 cm$^{-1}$, CH vibration of the methyl group located at 3100-2500 cm$^{-1}$ and OH vibration is located at 3600-3200 cm$^{-1}$.

### *2.5. Application of the synthesized material*

A research entitled “Synthesis of AC-NM-PZ composite as adsorbent for Cd2+Optimum conditions” [31], Adsorption of Cd (II) RSM was applied to develop an appropriate regression model to determine optimal values of pH, adsorbent dosage, and adsorption time in order to enhance the adsorption efficiency. The adsorption efficiency of AC, AC-NM, and AC-NM-PZ in optimum condition is shown in a contour plot shown The results are suitable with the data analysis using CCD where the optimum condition obtained were pH 6, adsorbent dosage 0.5 g, and adsorption time 25 minutes. Determined the optimum pH, adsorbent dosage, and adsorption time for the conventional method on Cd(II) adsorption using AC [33]. Values of the AC-NM were determined to be the following: pH 4, adsorbent dosage 0.5 g, adsorption time 5 minutes. AC-NM-PZ’s were the following: pH 8, adsorbent dosage 0.5 g, adsorption time 25 minutes.

The optimum condition was then used to determine the adsorption capacity and isotherm adsorption of the third adsorbent to Cd(II) metal ions.

In the study titled “activated carbon from rice hulls for the adsorption of two metals (Copper II and Cadmium II ions) from chemical waste solution” [22], using the constants of Freundlich and Langmuir isotherm, the temperature was calculated for 298 K and 313 K. The adsorption of Cu (II) and Cd (II) ions from aqueous solutions was found to be exothermic.

## 3. Results and Discussion

### *3.1 Activation of carbon and its characteristics*

The chemical activation of carbon materials is traditionally done through the use of alkali metal oxide or hydroxide as activation agent. This activation agents could interact directly with carbonaceous feedstock to form pore structure due to its capability to make chemical activation into one step process. In such method, we can effectively control the depth of activation by changing the activation agent’s adequate basicity. In their study they have used and compared different activation method such as coupling method and steam and KOH activation method.

Activation time of carbon is deemed to have great influence on the porosity and surface area of the material. As the result was shown on the study of

Xiao-dong Dai, et al with the title**:** *A novel method to synthesize super-activated carbon for natural gas adsorptive storage*,the change in the surface area initially increase as the activation time increases and they attained their peak at 2h but it then decreased afterwards [18].

Not only that, the activation time can also be attributed to the activation depth of the material. Meaning, acceleration of the increase in the activation time and the chemical activation initiation causes an even larger surface area of the material. But too long reaction time yields negative effect because the pore wall was continuously activated and resulted in partial collapse of the pore wall so that the surface area decreased conversely [18]. In their study, it was found that the chemical activation's optimum reaction time is 2h.

In their result they have found out that using coupling activation, 20% of the superactivated carbon's surface area increased which means that the coupling approach was able to increase the carbon activation. The reason for this might be that the steam interaction with the carbon precursor could remove the unorganized carbon in the material.

The basicity and/or the oxidative property of KOH in their study might have been accelerated by the steam at high temperature which means to say that the co-activation can be caused by the KOH and the steam leading to strengthening of the activation process.

On another related study, they have used sawdust derived hydrochar chemically activated by a mixture of potassium (K2C2O4) and melamine (C3H6N6) [20]. The Scanning Electron Microscopy (SEM) characterization in their work revealed that regardless of the preparation conditions, the activated particles retain the morphology typical in their sawdust-derived hydrochar sample, one example of that is the mixture of fibers and microspherules on their surface.

It is found that the morphology is completely transformed during the activation step of the original particles. The result obtained for the potassium hydroxide-activated samples were found to contrast this. After the activation, the original morphology retention promotes a potential advantage over the use of KOH especially when the morphology is an advantageous one such as that of spherical shape or nanosheet-like.

Giving closer attention to the output of their high-resolution transmission electron microscopy (HRTEM) particle analysis, it is evident that a porosity consisted of randomly distributed pores, which is usually of the activated carbons [25].

Their X-Ray Diffraction (XRD) and Raman spectroscopy showed the structure of the amorphous-like activated materials. XRD characterization patterns shows broad and low intensity (002) and (10) diffraction line patterns, in which the complete disappearance of the stacking of graphene is evident with the material that has the largest porosity proportion. On the other hand, the Raman spectroscopy graph on shows overlapping, broad and similar intensity D (~1346 $cm^{-1}$) and G (~1590 $cm^{-1}$) bands in the first order Raman spectra.

