Synthesis and Characterization of Magnetite Nanoparticles, Activated Carbon and their Composites

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ABSTRACT

Magnetite nanoparticle (MNP), Fe_3O_4 was prepared via co-precipitation method, activated carbon was produced from coconut coir pith through chemical activation process. As coconut coir showed maximum weight loss at temperatures lower than 500°C, it was carbonized at 400°C in a muffle furnace in the absence of air after which it was cooled and impregnated with H_3PO_4. The synthesized Fe_3O_4 was composited with powder activated carbon synthesized from coconut coir pith in two forms. The adsorbents synthesized were characterized by physico-chemical and spectroscopic methods. The physico-chemical parameter employed include, Brunauer Emmett and Teller (BET) surface area, percentage yield, bulk density, pH, pzc, surface area, iodine value, moisture contents, volatile components, while the spectroscopic methods include Scanning electron microscopy (SEM) coupled with Energy Dispersive X-ray (EDX), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR).
The surface areas of MAG, ACT, MAG-AC (1:3) and MAG-AC (1:5) composites were found to be 276.956, 833.641, 444.095 and 454.569 m2/g, respectively which falls within the range of their specific surface area with the pore volume and pore sizes of (10.97, 32.86, 17.27 and 15.73 cc/g) and 3.015, 3.148, 3.091 and 3.335 nm respectively. The synthesized adsorbents can be used for a variety of environmental application including treatment of drinking water, removing colour from industrial effluents and removal of heavy metals due to their high surface area and porosity.

Keywords: Magnetite, Activated carbon, Nanocomposite, SEM, TEM, XRD, BET, FTIR.

1 INTRODUCTION

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case [1]. Nanoparticles often have unexpected visible properties because they are small enough to confine their electrons and produce quantum effects. This provides a tremendous driving force for diffusion, especially at elevated temperatures.

Activated carbon (AC), a general adsorbent for removal of wide range of pollutants from water, has some important advantages such as special structure and high adsorption capacity which have highlighted the AC application in many treatment plants [2].
This activated carbon can be commercial or synthetic depending on the choice of study. In this study synthetic one was chosen which was synthesized from agricultural waste, a rich source for activated carbon production due to its low ash content, abundant availability, and reasonable hardness [3], therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems such as disposal of waste and also to reduce the preparation costs [4]. The use of activated carbon prepared from agricultural waste product and iron oxide as adsorbents has been recently focused due to their availability in large quantity and environmental friendly.
Magnetite-activated carbon nano-composite is one of the most promising and effective adsorbents for the remediating of pollutants from the environment. Recently, a great deal of attention has been focused on the synthesis and application due to their small particle size, large surface area, high efficiency, ease of preparation and supra-magnetic in nature which makes it to be easily separable. Some of the major attractive features are related to large and controllable surface area, low-cost of production, non-toxicity to some extent, and ability to work in classical process with mechanical mixing of the contaminated aqueous media. The high surface area to some extent compensates the increase in the mass transfer resistance due to the stagnant liquid layer attached to the solid surface. This nano-composites offer a great applicability in many industries for treatments of contaminant and pollutants.
Nano materials (nano-particles and nano-composites) characterization is therefore necessary to establish understanding and control of nano-particle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy

(TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), x-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionizationtime-of-flight mass spectrometry (MALDI-TOF), ultraviolet-visible spectroscopy etcetera [5].

2 MATERIALS AND METHODS

2.1 Synthesis of Adsorbents

All reagents used in this work were of analytical grade and were used without any further purification.

2.1.1 Preparation of activated carbon

Activated carbon was prepared from coconut coir pith, 100 g of the coconut coir pith was reduced into smaller sizes and carbonized at a temperature of 400^{o}C for 1 hour in a stainless steel reactor placed in a furnace in the absence of air. The char produced was then activated with an aqueous solution of 1M concentrated phosphoric acid with an impregnation ratio of 1:5 (activation chemical). The mixture was mixed in a mechanical mixer for 1 hour to ensure the mixture was properly mixed. After that, the mixture was dehydrated in an oven at a temperature of about 105^{o}C for 24 hours, cooled to room temperature and washed with hot distilled water to remove any undiluted residue of ortho-phosphoric acid and then re-dried, ground and sieved to get the desired particle size and stored in plastic containers for further use.

