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REMOVAL OF LEAD (Pb^{2+}) IONS FROM AQUEOUS SOLUTION BY ADSORPTION USING SUGARCANE BAGASSE ACTIVATED CARBON COATED WITH MAGNETIC NANOPARTICLES

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ABSTRACT

An experiment to remove lead (II) ions through adsorption from its aqueous solution using Sugarcane Bagasse Activated carbon (SBAC) was carried out. As one of the ways employ to reduce the high cost of treatment of industrial effluents. Agricultural wastes could be considered as suitable material for the production of Activated Carbon due it high carbon contents, environmentally friendly and low cost of production. In this work, activated carbon was produced by chemical activation with sulphuric acid (H_2SO_4) of sugarcane bagasse materials. It was then coated with magnetic nanoparticle (Fe_3O_4) prepared by chemical precipitation of Fe^{2+} and Fe^{3+} salt from aqueous solution and tested for its efficiency as an adsorbent for the removal of Lead(II) ion from aqueous solution .The surface morphology, structural and functional groups present were investigated using scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. Shift and disappearance of some adsorption bands in the sugarcane bagasse activated carbon coated with magnetic nanoparticles testify the formation of the composite. Optical properties were determined using UV Vis spectroscopy shows a wavelength ($\lambda_{\max}$)of 400nm. Adsorption parameters such as effect of pH, contact time, initial concentration of Lead ion and adsorbent dosage were studied. Neutral medium was the optimum pH condition needed for the removal of lead with the percentage removal efficiency of 91%. It was found to be highly efficient at 0.4g of the dosage and at contact time of 60 minutes. This sugarcane bagasse is useful in adsorbing heavy metal in an aqueous solution.

Keywords: Adsorption**,** Activated carbon, Magnetic nanoparticles, Lead (II)

INTRODUCTION

Heavy metals are natural elements characterized by rather their high atomic mass and high density as well. Although typically occurring in rather low concentration, they can be found all through the crust of our planet. Commonly, a density of at least 5 g cm^{-3} is used to define a heavy metal and to differentiate it from others, "light" metals *(*Saleh *et al*, 2018). Heavy metals are quite different from organic waste pollutants and persistently continue to remain as non-biodegradable species in the environment which undergo bioaccumulation and biomagnifications in organisms (Muhammad et al, 2018). Bioaccumulation itself is a process through which concentration of a chemical in biological organism increase over time above the chemical's level in the environment (Alexander, 2019). As trace elements, some heavy metals (e.g. Copper, Selenium, Chromium, and Zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can be poisonous (Mohsen A. Hashem, 2007).

Studies of humans as well as laboratory animals have reported the adverse effects of lead on the blood, kidneys, nervous, immune, and cardiovascular systems (Ab Latif Wani et al, 2015). Serious brain and nervous system damage resulted due to prolong exposure (Tan et al, 2014).EPA has considered lead to be a probable human carcinogen, and under more recent assessment guidelines, it would likely be classified to be carcinogenic to humans.

Activated carbons are extremely versatile adsorbents with major industrial significance. The world consumption of activated carbons is steadily increasing and new applications are always emerging, particularly those concerning environmental pollution remediation, which should help to sustain demand for them (Kaghazchi , 2007). Important applications are related to their use in water treatment for the removal of flavor, color, odor and other undesirable organic impurities from water. It is also used in industrial wastewater and gas treatment due to the necessity for environmental protection and also for material recovery purposes (Kaghazchi, 2007).

However, the cost of the commercial activated carbon has remained high, limiting its applicability. The use of low cost raw materials such as agricultural wastes for the production of activated carbon can go a long way towards reducing the cost of commercial one. Moreover, transforming agricultural wastes into valuable end products may lead to crops value addition as well as reducing problems of solid waste management.

Yearly, sugar manufacturing industries in Vietnam disposed of thousands of tons of sugarcane bagasse as a waste after extraction and processing of sugar (Tran Van Thuan et al 2016). Consequently, untreated sugarcane bagasse elimination is not only responsible for useless loss of a large amount of carbonaceous precursors, but also might cause several serious environmental issues. Accordingly, utilizing sugarcane bagasse for the purpose of low cost activated carbon preparation is one of potential approaches towards green production.