The value obtained in their analysis has the value of 1.44 and 1.45 for HCOxK-2.7-2 and HCOxK-3.6-2 respectively for the degree of disorder in their carbon material using the ratio of integrated intensities $I_D/I_G$. The results obtained for those that are activated with KOH or melamine and KOH mixture and other kinds of AC were all found to be similar with the data obtained with other hydrochar materials [20].

In the study conducted by Sevilla et al., the disorder in the carbon molecules in their sample could be lessened and their activation enhanced if they have integrated steam in their method. As stated in the study of Xiao-dong Dai, et al, it could make a stronger activation on the porous material.

Table 1 shows the comparison between the works cited on the synthesis of super activated carbon and conventional activated carbon. The table shows the processes undertaken in the synthesis of such. This differentiates the methods and materials used and whether they were able to enhance the adsorptive property of the final product or not.

Superactivated carbon, a better counterpart of activated carbon with nanoscale particles has an approximate Iodine adsorption value of 6, 198 mg Iodine per gram of carbon [40]. SAC shows adsorption of large portion of iron and large adsorption percentage of copper, zinc and manganese was observed from the SAC impregnated with nanosilver [50]. SAC alone adsorbs less metal ions than the SAC with nanosilver [41].

### *3.2 Nanomagnetite adsorption*

Nanomagnetite is hydrophobic in nature, leading to the coverage of magnetite surface with polymer to be in an aqueous solution due to the hydrophobic interactions present. It was noted that polymer-coated nanoparticles have lower dispersity than naked magnetite particles. It was reported that the polymer-coating increased the monodispersity of the nanomagnetite particles.

Using Electron Spin Resonance (ESR), the unpaired electrons in the structure of a molecule or molecule parts show magnetic property and can be determined. Therefore, the use of ESR analysis can determine the presence of magnetite in the nanoparticle structure. In their analysis it was found that the polymer alone doesn’t exhibit any magnetic property without the presence of any magnetic structure.

Higher signal intensity was observed in the nanomagnetite particle against applied magnetic field than the sample coated with polymer particles since the magnetic units in the sample can be penetrated by polymer and cause a decrease in interaction force when run under the ESR [25].

According to, “Magnetic field applied to the materials with unpaired electrons exhibits ΔE energy difference between energy levels depending on the magnetic moments. It is defined as $\Delta E = g^* \beta^* H$ where g is electron spin g-factor (Lande’ g-factor), the constant β which is called Bohr magneton and H is applied magnetic field. When this energy difference is equal to microwave energy, it is called as resonance magnetic field (Hr). Resonance field in the ESR spectrum is defined as magnetic field value when signal intensity is zero, in other words maximum microwave energy absorbed. Spectroscopic splitting factor, g, is given as material's specific property [25]."

Table 2 shows comparison of the reagents and procedures used in different studies. It also shows whether the materials is efficient in its application or not.

This finding won't have much contribution to the study that will be conducted since the use of polymer will not be incorporated in the experimentation. Although, the computation for the ΔE energy difference can be used given that we will be able to use ESR for comparison of the difference in energy levels of magnetic moment of different composition of our nanomagnetite composite.

### *3.3 Nanomagnetite composites for adsorption of heavy metals (Cd, Cr, Pb and Fe)*

In the study of Pratiwi et al, they synthesized activated carbon nanomagnetite composite that is impregnated by pyrazolone to modify the adsorption of the material when it comes to Cd(II) adsorption. Although this doesn't seem to be so successful as their results have shown that the activated carbon-nanomagnetite-pyrazolone composite material was shown to have lower adsorptivity than the activated carbon-nanomagnetite composite alone. But, it was observed that the AC-NM-P composite have had higher adsorptivity than the activated carbon material only.

Activated carbon with immobilized nanomagnetite can increase the surface area of the activated carbon and can also cause an increase in its adsorption capacity.

Some specific ligands can modify the surface of nanomagnetite to improve the adsorption efficiency of heavy metals. One example of this is the EDTA immobilized NM and this was applied to Cu, Cd, Co and Pb metal ions successfully. But, the specificity of its adsorption is still not completely incorporated because the extraction percentage of these metals did not differ significantly [30].

From these results, we can theorize that further addition of material on an activated carbon-nanomagnetite composite may weaken its adsorptive capacity. This may be due to the material added to it is taking the place of the material that will supposedly be adsorbed by the AC-NM composite. Nanoparticle poly-dispersion and size control is critical because nanocrystal properties strongly depend on the dimension of nanoparticles [37]. Magnetite particles having the size of around 30nm have characteristics that exhibit super paramagnetic properties and large surface area that becomes permanently magnetized with an external field support but doesn't do so otherwise. Also, because of this feature, the particles were made prone to magnetic fields [38].

