

Manganese oxide-modified biochar (MBC) for arsenic and lead adsorption from groundwater

W. Alalid^{a,d}, F.A. Alseroury^a, T. Almeelbi^b, M.A. Barakat^{b,c*}

^aDepartment of Physics, Faculty of Science, King Abdulaziz University, Jeddah, KSA, Saudi Arabia

^bDepartment of Environmental Sciences, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, 21589, KSA, Saudi Arabia

^bDepartment of Environmental Sciences, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, 21589, KSA, Saudi Arabia

^cCentral Metallurgical R&D Institute, Helwan 11421, Cairo, Egypt

^dDepartment of Physics, Faculty of Science, Aljouf University, KSA, Saudi Arabia

Abstract - This study investigates the preparation of modified biochar manganese oxide for adsorption and removal of both arsenic As(V) and lead Pb(II) ions from groundwater. Biochar is a potential adsorbent material of thermal decomposition of organic material under the limited supply of oxygen (O) at temperatures between 350 and 700°C. In this experiment, batch adsorption experiments were conducted as a function of pH, contact time, adsorbed dose and initial concentration. The biosorbent was characterized before and after the adsorption processes by electron microscopy and Fourier spectroscopy within two methods (XRD) which is a laboratory-based technique commonly used for identification of crystalline materials and analysis of unit cell dimensions, and (FTIR) to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral-resolution data over a wide spectral range. Results showed that the best sorption conditions are perceived at pH interval of 5–7 for both lead and arsenic ions. Equally, an important uptake decrease is caused by the rise or fall of pH. Biochar properties are affected by the low temperature generally has lower pH, higher water holding capacity, lower specific surface area, more carboxylic and phenolic hydroxyl functional groups and higher cation exchange capacity. The equilibrium times obtained for Lead and Arsenic were reached in a short period of contact time. For both Pb(II) and As(V) ions; adsorption capacity increased with the increase of solution concentration.

I. INTRODUCTION

One of the most serious environmental issues is groundwater pollution by heavy metals. However, removing these heavy metals using the conventional methods like chemical precipitation, ion exchange, membrane evaporative processes is expensive and ineffective. Physical adsorption appears as a potential alternative to the classic techniques.

Industrial effluents and pollutants resulting from the intensive use of fertilizers, pesticides, sanitation, agricultural and pharmaceutical products are the major causes of environmental pollution. These pollutants have the ability to concentrate along the food chain and accumulate in certain organs of the human body. It is therefore essential to eliminate these toxic elements present in the various industrial effluents or to reduce their quantity below the acceptable thresholds defined by the standards. Therefore, removal of toxic heavy metals from aqueous solution via different technologies has long been recognized as an efficient and crucial process^{1,2}. Numerous approaches have been proven to be the most effective technologies³. These include: ion exchange, filtration, coagulation and adsorption). Due to the growing need for economic large-scale water treatment applications, it is seriously important to develop a new, cheap, stable and reliable sorbent.

Lead Pb(II) and arsenic (As(V)) are ubiquitous contaminants in soil and aqueous solution environment. They have extensive effects on several systems in the human body; such as they threaten the nervous, endocrine, renal, musculoskeletal, immunological, as well as the cardiovascular systems^{4,5}.

studies explored biochar application and investigated the ability of biochar to tackle heavy metals ground water contamination considering its wide availability and reliability of feedstock, physicochemical surface characteristics and lower cost^{6,7,8}. In addition; Biochars having high surface area and pore volumes have a great affinity for metals. In other words, the metallic ions can be physically sorbed onto the surface of the char and retained within the pores⁹. Many biochars' surfaces are negatively charged and are more likely to sorb positively charged metals by electrostatic attractions, ligands surfaces have negatively charged and can sorb metals positively have charged through electrostatic attractions. Moreover, the surface functional groups of the biochar

can also interact with various heavy metals by forming solid mineral phases precipitates¹⁰. Wang et.al¹¹ showed that Biochar/manganosite (iMPB) and biochar/birnessite BPB) composites showed enhanced sorption for As(V) and Pb(II). Sorption capacities of MPB (0.59 and 4.91 g/kg) and BPB (0.91 and 47.05 g/kg) were significantly higher than that of the unmodified biochar (0.20 and 2.35 g/kg).

The aim of this work was to prepare a modified biochar and investigate it's efficiently for lead and Arsenic removal from groundwater.

II. MATERIALS AND METHODS

1.1. Materials

The following materials have been used in the study; Biochar, Manganese(II) chloride tetrahydrate(MnCl₂.4H₂O). All chemicals were analytical reagent grade. Deionized water was used for preparing of the aqueous solutions.

The Biochar was prepared at the lab as follow:

Biochar preparation

Dates tree waste was dried at 60 C for 24 h and then cut into a particle size of 2-4 cm. The dried particles were then burnt in a pilot-scale pyrolysis reactor in the absence of O₂ at 400 C for 4 h. The obtained biochar was ground and passed through 0.25 mm sieve (60 mesh).

MBC preparation

The biochar was dried in the oven at night at temperature of 80°C. Then squeezed and filtered to yield a uniform 0.425–1 mm size fraction. A solution of 3.15 g of KMnO₄ in 50 ml of deionized water was prepared, and added to 5g of biochar. The resulting mixture was stirred for 2 h. Thereafter, the suspension was boiled for 20 min, and then 3.3 mL of concentrated HCl was added. Next, stirring was continued for 10 min. The reaction mixture could cool slowly to room temperature and then filtered through 0.22 μm nylon membrane. Biochar were gently washed with deionized water three times, dried at 80 °C at night.