When choosing a precursor the following properties are of importance: specific surface area of the pores, pore volume and pore volume distribution, composition and size of granules, and chemical structure/character of the carbon surface (Pradhan and Subhashree, 2011). Choosing the correct precursor for the right application is very important because variation of precursor materials allows for controlling the carbons pore structure.

Applications of iron oxide nano materials as magnetic particles was extensively studied because of nano-scale size, high surface area, super-paramagnetism, ease of synthesis, and option for coating or modification (R. Wannahari et al, 2006) . Powders of small particle size necessarily possess high specific surface areas. Therefore, the specific surface area itself could also be considered a dimensional property. High surface areas are attractive in various applications.

MATERIALS AND METHODS

Reagents

Analytical grade reagents were used throughout. They include $Pb(NO_3)_2$ as a source of Pb^{2+},ferric chloride, ferrous chloride, ammonia solution, hydrochloric acid, sodium chloride and dimethyl glyoxime.

Sample Collection

The samples of Sugarcane Bagasse were collected from Dutsin-ma market, Katsina State and other selling units within its environs.

Preparation of 1000ppm Lead (II) Nitrate Stock solution

A stock solution of 1000ppm of lead nitrate was prepared by dissolving the 1.5992g of the lead nitrate in 1000mlof distilled water in a standard flask (Dada et al, 2013). Other experimental solutions of desired concentrations were obtained by dilution of stock solution using distilled water according dilution principle.

Preparation of Sugarcane Bagasse Activated Carbon (SBAC)

The sugarcane bagasse obtained were double washed with distilled water and dried in hot air oven at 120°C for 3 hours and then grounded with mortar and pestle into fine particles for easy activation. The activation was carried out in a beaker by soaking thoroughly 100g of the dried sludge in 450ml of concentrated sulphuric aci0d and heated to 200°C with continuous agitation for 1 hour. After agitation, the mixture started to solidify producing a carbon like material and it was then stopped. The resulting carbon was then allowed to cool to room temperature, washed with distilled water before soaking it into dilute NaOH solution for 30 minutes and again washed with distilled water (S.S. Imam and M. Abdullahi,2017) .The product was allowed to dry, sieved through 100µm sieve and stored in a closed container.

Preparation of Sugarcane Bagasse Activated Carbon Coated Fe_3O_4 (AC- Fe_3O_4)

Chemical precipitation technique was employed here (Ahmad A. A. et al , 2006). 2.1g of $FeSO_4.7H_2O$ and 3.1g of $FeCl_3.6H_2O$ were accurately weighed and dissolved in a 250ml beaker under inert atmosphere in 80ml of double distilled water with vigorous stirring using a mechanical stirrer. While the solution was heated to 80°C, 10ml of NH_4OH solution (25%) was added. For complete growth 10g of the prepared sugarcane bagasse activated carbon was added and reaction continued for 30 minutes (P. Panneersalvam et al, 2010) .The resulting suspension was cooled down to room temperature and then repeatedly washed with distilled water to remove unreacted chemicals. The product was dried in an oven at 50°C for 2h, tested using a magnetic rod and then stored in a closed container ready for use.

The reactions that occur in the production are shown in chemical equations (1) and (2).

$$FeSO_4.7H_2O + 2FeCl_3.6H_2O + 8NH_4OH \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 6\ 17H_2O \qquad (1)$$

$$Fe_3O_4 + AC + 17H_2O \rightarrow AC\text{–}Fe_3O_4 \qquad (2)$$

Adsorption Test of Pb^{2+}

For all the experiments batch adsorption technique was used at room temperature on a mechanical shaker at 150rpm using 250ml capped erlenmeyer flasks. The influence of pH was studied by varying it over a range of 3 -1 1. While 0.1M NaOH and 0.1M HCl were used for pH adjustment, using a pH meter (Systronics made). Adsorbent dosage at 0.1, 0.2, 0.3, 0.4 and 0.5g, initial Pb^{2+} ions concentration (150, 200, 250, 300 and 3500ppm) and contact time 0, 15, 30, 45, 60, 75,90, 105, 120 and 135min on the performance of AC–NP (Fe_3O_4) were evaluated in order to optimized them. After the adsorption process, the contents were filtered using a whatman filter paper no. 42, four drops of Dimethyl glyoxime were added to the supernatant solution which was analyzed using a UV-visible spectrophotometer (T-60 PG instrument) by recording the absorbance changes at wavelength of 445nm (Aguadoj et al, 2009). The amount of lead (II), Pb^{2+} adsorbed per unit weight of SBAC- Fe_3O_4 adsorbent at time t‟, qt(mg/L) and percentage Lead Pb^{2+} adsorption capacity was calculated using equations (3) and (4) :