In the study of Predescu et al, the size and morphology of the obtained nanoparticle samples were observed under the microstructural analysis of SEM, TEM and XRD. The reactivity of nanomagnetites decrease as the size of the particle decreases [37]. In their controlled analysis process, they were able to obtain particles more compact than 30nm (around 2nm scale) that led them to the conclusion that it has increased removal efficiency [37].

The ion adsorption increases as the adsorbent dosage increases. Lasheen et al, compared the heavy metal adsorption property of nanomagnetite and magnetite-kaolinite nanocomposite. It was then found that the heavy metal ion removal has increased as the composite and nanomagnetite doses increase [39]. The equilibrium was achieved when the doses was up to 2g/L.

As for the effect contact time it was shown that the adsorption of the heavy metals under study gradually increases as the contact time increases. It then eventually reached equilibrium at 60 minutes using nanomagnetite and 120 minutes using Mag-KL nanocomposite. They have tested their synthesized material on the $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, and $Ni^{2+}$ metal ions. After the experimentation, it was found that the removal percentage was: 90% for $Cu^{2+}$, 88% for $Pb^{2+}$, 85% for $Cd^{2+}$ and 83.2% for $Ni^{2+}$ using Mag-KL nanocomposite. On the other hand, there has been 95.8% for $Cu^{2+}$, 94% for $Pb^{2+}$, 92.8% for $Cd^{2+}$ and 92% for $Ni^{2+}$ metal ion removal using nanomagnetite alone [39].

Using a mass balance, the equilibrium adsorption capacity of the metal can be calculated according to the following equation:

$$q_e = (C_o - C_e)\, V/m \quad [39]$$

Where $C_o$ is the initial metal ion concentration in mg/L, $C_e$ is the equilibrium concentration of metal ion in the solution in mg/L, $V$ is the volume of the sample (L), and $m$ is the mass of the adsorbents in (g).

The percent removal of metal ions on an adsorption process can be determined by the equation:

$$\%Removal = \frac{qtotal}{Mtotal} x\ 100$$

### 3.4 Desorption of metals from activated and superactivated carbon

The increase in temperature also increases the desorption in all cases. This indicates that high temperature favors desorption [44]. The desorption enhancement with temperature is due to the breakage of bonds between the activated carbon surface and sorbate ions or the possible increase in pore intraparticle diffusion rate into the pore at higher temperature of the sorbate ions as an endothermic process [43].

For Mag-KL nanocomposite and nanomagnetite, $HNO_3$ solution was used for metal desorption. On its process, the metal loaded with adsorbent mixture was combined with 10mL of 5M of $HNO_3$. In Mag-KL nanocomposite, it was found that the desorption efficiencies in different metals is found to be 90% while the nanomagnetite has 96% desorption efficiencies [39]. Cycles of desorption and adsorption were done on both the materials. After each cycle, the adsorbents were thoroughly washed with distilled water to neutrality. They were then dried and reconditioned for the next adsorption-desorption cycle. Recycled sorbent efficiencies for metal removal are just the same with the newly-made ones even after recycling them five times [39].

### *3.5 pH effect on adsorption of SAC*

One of the most important parameters in metal sorption control is the pH of the material [43]. The pH solution control can be done using the addition of sulfuric acid (to increase acidity) and sodium hydroxide (to make the solution basic). Change in the pH of the solution causes an increase in the carbon surface's negative charge and in the formation of different ionic species. Pure SAC shows great adsorptive capacity on $Fe^{2+}$ metal ion adsorption [41]. Different SAC and nanosilver ratios was used on the study of Bernaldo et al, from there they have hypothesized that the varying pH on each combination of the adsorbent solution could be the reason for high $Fe^{2+}$ sorption. SAC was found to be more basic than the SAC-NS due to their use of reducing agent (tri-sodium citrate) for the impregnation

***Table 1** Comparison of synthesis components of activated and superactivated carbon of the cited studies*

| Title | Materials | Procedure | Activating agent | Enhanced adsorption | References |
|---|---|---|---|---|---|
| A novel method to synthesize super-activated carbon for natural gas adsorptive storage | Petroleum coke | They used chemical activation using alkali hydroxides as activation agent | KOH with steam as co-activator | Yes | [18] |
| Beyond KOH activation for the synthesis of activated carbons from hydrochar | Hydrochar | Chemically activation using $KC_2O_4.H_2O$ and melamine | KOH | Yes | [20] |
| Synthesis of activated carbon-nanomagnetitepyrazolone(1-phenyl-3-methyl-5-pyrazolone) composite as adsorbent for Cd2+ | Activated carbon with nano magnetite (FeCl3.6H2O) | Hydrothermal method | None | Yes (bioadsorption) | [30] |
| Synthesis of carbon nanoparticles using one step green approach and their application as mercuric ion sensor | Coconut milk | Thermal pyrolysis method | None | Yes | [19] |

of nanosilver. The optimum adsorption pH for $Fe^{2+}$ is at pH 2 [42]. Since SAC-NS has higher pH than SAC, it was able to adsorb less $Fe^{2+}$ ions than SAC particles alone.