1.2. Adsorption experiment

Effect of pH experiment: This part of the experiment was performed to verify the effect of pH effect at Adsorbent dose = 0.25g ; contact time = 24hours. pH was tested for pb(II) ions and As(V) ions at pH range of 3-9 under constant agitation at 150 rpm and room temperature.

1.2.1. Effect of contact time experiment: The effect of time was investigated by agitating 0.25 g of adsorbent at pH 3,5,7 and 9 in 50 mg/lof pb(II) and 10 mg/lof As(V) solutions over time periods of 0.5-hr, 1-hr, 2-hr, 4-hr, 8-hr, 24-hr at constant agitation speed of 150 rpm.

1.2.2. Effect of initial heavy metal concentration: concentrations of 10 mg/L, 50 mg/L, 100 mg/L, and 200 mg/L were prepared for pb(II); while concentrations of 1 mg/L, 50mg/L, 10 mg/L, and 20 mg/L were prepared or As(V). 0.25 g of MBC at fixed pH=7 was added into 100 mL of solutions for 24h in order to assess initial metal concentration.

After shaking, the samples were filtered using 0.22 μm nylon membrane then collected and dried at 80C at night. The adsorption capacity of pb(II) and As was calculated using this formula:

$$q_e = (C_i - C_e) \times V/m$$

where q_e is the equilibrium adsorption capacity, C_i (mg/l) and C_e (mg/l) are respectively the initial metal concentration and concentration at equilibrium, m is the mass of adsorbent in (g) and V is the volume of the solution in (L).

1.3. Sorbent characterization

FT-IR spectroscopic analysis was performed for the determination of functional groups present on the surface of adsorbent both before and after adsorption process (Thermo Scientific™ Nicolet™ iS™10 FT-IR spectrometer). FT-IR spectra were recorded in the mid infrared range between 4000 and 400 cm⁻¹. The surface morphology was also studied before and after adsorption by SEM-FESEM (Jeol JSM-7600F) machine.

III. RESULTS AND DISCUSSIONS

1.4. Materials Characterization

3.1. IFT-IR spectroscopic analysis

FT-IR spectroscopic analysis was performed in order to identify the functional groups present on the surface of adsorbent both before and after adsorption of Arsenic and lead.

The FTIR spectra ($400\text{--}4000\text{ cm}^{-1}$) before and after adsorption of As(V) at different concentrations are shown in Figure 1.

The bands around 3411.13 cm^{-1} correspond to O–H stretching vibrations, 2963.56 , and 2869.62 cm^{-1} indicate presence of methylene $\text{--CH}_2\text{--}$ bridge deformation vibration¹². The region from 1745 to 1504 cm^{-1} suggest the presence of the carbonyl stretching vibration band C=O or C=C stretching.

Asymmetric stretching vibrations of As–O bond are confirmed by the presence of two peaks around 1580 and 850.21 cm^{-1} . A broadband at low-frequency range around 542.48 cm^{-1} corresponds to Mn–O vibrations¹³. In addition, Mn–O vibrations band showed a diminution with the increase in amounts of MBC after the adsorption of As. This potentially could be explained by the important role of Mn in MBC and the interaction between Mn–O and As.

The FTIR spectra of the MBC before and after pb(II) adsorption are illustrated in Figure 2. Similarly, to the expected spectrum of Arsenic, bands at 3144 cm^{-1} and 1347.28 cm^{-1} could be due to the --OH stretching and the more prominent peak at associated with --OH vibrations. Peaks at 2987 cm^{-1} , 2883.46 cm^{-1} , 1606.23 cm^{-1} and 1533.88 cm^{-1} correspond to CH_2 deformation vibrations, C=C, and carbonyl C=O. The low-frequency region around 520 cm^{-1} corresponds to Mn–O vibrations. The Comparison of FTIR before and after adsorption of pb(II) ions suggest the attachment of pb^{2+} to OH group and other function. Moreover, the spectrum in Figure 2 indicates clearly the transmittance drops with variation of concentration. These results are in accord with those in section 3.2.

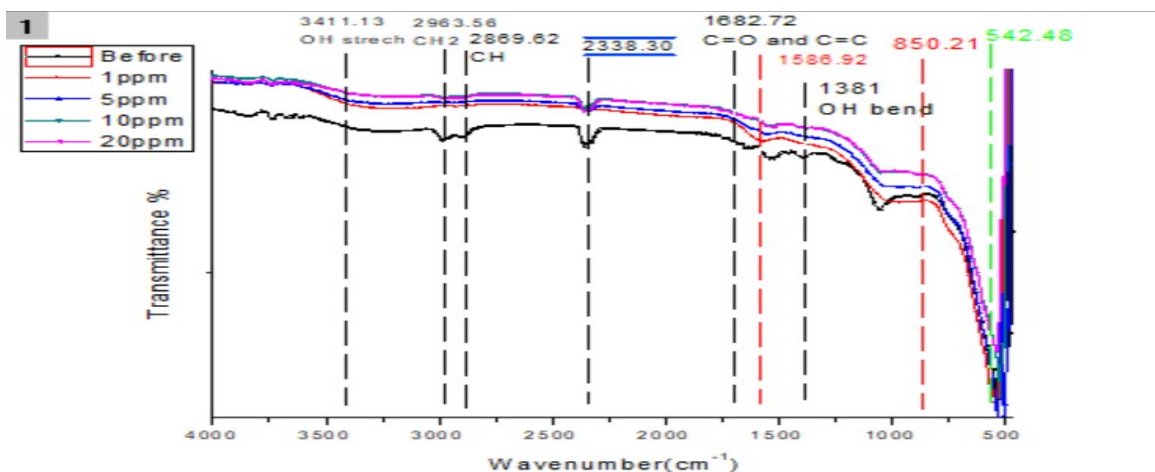


Figure 1: FTIR spectra MBC before and after Arsenic adsorption at different concentration.