$$Amount\ of\ Lead\ Pb^{2+}\ adsorbed\ (q_t) = \frac{V(C_o - C_t)}{M} \qquad (3)$$

$$Percentage\ removal\ of\ Lead, Pb^{2+} = \frac{(C_0 - C_t)}{C_t}\ x\ 100 \qquad (4)$$

Where C_o, *is the initial Lead* Pb^{2+} *concentration (mg/L), Ct is the concentration of Lead* Pb^{2+} *at any time t, V is the volume of solution (ml) and M is the mass of AC-*Fe_3O_4 *(gm).*

RESULTS AND DISCUSSION

Characterization of Adsorbent

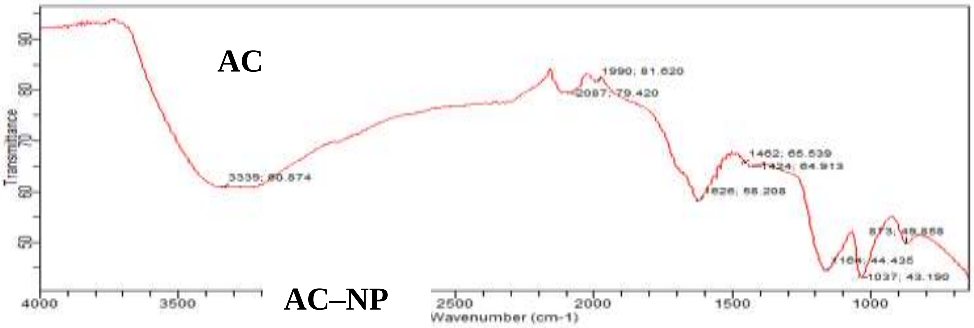


Figure 1:FTIR spectra of AC (Activated Carbon Only)

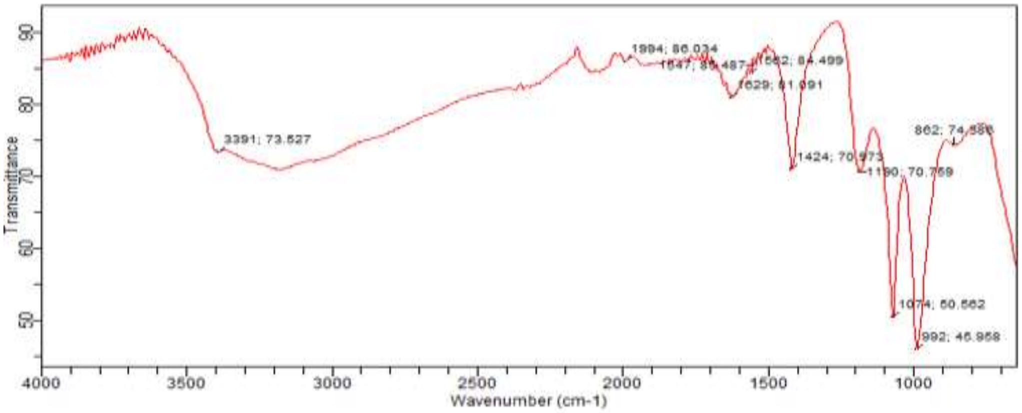


Figure 2*:* FTIR spectra of NP (Nanoparticle only)