2.1.2 Synthesis of Fe_3O_4 Nano-particles

Magnetite nano-particle was synthesized according to method of Jean-Pierre et al, 2014 [6]. A 200 ml of deionized water measured into a round bottom flask, was deoxygenated by bubbling N_2 gas for 30 minutes, 50 ml of ammonium hydroxide (NH_4OH) (IM) was the added and the mixture was stirred for 10 minutes at 1000 rpm using mechanical agitation. After which 10ml of 0.1 M ferrous chloride ($FeCl_2.4H_2O$) and 20 ml of 0.1M ferric chloride ($FeCl_3.6H_2O$) was added in ratio 1:2 respectively; the reaction mixture generated a black precipitate immediately which was stirred and aged for 24h before filtration. The product obtained was washed severally with de-oxygenated- de-ionized water for it to be in pure form and then dried at 45^{o}C for 4 hours.

Chemical equation of reaction

The main aim of this research work is to prepare and characterize activated carbon produced from coconut coir pith, magnetite and their composites as adsorbents in order to understand their mechanisms and properties.

$$FeCl_2 + 2FeCl_3 + 8NH_4OH \longrightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O$$

2.1.3 Synthesis of Fe_3O_4-AC composites

The Fe_3O_4-activated carbon magnetic nanoparticles (AC-Fe_3O_4 MNPs) were synthesized using modified procedure of Do et al. 2011[7] in the ratio 1:3 and 1:5. 40 g of activated carbon was impregnated into nitric acid (63%) for 3 hours at 80^{o}C in an ultrasonic bath. The sample was filtered, allowed to dry at room temperature and subsequently, 15 g and 25 g of obtained powder was weighed each into a 200 ml solution of Fe_3O_4 and placed in ultrasonic vibration for a 1 hour at 80^{o}C. The product formed was filtered, dehydrated in an oven at 105^{o}C for 1 hour and then heated in a furnace at 750^{o}C for 3 h for the formation of AC-Fe_3O_4 magnetic nanoparticles. Finally, the synthesized adsorbent was washed with deionized water severally, then dried at 105^{o}C and kept in desiccator for use.

2.2 Characterization of the Adsorbents

The adsorbents were characterized by physico-chemical methods; bulk density, pH, point of zero charge (PZC) for the three adsorbents while iodine number, volatile, ash and fixed carbon contents was included for that of activated carbon. Spectroscopic analysis such as Scanning electron microscopy (SEM) was observed to know the morphology of the exterior surface of synthesized adsorbents, Energy dispersive X-ray to know the elemental composition present in the synthesized adsorbents, Transform electron microscope to confirm the morphology and the shape of the magnetite (JEOL Model 1010 series), (Nanosizer to know sizes of the adsorbents, X-ray diffraction (GBC eMMA XRD model) was done using Cu-Kα radiation, λ = 1.54059A at 25°C to confirm the crystallinity nature of the magnetite and the composite. The specific surface area of the adsorbents was measured using BET surface area analyser (NOVA 4200) and the Fourier Transform Infrared (SHIMAZDU) spectroscopy was applied in order to determine the functional groups on the surface of the adsorbent over 500 – 4000 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Physico-chemical Properties

The percentage yield for the MAG, ACT MAG-AC (1:3) and MAG-AC (1:5) ranged from 36.5 to 98.5 % with the MAG-AC (1:5) having the highest yield percent and MAG having the lowest yield percent as it can be seen in Table 1.

The coconut coir pith could serve as a very good precursor for the production of activated carbon due to its very low value in ash content and moderate value of fixed carbon constituents. Moisture content, according to Azizian, 2004 [8] has a relationship with porosity (α) of a given carbon. Adsorbent with high moisture content is expected to swell less, thus retarding pore size expansion for adsorbate uptake.The moisture content of ACT was found to be 2.9 % while the volatile content was found to be of 38.5 %. This is responsible for the decomposition of the organic materials to release volatiles and development of microporous structures [9]. Report has shown that low volatile matter content implies the high porosity of the adsorbent since volatile matter remains clogging in the carbon pores [10]. Ash is a measure of inorganic impurities in the carbons [11]. The ash content of activated carbon was found to be 3.8 % which is in range of most ash content of agricultural waste reported [12].Fixed Carbon content is the residual amount of carbon present in the sample. The result obtained shows that carbon content is 54.8 %. This is in concordance with the findings of Azizian, 2004 in which most of the carbon composition of A.C falls within 50-90 % [8].