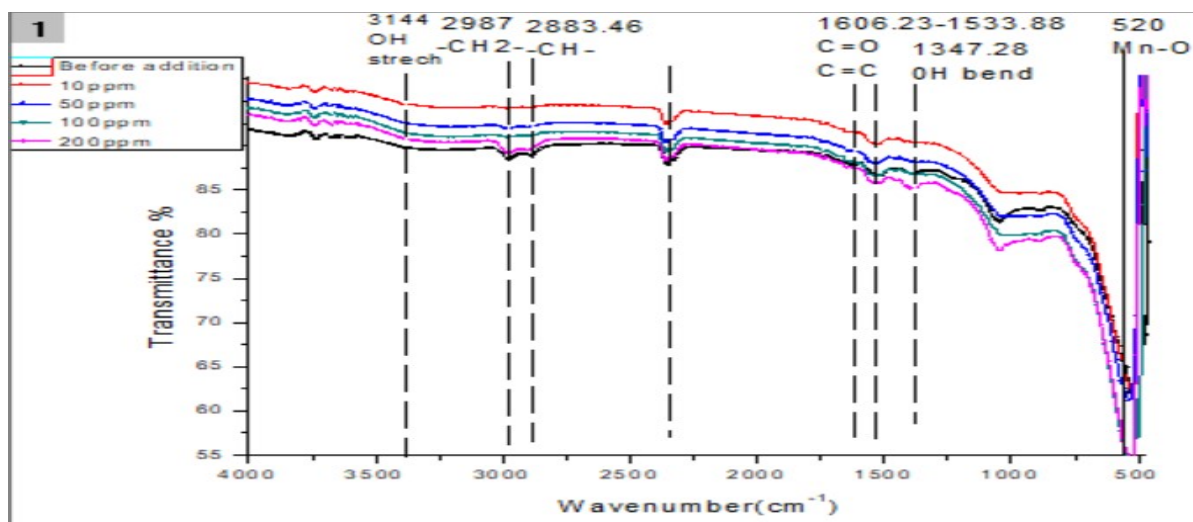


Figure 2: FTIR spectra MBC before and after lead adsorption at different concentration.

3.1.1 SEM analysis

Scanning electron microscope (SEM) has been assessed in order to observe and evaluate changes in the morphology before and after adsorption of pb(II) and As(V) SEMs as shown in Figure 3 below. The micrograph (a) and (b) of sorbent show nano porous with irregular surface and shape. Particle size of sorbent is an important factor to be considered in biosorption. In addition, their irregular surface enhanced good capacity for adsorption. SEM micrographs of MBC surfaces after the biosorption of Lead (II) ions and Arsenic (V) at different magnifications are shown in Figure 3. Images indicated that metals have filled pores and the adsorption process depends clearly to initial metal ions concentration.

After Arsenic adsorption; it is clear from the Fig.3c and 3d that the surface morphology changed, and pores were filled in As(V) ion and new spherical particles appeared.

Fig 1 confirms results in paragraph 3.2.1 and show that the surface was filled by many well small-sized nanoparticles with uniform spherical shape. Similarly, surface morphology using the SEM technique showed distinct changes between before and after the adsorption processes accumulation of pb(II) on the surface were observed Fig.3e and 3f. It is clear from micrographs that after adsorption process caves and pores became filled with pb (II) ions this is due to the physico-chemical interaction between the lead ions and the surface functional groups present on MBC.