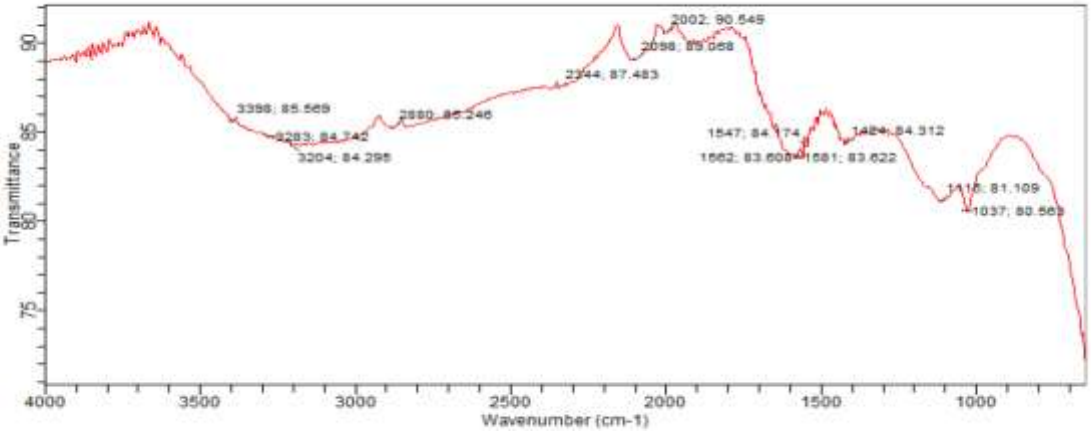


Figure 3:FTIR spectra of AC–NP(Activated Carbon coated with Nanoparticle)

The FTIR spectra of AC, NP and AC–NP were recorded in the range of 650cm^{-1} to 4000cm^{-1} using KBr disc for reference. Figure 1 shows the IR spectrum of AC. The band at 3339cm^{-1} is due to asymmetric stretching of bonded -OH groups. The band at 2087 is a combination of hindered rotation and O–H bending (water), the band observed at 1462cm^{-1} could be assigned to the paraffin group, the band at 1424cm^{-1} is a sigma (CH_2) of polysaccharide and cellulose and the band at 1626cm^{-1} is an Amide Region. The band at 1164$cm^{-1}$is mainly from the C – O stretching mode of C – OH groups (H. Kaur,2013).The band 1037$cm^{-1}$is a skeletal cis conformation of v(CH_2OH) and also represents the C=O stretching couple with C – O bending while the band at 873cm^{-1} is a form of helix conformation.

When comparing the spectra in AC and NP, additional peak is more in NP than AC various functional groups were detected on the surface as shown in figures above. An obvious observation also, was the shifting, disappearance or appearance of new peaks. Most importantly, the newer peak observed at 992cm^{-1} is related to C – O ribose, and C – C group, and the peak around 33391cm^{-1} was assigned to t(A. C. S. Talari et al, 2017). The stretching –OH asymmetric (the bend of second order) group on the surface of the magnetite Additional peak was show at the band of 1190cm^{-1} which contains a functional group of phospholipids.

In figure 3, (AC – NP) which has more spectrum than AC and NP this is because AC is coated with NP. The absorption peak around 3398cm^{-1} is indicative of the existence of a bonded of stretching hydroxyl group. The band at 3283 and 3204cm^{-1} are N – H stretching of amide and O – H stretching of carbohydrates, the band observed at 2880 to 2002cm^{-1} are assigned to stretching of C – H bond. New functional groups was observed at the band of 1581cm^{-1}which is ring C – C stretch of phenyl group and at the band of 1424cm^{-1} is the carboxylic acid of polysaccharides and pectin.

UV/VIS Spectrum

UV-Vis spectroscopy was used for the examination of optical properties of the synthesized nanoparticles. Iron oxide nanoparticles spectrum observed in figure 4 below shows the characteristic absorption peak of the sample is noted that is 400 nm. This is attributing as intrinsic band gap absorption of Fe_3O_4 from this peak it can be analyzed that there are uniform distributed nanoparticles and mostly particles are in nano size (Zak KA et al, 2010). The supporting point is that there is no other peak is observed in whole a spectrum that meansFe_3O_4 has successfully formed. (Abbas Q, 2019).