The bulk density of any sample plays a great role on adsorbate uptake. Generally, higher density carbons hold more adsorbate per unit volume [13]. From table 1, the bulk density of the MAG is the highest (4.29 g/ml) and that of activated carbon is the lowest (1.07 g/ml). The higher bulk density of the MAG can be due to its compactness in nature because of its crystal form especially when in nano sizes are prone to agglomeration which makes the particle to tightly fuse together and occupy every available space

Physicochemical Parameters	Magnetite (MAG)	Activated carbon (AC)	MAG-AC composite (1:3)	MAG-AC composite (1:5)
Appearance	Black	Black	Black	Black
% Yield	36.65	60	96.5	98.5
Bulk Density	4.89	0.298	2.35	1.07
Ph	8	6.8	6.5	6.3
PZC	7.8	6.2	ND	ND
Fixed carbon	ND	54.8	ND	ND
Volatile component	ND	38.5	ND	ND
Moisture content	ND	2.9	ND	ND
Ash content	ND	3.8	ND	ND
Iodine Value	ND	812.16mg/g	ND	ND
Surface area (m^2/g)	278.956	833.641	444.	454.569
Micro-pore volume (cc/g)	1.097×10^1	3.286×10^1	1.727×10^1	1.573×10^1
Pore size (nm)	3.015	3.148	3.091	3.335

Table 1: Physicochemical Properties of MAG, ACT, MAG-AC (1:3) AND MAG-AC (1:5) Adsorbents

The iodine number is a measure of activity level, the higher the number, the higher the degree of activation and the development of the microporous structure. It is often reported in mg/g. Iodine number may also be used as an approximation of surface area. Some types of carbons have been reported to be between 600 mg/g and 1100 mg/g The iodine number of AC adsorbent was found to be 812.16 mg/g.

The surface areas of MAG, ACT, MAG-AC (1:3) and MAG-AC (1:5) composites were found to be 276.956, 833.641, 444.095 and 454.569 m^2/g, respectively which falls within the range of their specific surface area with the pore volume and pore sizes of (10.97, 32.86, 17.27 and 15.73 cc/g) and 3.015, 3.148, 3.091 and 3.335 nm respectively. The surface area of the MAG, MAG-AC (1:3) and MAG-AC (1:5) are lesser to that of ACT. This fall could be attributed to the occupation of almost the

entire pores of AC with Magnetite nanoparticle resulting in less accessible pores [2].

3.2 Spectroscopic Properties of the Adsorbents

XRD analysis was performed to examine the crystal structure of the synthesized MAG and MAG-AC (1:3). The typical XRD pattern of the adsorbents is shown in Fig. 1a & 1b. From the spectra shown below for magnetite, peaks are found at positions of 6.07 º , 19.04 $^{\theta}$, 35.85 $^{\theta}$, 40.70 $^{\theta}$, 54.13 $^{\theta}$ and 63.49 $^{\theta}$ which are in good agreement with values found in literatures. The appearance of a broad peak at 2θ = 35.85º [3, 14, 26] and 15.65 and 26.70 could be interpreted as the evidence for the presence of Fe_3O_4 crystalline phase. The composite shows some distinct spectral which are found at peaks 15.65 º, 22.66 º 26.70 º and 39.87 º because of the slight shift in the peaks due to activated carbon. The main peak at 2θ = 15.65 and 26.70 º corresponds to carbon. It can also be seen from the diffractograms obtained for MAG that it has a higher degree of crystallinity than that of the composite.