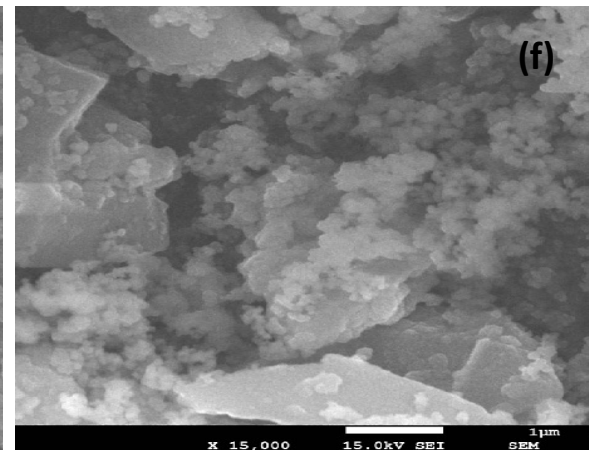
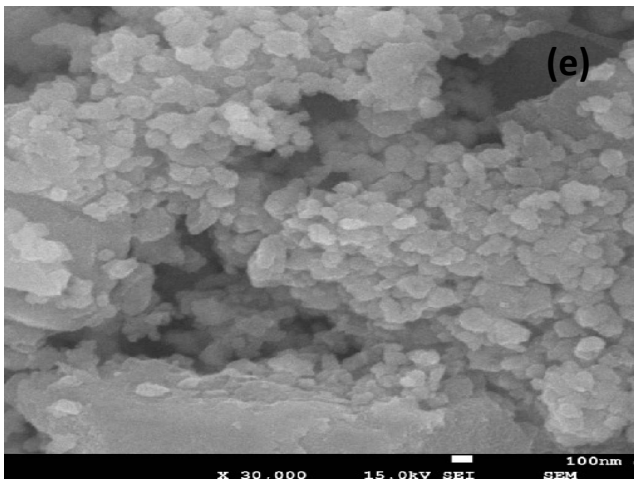
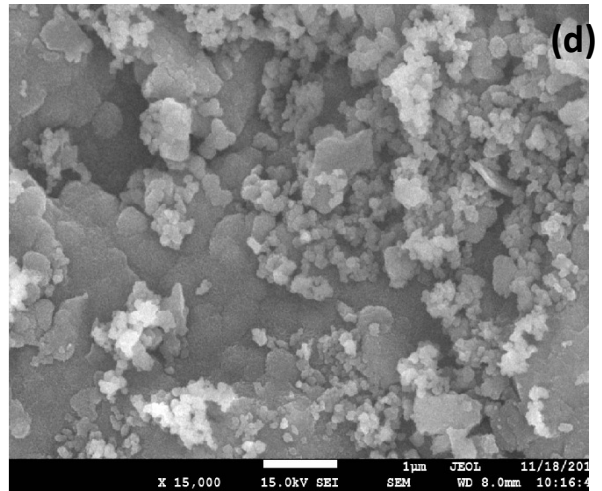
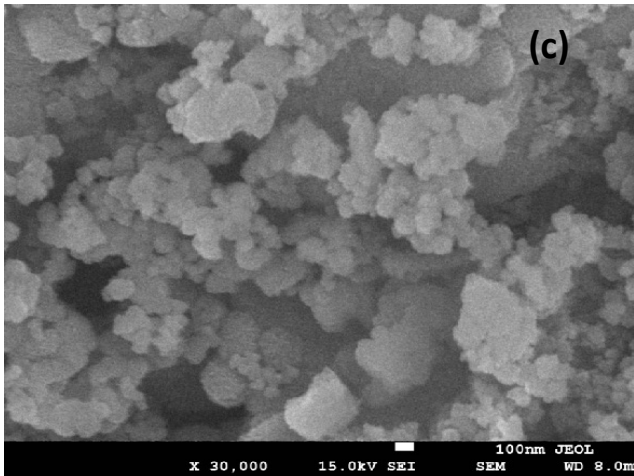
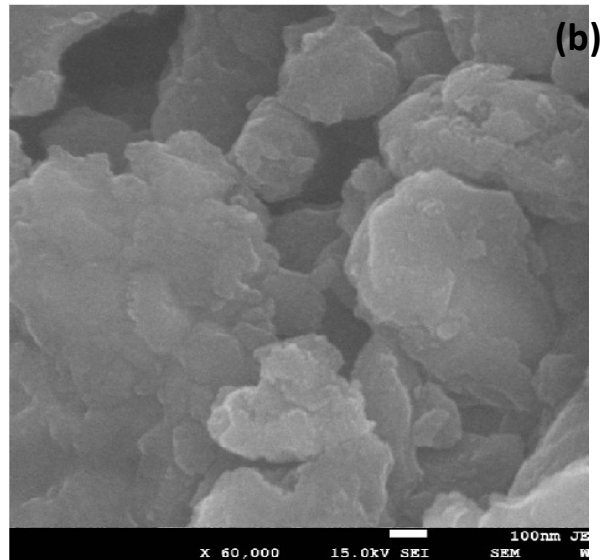
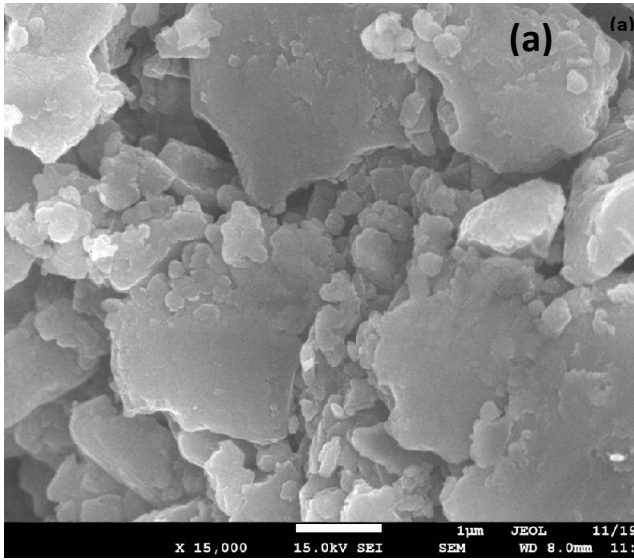


Fig 3: SEM images of (a,b) before adsorption of As(V) and pb(II) respectively; (c,d) after adsorption of As(V); (e,f) after adsorption of As(V).

1.5. Adsorption of Lead and Arsenic

1.5.1. Effect of pH

PH is one of the most crucial parameters for adsorbing metal ions from aqueous solution. In other words,; it has an effect on the metal ions solubility, the concentration of the counter ions on the functional groups of the adsorbent and the degree of ionisation of adsorption during reaction.

The effect of pH at an initial metal ions concentration of 10, 50,100 and 200ppm in 100mL solution, constant adsorbent dose of 0.25g and agitation period of 24 hours at varying pH ranges has been examined. The experimental data obtained are presented in (Fig.4.)