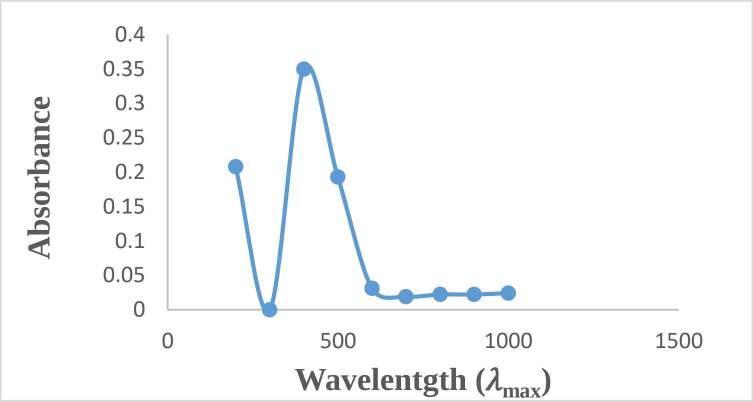
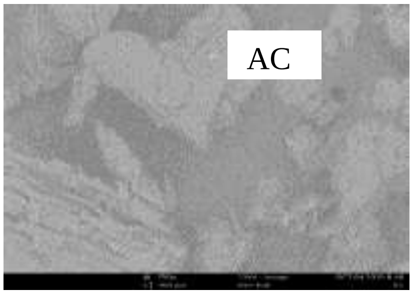


Figure 4: Wavelength of Maximum Absorbance **(**λ_{max}**)** of Nanoparticles

SEM Characterization

Surface morphology of NP (Nanoparticles), AC and AC-NP were visualized using Scanning Electron Microscopy (SEM). Measurements were taken using SEM-Quanta. The images were taken with an emission current of 100µÅ by the Tungsten filament at a magnification of 750x and an accelerator voltage of 15kV. Figure 5 (AC), 6 (NP) and 7 (AC–NP) shows the SEM micrographs of AC (sugarcane bagasse activated carbon), Fe_3O_4 (Nanoparticles), and AC–NP.

The AC exhibits homogeneous rough, dense and uneven surface morphology with a series of overlaps as shown in figure 7 (AC–NP) shows the parent AC covered with Fe_3O_4 (NP). The surface of the figure 5 shows the surface of AC alone (M.A. Tadda et al, 2016).



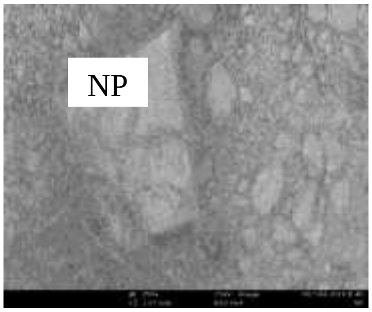


Figure 5: Sugarcane Bagasse Activated Carbon (AC) *Figure 6:Magnetic Nanoparticles (NP)*

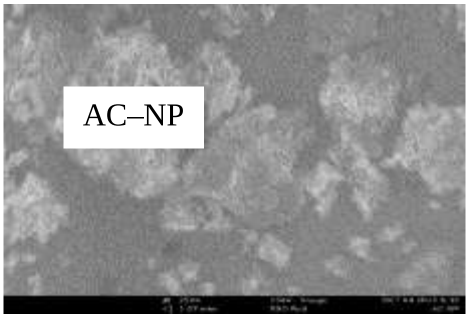


Figure 7: Sugarcane Bagasse Activated Carbon Coated with Nanoparticle (AC-NP)

Effect of pH

pH of the medium plays a vital role in the determination of adsorption capacity of any adsorbent. The pH was determined at room temperature using a portable pH meter (H19813 – 6 USA HANNA Instruments) and calibrated using 4.0 buffer tablet. It was experimented over a range of pH values of 3-11 which is adjusted using dilute solutions of nitric acid (HNO_3) and sodium hydroxide (NaOH). Optimum adsorption was noted at the pH value of 7, that is neutral which implies there less competition with hydrogen ions for the negative adsorption site at the adsorbent surface with Pb^{2+} ions.