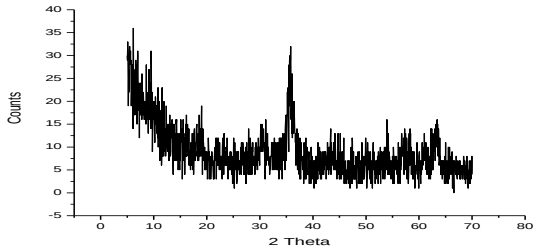

Figure 1a: X-ray Diffractogram of MAG

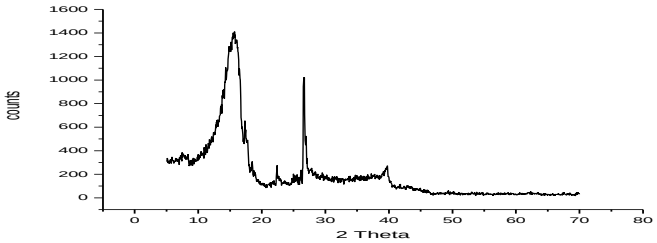

Figure 1b: X-ray Diffractogram of MAG-AC

The SEM micrograph of AC, MAG, MAG-AC (1:3) and MAG-AC (1:5) representing the surface morphology of the synthesized adsorbent is illustrated in Figure 3a. Large and well-developed pores which looks like honey comb were clearly found on the surface of the activated carbon.

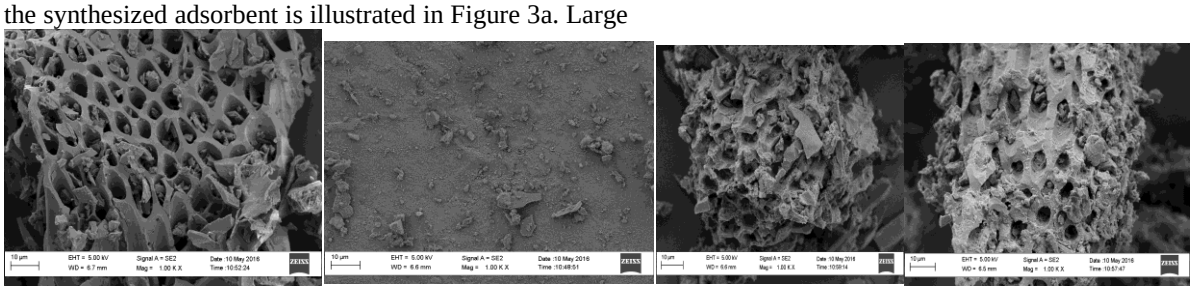

Figure 2: SEM micrograph of ACT, MAG, MAG-AC (1:3) and MAG-AC (1:5) respectively

The TEM micrographs of magnetite at different magnifications as shown in figure 3 below reveal a rod-like shaped particle with ranges of diameter, the particle is seen to have smooth surface which could enhance adsorption properties.

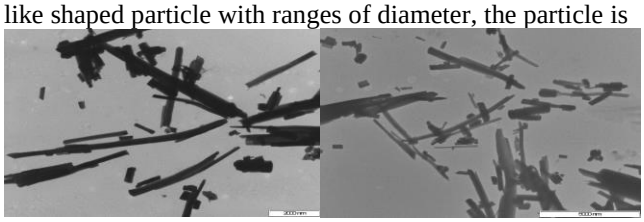

Figure 3: TEM micrograph of magnetite

Conclusion

Fe_3O_4 magnetic nanoparticles, activated carbon and the composites with excellent properties have been successfully prepared by chemical co-precipitation, chemical activation and in-situ methods respectively. The surface area of the MAG, MAG-AC (1:3) and MAG-AC (1:5) are lesser to that of ACT. This fall could be attributed to the occupation of almost the entire pores of AC with Magnetite nanoparticle resulting in less

accessible pores. Fe_3O_4 magnetic nanoparticles prepared under the standard conditions are non-porous in nature, relatively smooth with irregular shapes, large and well-developed pores which looks like honey comb were clearly found on the surface of the activated carbon while the porous nature of the synthesized composites is an implication of large surface area and high adsorption capacity. Formation of the magnetic-AC was also confirmed by the presence of several mono-disperse magnetite nanoparticles embedded in activated carbon pores with needle-like shapes. Due to the presence of high surface area, porosity, the synthesized adsorbents, can be used for a variety of environmental application including treatment of drinking water, removing colour from industrial effluents and removal of heavy metals.

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