(Pb)

(As)

Ph	10 ppm	50 ppm	100 ppm	200 ppm
7	7.7	7.1	7.2	7.8
9	9.006	9.003	9.003	9.01
5	5.020	5.009	5.016	5.001
3	3.00	3.01	3.006	3.011

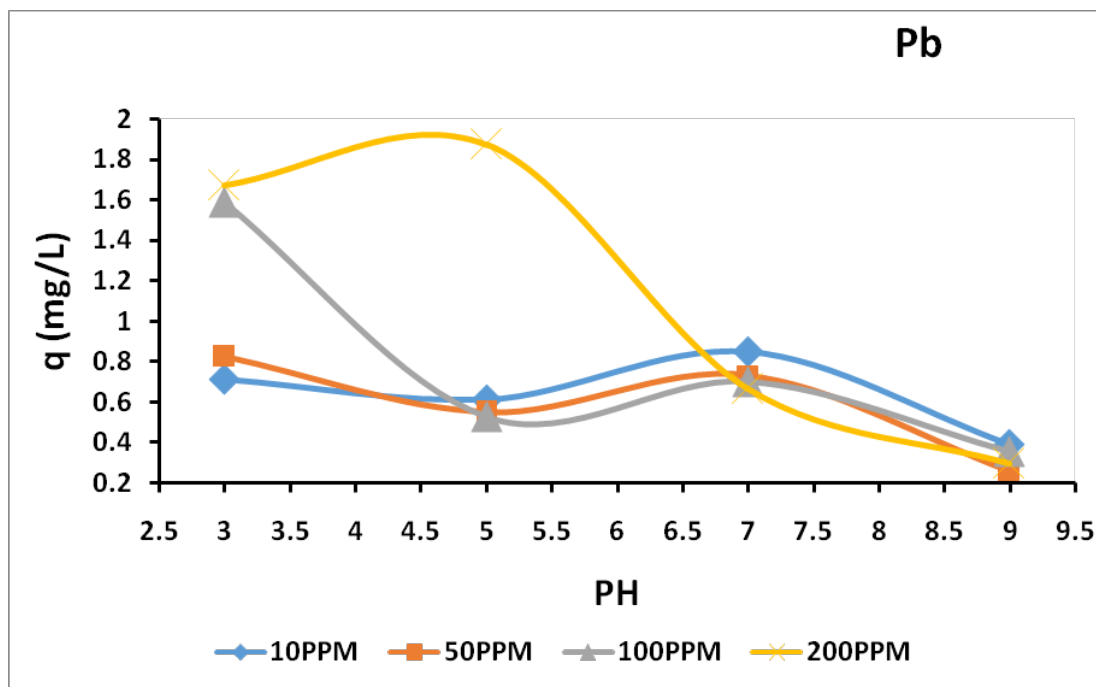
PH	1ppm	5ppm	10ppm	20ppm
7	7.0	7.1	7.10	7.11
9	9.03	9.02	9.017	9.012
5	5.022	5.017	5.04	5.02
3	3.013	3.006	3.010	3.006

As shown in Fig. (4) the efficiency of lead ion removal was highest at pH 5-7 values. Although, results show an uptake decrease by either raising or lowering pH. Similar trend for the effect of pH on adsorption of heavy metals (i.e adsorption decreases with increase in pH) has been reported by Hongbo et. al¹⁴.

The decline of adsorption of pb (II) ions at higher pH>7 may be assigned to the formation of their hydroxides which build precipitate and avert further adsorption as stated by Xiao and Ju-Chang¹⁵. On the other hand, the lead ion uptake for pH=3 is low in this acidic medium. This can be allocated to the existence of H⁺ ions.

Effect of pH on Arsenic As efficiencies was also studied in Fig. (4) at varying As (V) initial concentration of 1ppm, 5ppm, 10ppm and 20ppm in 100 ml solution.

Indeed, the best sorption conditions were observed at pH interval 5–7 for As(V) when H₂AsO₄ is the predominant form in the solution then showed a decline under highly alkaline conditions. A maximum absorption efficiency was found at pH = 5 for 20ppm arsenic initial concentration.



1.5.2. Effect of contact time

The effect of contact time on the removal efficiency of Lead and Arsenic metals was studied at various solution pH values in the range 3-5-7-9. Fig. (5.a) and Fig. (5.b).

As shown in Fig. (5.a) and Fig. (5.b), the adsorption capacity of both Lead and Arsenic were strongly pH dependent.

The equilibrium time is reached after 2 hours for pb (II) and 1 hours for As(V). The equilibrium times obtained for both Lead and Arsenic are short by contributions at certain times reported in the literature¹⁶. However, the rapid adsorption kinetics during the first minutes of reaction can be interpreted by the fact that at the beginning of adsorption, the number of active sites available on the surface of the adsorbent material is much greater than that of the sites remaining after a certain time¹⁷.