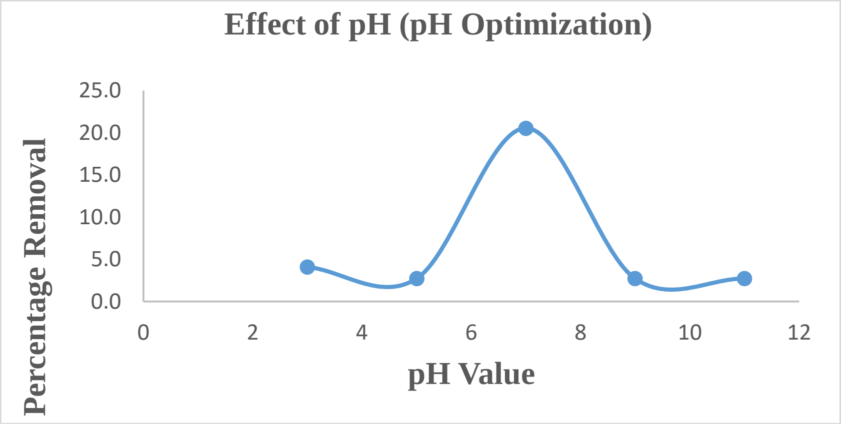


Figure 8: Effect of pH (pH Optimization)

Effect of Initial Adsorbent Dosage on Lead Pb^{2+}concentration Removal

Adsorbent dosage is a very important parameter in the determination of adsorption capacity. To determine its effect, experiments were conducted by varying the adsorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5g) in the sample solution of a fixed initial adsorbate concentration of 400ppm, at room temperature, 150 rpm shaking speed and pH 7.0. As the adsorbent dosage increases, the surface area of the adsorbent will be increased. Hence, more adsorption sites are available to absorb Lead Pb^{2+} from aqueous solution. Therefore, the equilibrium time will be shorter at higher adsorbent dosage.As seen in the figure below optimum amount was found at 0.4g.

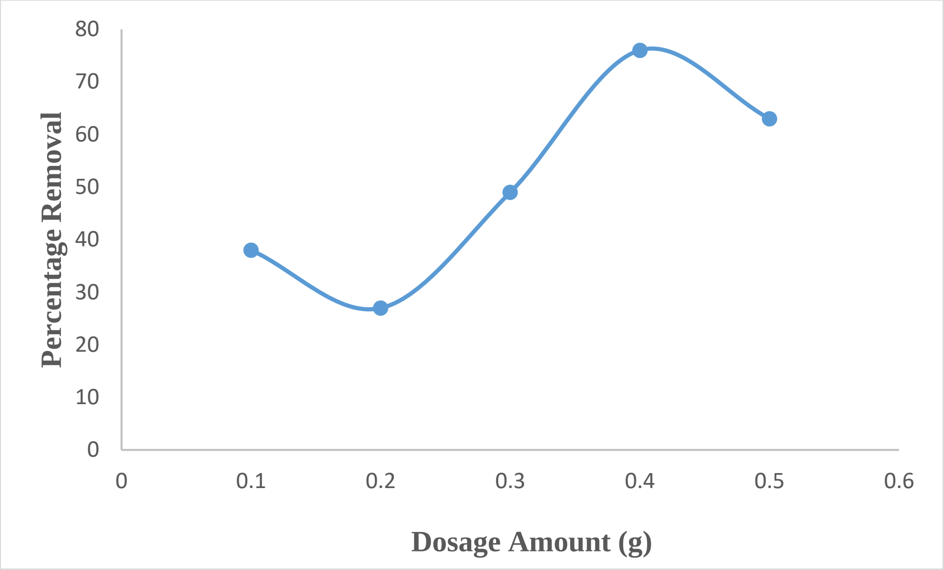


Figure 9: Dosage Optimization

The effect of Lead (II) initial concentration

The influence of the initial concentration of the adsorbate was carried out at a fixed adsorbent dosage of 0.4g, room temperature, pH 7.0, 150rpm and at different concentrations of Lead Pb^{2+} (150, 200, 250, 300, 350ppm) at constant time of 30 minutes. As shown in the figure 10 below, the percentage adsorption increases as the concentration increases and start reducing at beyond 250ppm. Because at low adsorbate/adsorbent ratio, there high availability of adsorption sites, which however, decreases as the ratio increases, thereby decreasing the efficiency (S.S.Imam and M.Abdullahi,2017)..