Metal ion adsorption from aquatic environment using activated carbon is governed by nonelectrostatic and electrostatic interactions. Electrostatic interaction generated on carbon come mainly from the surface charges after it was immersed into water and the ions on the solution. Different nature of nonelectrostatic interaction can be observed, but predominantly it is of the van der Waals type.

The adsorption efficiency of heavy metals is mostly dependent of pH value. In a study about cadmium (II) and lead (II) [48], was found that the

***Table 2*** *Comparison of synthesis components of magnetite of the cited studies*

| Title | Materials | Procedure | Activating agent | Enhanced adsorption | References |
|---|---|---|---|---|---|
| Synthesis of magnetite nanoparticles in the presence of amino acids | ($FeSO_4$ $7H_2O$) and ($Fe(NO_3)_3$ . $9H_2O$ | The magnetite is obtained by the decomposition of polynuclear aminoacids complex compounds of Fe3+ and Fe2+, at pH 11. | KOH with steam as co-activator | Yes | [23] |
| Statistical optimization of effective parameters on saturation magnetization of nano magnetite particles | $FeCl_3$ . $6H_2O$ and FeCl . $4H_2O$ | Co-precipitation method | KOH | Yes | [28] |
| Performance of nano magnetite for removal of selenium from aqueous solutions | iron (III) sulfate [$Fe_2(SO_4)_3$] and Iron (II) sulfate ($FeSO_4$ .$7H_2O$) | Co-precipitation method | None | Yes | [24] |
| Synthesis and characterization of nanomagnetite particles and their polymer coated forms | $FeCl_3$ . $6H_2O$ 99% and $FeCl_2$ . $4H_2O$ 99% | Co-precipitation method | None | Yes | [25] |

optimum adsorption for those metals is at the pH of 10 [47]. The maximum adsorption of chromium was found to be at pH 6 [48].

### *3.6 Kinetic and isotherm analysis for metal adsorption*

To determine the adsorption process order (first order, second order, pseudo-first order and pseudo-second order), linearized kinetic models will be plotted after the identification of the adsorbed metal ion concentration [48]. One of the initial models of isotherm is the Langmuir Isotherm for the adsorption of species into a simple surface. This model was brought forth by Irving Langmuir in 1916 [45]. Languir model assumes that there is a monolayer uptake of metal ions and that the sorption energies to be equivalent in each site of sorption [46]. Adsorbate interaction with the bioadsorbent adsorption process can be described by adsorption isotherm.

The percentage removal of an adsorbent can be identified with the use $_2$of kinetic modelling experiments and the mechanism of the metal ions adsorbed on the sorbent [49].

## 4. Conclusion

Activation time, activating agents, and activation method have great contribution to the efficiency and adsorptive capacity of the synthesized activated or superactivated carbon material. Although limits on these must be set to achieve the optimum activation the carbonaceous material. Otherwise, some consequences such as degradation of the material might occur. Several activation methods in particular, the coupling activation and the usage of steam along with KOH activation was proven to increase the surface area of the synthesized AC/SAC, increase the activation process and remove the unorganized carbon in the material. The integration of an immobilized nanomagnetite particles on an activated or superactivated carbon can increase the surface area and adsorption capacity of AC and SAC. The adsorption capacity of a nanomagnetite particles can be determined by its efficiency in adsorption and removal of various materials from an aqueous solution.

Various modifications can be done on activated and superactivated carbon, nanomagnetite, and their composites to enhance and increase their function. Most supported activated AC and SAC have yielded a better adsorptive capacity. Although, as more material is incorporated to the composite of the activated carbon and nanomagnetite, seem to weaken the adsorptive capacity of it. The adsorbed metal ions on a nanomagnetite and various magnetite nanocomposite can be desorbed using $HNO_3$ solution and the materials can then be used again in the same process. The constant efficiency of the materials on metal removal even after series of recycling have proven that they are economic and convenient to use. Certain factors such as pH and temperature could still alter and enhance on the process.

The use of nanocomposite of SAC/AC and another sorbent is very cost-efficient due to the possibility that the adsorbed ions will be desorbed and the material to be recycled. Since no significant change in adsorption efficiency was found to be the effect of desorption process done multiple times on the same synthesized nanocomposite sorbent so far, we can say that the competency of the use of nanocomposite in the industry will be very promising.There is still a great deal of possible modification about magnetite, activated carbon and their possible composites. The researchers suggest, that those who take interest on the study to try to mix and match other potential material with these sorbents and try to unfold endless application of these in the modern world.

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