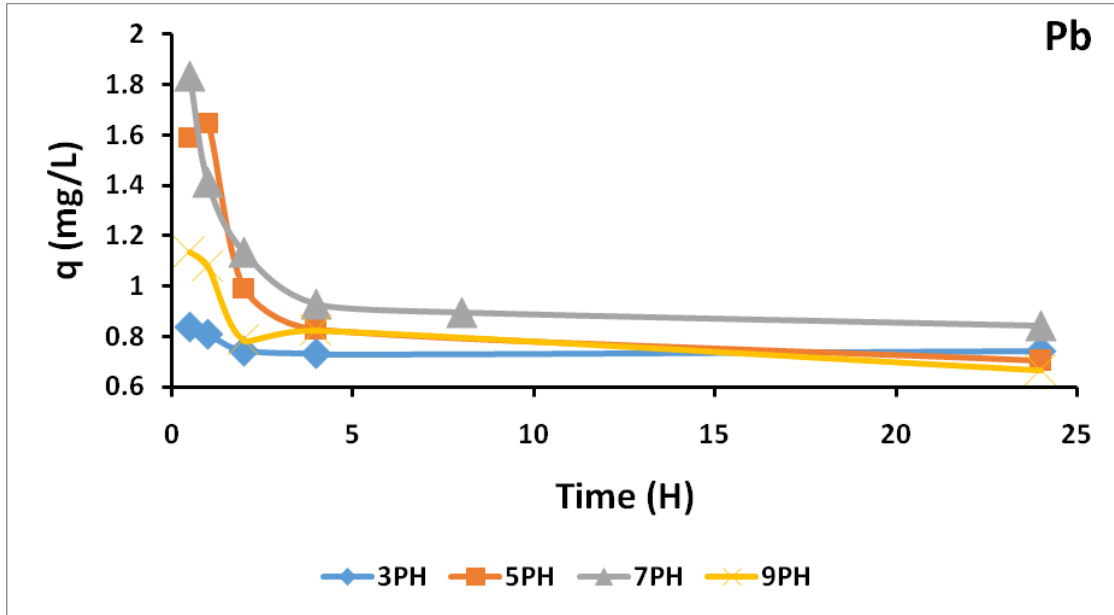


Fig.(5.a). Effect of contact time on adsorption of pb(II) at various pH

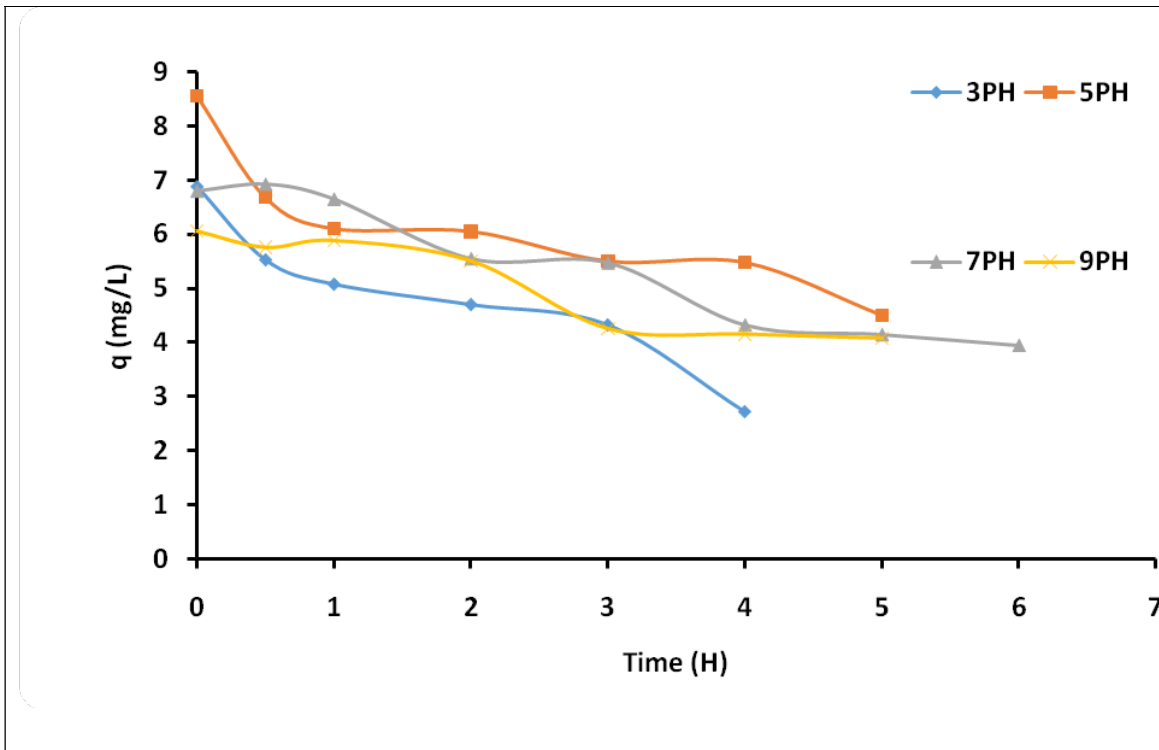


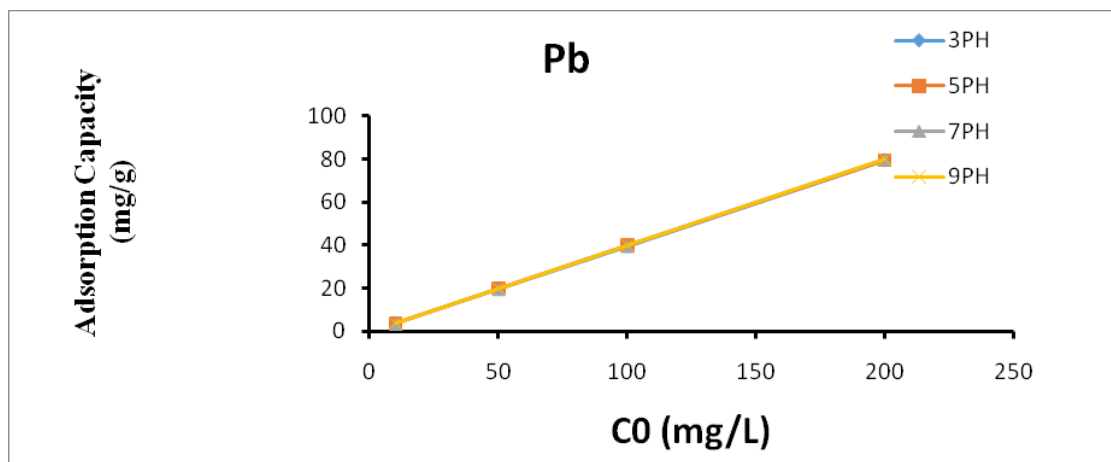
Fig.(5.b). Effect of contact time on adsorption of As(V) at various pH