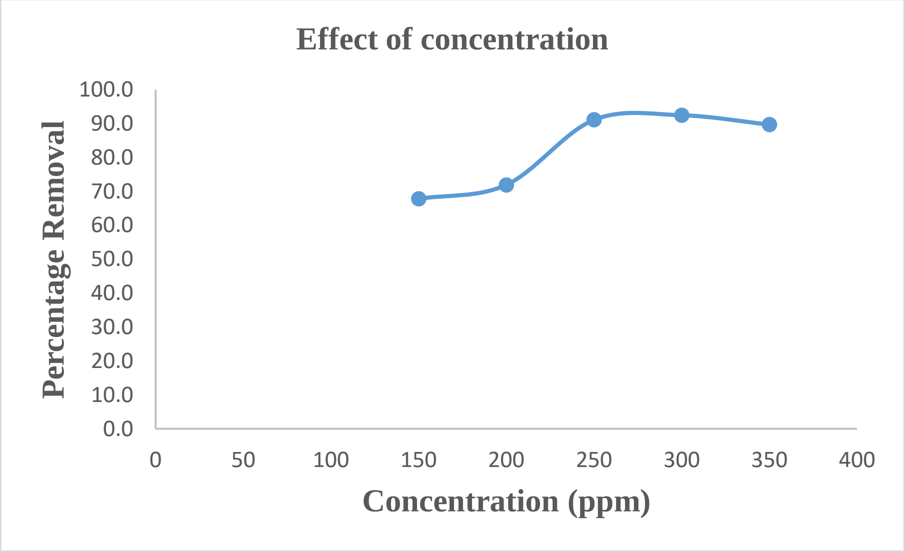


Figure 10: The effect of Lead Pb^{2+} initial concentration

Effect of Time

The optimum time for the adsorption of Lead Pb^{2+} onto SBAC-Fe_3O_4 was experimentally investigated over a period of 135minutes as seen in figure 11 below.250ppm and 0.4g were used as the concentration of lead (II) ions and adsorbent dosage respectively at neutral medium. At 60 minutes, 80% of the adsorbate was adsorbed and it appeared to be the highest. It can therefore be deduced that beyond one hour the attractive force became very weak.

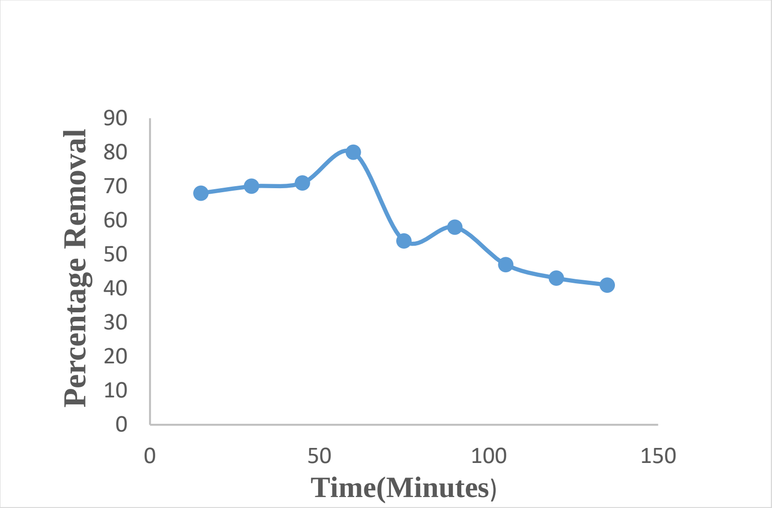


Figure 11: The effect of time Lead Pb^{2+}

CONCLUSION

This research show high yield of the activated carbon from Sugar Cane Bagasse and a good performance in adsorption of lead ions (Pb^{2+}) when it is coated with magnetic nanoparticles. The most important things to consider here is apart from using a waste to treat a waste; other parameters such adsorbent dosage, pH of the medium and contact time among others were all found to be very promising. SEM and UV/VIS spectrometry revealed the dimension of the adsorbent in nano-scale. It is also useful as an indicator of the potentials of the adsorbent being in adsorbing any heavy metal in aqueous solution and to reduce industrial cost for the treatment.

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