1.5.3. Effect of initial pb (II) and As(V) concentration on adsorption isotherm

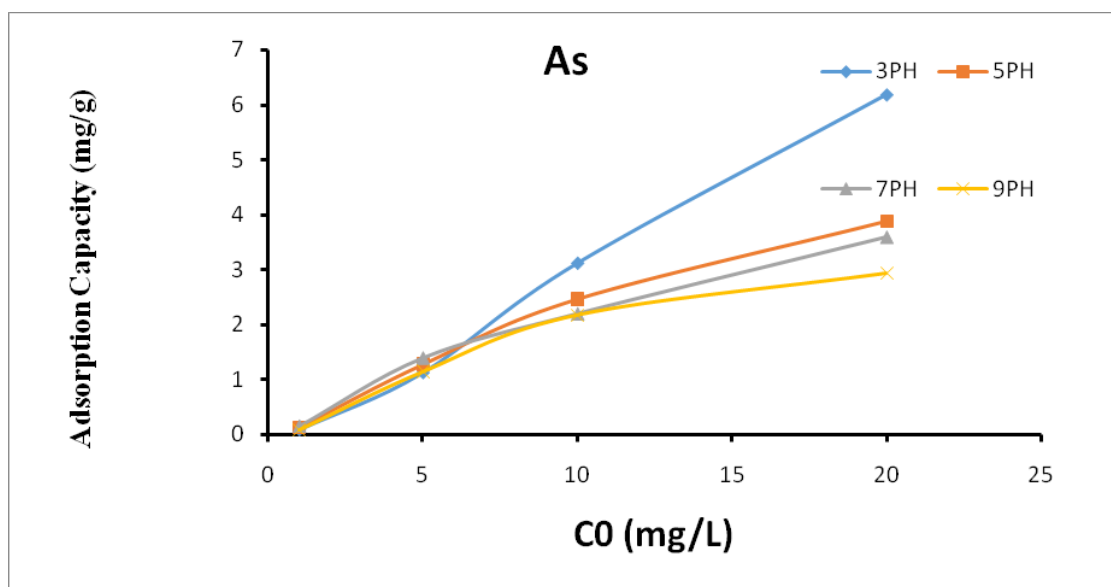
The plot of adsorption vs. the initial concentration of pb (II) and As(V) at varying range of pH of solution are represented in Fig. (6.a) and Fig.(6.b).

The results shown in Fig. (6.a) and Fig. (6.b) reveals that the adsorption begins at a low concentration, and with increasing metal ion concentration the amount of metal ion adsorbed increases for both pb(II) and As(V). The initial concentration may provide the driving force to overcome the resistance to the mass transfer of metal ions between adsorbed and adsorption. For this reason, the initial concentration was high and then the driving force was high too, and therefore the adsorption capacity would be high.

Although the increase in pH have no effect on the adsorption of lead ion Fig (6.a), it's clear from the plot that the decrease in pH causes increased adsorption of the Arsenic ions Fig (6.b). These results can be explicated by the decrease in the expansion of the adsorbent surface which may reduce the electrostatic attraction between the As(V) species and the adsorbent surface. Consequently, adsorption may occur and a resulting decrease in the removal proportion of As(V) is also possible.



Fig(6.a) Effect of pH and initial concentrations on the adsorption capacity of Pb(II) from aqueous solution. (adsorbent amount = 0.25g).



Fig(6.b) Effect of pH and initial concentrations on removal of As(V) from aqueous solution. (adsorbent amount = 0.25g).

IV. CONCLUSION

To summarize, Manganeseoxide modified biochar (MBC) has been synthesized. Indeed, modified Biochar reveals a better sorption of As(V) and Pb(II) and is dependent on pH, contact time, lead-concentration and Arsenic. Accordingly, the results signify that the best sorption conditions are perceived at pH interval 5–7 for both lead and arsenic ions. Equally, important results show that there is an uptake decrease caused by the rise or fall of pH. Furthermore, Pb (II) and As(V) ions were rapidly recovered in a short period of contact time, this can be understood by the high removal at pH=5 and pH=7. The results also show that when the ion concentration of the initial metal is increased, the quantity of the metal ion adsorbed rises for Pb (II) and As(V).

REFERENCES

- [1] C. Femina Carolin, P. Senthil Kumar, A. Saravanan, G. Janet Joshiba, Mu. Naushad (2017). Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *Journal of Environmental Chemical Engineering*, 5, 2782–2799.
- [2] Radaideh JA, Abdulgader HA, Barjenbruch M (2017). Evaluation of Adsorption Process for Heavy Metals Removal found in Pharmaceutical Wastewater. *J Med Toxicol Clin Forensic Med* Vol.3 No.2:9 Lisa N, Kanagaratnam B, Trever M (2004). Biosorption of Zinc from aqueous solutions using biosolids. *Adv. Env. Res.*, 8,629-635.
- [3] Mohammad Kashif Uddin (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal*, 308 438–462.
- [4] Singh N, Kumar D, Sahu AP(2007). A review Arsenic in the environment: effects on human health and possible prevention. *J Environ Biol.*, 28, 359-65.
- [5] Belinger, D. C (2005). Teratogen update: lead and pregnancy. *Birth Defects Research a Clinical and Molecular Teratology*, 73, 409–420.
- [6] Hongbo P, Peng G, Gang C, Bo Pan, Jinhui P, Baoshan X (2017). Enhanced adsorption of Cu(II) and Cd(II) by phosphoric acid-modified biochars. *Environmental Pollution*, 229: 846-853.
- [7] Zhihong Yu, Li Z, Yifan H, Zhengguo S, Weiwen Q (2015). Effects of a manganese oxide-modified biochar composite on adsorption of arsenic in red soil. *Journal of Environmental Management*, 163: 155-162
- [8] Lukáš T, Veronika V, Ivo Š, Martina V, Sylva Č, Michael K (2016). Lead and cadmium sorption mechanisms on magnetically modified biochars. *Bioresource Technology*, 203, 318-324.
- [9] Obemah D. N, Baowei Z (2014). Biochar Preparation, Characterization, and Adsorptive Capacity and Its Effect on Bioavailability of Contaminants: An Overview. *Advances in Materials Science and Engineering*.
- [10] Wang S G, Zimmerman A, Li Y, Ma L, Harris W, Migliaccio K (2014) Removal of arsenic by magnetic biochar prepared from pinewood and natural hematite. *Bioresources Technology*.10.104
- [11] Shengsen Wang, Bin Gao, Yuncong Li, Ahmed Mosa, Andrew R. Zimmerman, Lena Q. Ma,
- [12] Willie G. Harris b, Kati W. Migliaccio(2015). Manganese oxide-modified biochars: Preparation, characterization, and sorption of arsenate and lead. *Bioresource Technology* 181 13–17.
- [13] Li Zhou, Yifan Huang, Weiwen Qiu, Zhanxiang Sun, Zhongqi Liu, Zhengguo Song(2017) Adsorption Properties of Nano-MnO₂-Biochar Composites for Copper in Aqueous Solution. *Molecules*, 22(1), 173
- [14] López R V, Moreno C C, Rivera U J, Radovic L R (2003). Ionic strength effects in aqueous phase adsorption of metal ions on activated carbons. *Carbon*, 41, 2020–2022.
- [15] Li H D, Xiaoling da S, Evandro D O, Letuzia C, Yanshan M L. (2017). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. *Chemosphere*. 178. 466-478.
- [16] Xiao F, Ju-Chang HH (2009). Comparison of biosorbents with organic sorbents for removing Copper (II) from aqueous solutions. *J. Environ. Man.*, 90: 3105-3109.
- [17] Zhengang Liu, Fu-Shen Z (2009). Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. *Journal of Hazardous Materials* 167, 933–939.
- [18] Chawla S, Uppal H, Yadav M, Bahadur N, Singh N (2017) Zinc peroxide nanomaterial as an adsorbent for removal of Congo red dye from waste water. *Ecotoxicology and Environmental Safety* 135, 68–74.
- [19] Wan S, Wu J, Zhou S, Wang R, Gao B, He F (2018) Enhanced lead and cadmium removal using biochar-supported hydrated manganese oxide (HMO) nanoparticles: behavior and mechanism. *Sci Total Environ* 616-617:1298–1306.
- [20] Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B., (2008). Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. Asabe* 51, 2061–2069.
- [21] Jppolito, J.A., Novak, J.M., Busscher, W.J., Ahmedna, B.M., Rehrah, D., Watts, D.W., (2012). Switchgrass biochar affects two aridisols. *J. Environ. Qual.* 41, 1123–1130.
- [22] Abd Allah A (2011) Physico-Chemical Studies Concerning Naturally Occurring Radionuclides and Heavy Metal Concentrations in Groundwater. A Thesis of Master of Science Degree. Beni Suef University.
- [23] N. Ahmad, M.S. Jaafar, T. Nasir, M. Rafique (2018) Determination of radon concentration and heavy metals (Ni, Pb, Cd, As, Cr) in drinking and irrigated water sampled from Kulim, Malaysia. *International Journal of Radiation Research*, July 2018. Volume 16, No 3:341-349.
- [24] Al-Nafiey MS, Jaafar MS, Bauk S (2014) Measuring radon concentration and toxic elements in the irrigation water of the agricultural areas in Cameron Highlands, Malaysia. *Sains Malaysiana*, 43: 227-231.
- [25] Darko, G., Ansah, E., Faanu, A. and Azanu, D. (2017) Natural radioactivity and heavy metal distribution in reservoirs in Ghana. *Pollution*, 3(2): 225-241.
- [26] Gjoka, F., Felix-Henningsen, P., Wegener, H.R., Salillari, I. and Beqiraj, A. (2011). Heavy metals in soils from Tirana (Albania). *Environ. Monit. Assess.* 172, 517-527. doi:10.1007/s10661-010-1351-5.
- [27] Jie Liang, Xuemei Li, Zhigang Yu, Guangming Zeng, Yuan Luo, Longbo Jiang, Zhaoxue Yang, Yingying Qian, and Haipeng Wu. (2017) Amorphous MnO₂ Modified Biochar Derived from Aerobically Composted Swine Manure for Adsorption of Pb(II) and Cd(II). *ACS Sustainable Chem. Eng.*, 5 (6), pp 5049–5058.
- [28] Meththika Vithanage, Indika Herath, Stephen Joseph, Jochen Bundschuh, Nanthi Bolan, Yong Sik Ok, M.B. Kirkham, Jörg Rinklebe. (2016) Interaction of arsenic with biochar in soil and water: A critical review. *Carbon journal*. Volume 113, Pages 219-230
- [29] Wang S, Gao B, Li Yuncong, Mosa Ahmed, Zimmerman A, Ma Lena, Harris Willie, Migliaccio Kati. (2016) Manganese oxide-modified biochars: Preparation, characterization, and sorption of arsenate and lead. *Bioresource Technology*, Volume 181, Pages 13-17.

- [30] Yang, A., Zhu, Y., & Huang, C. P. (2018). Facile preparation and adsorption performance of graphene oxide-manganese oxide composite for uranium. *Scientific reports*, 8(1), 9058. doi:10.1038/s41598-018-27111-y
- [31] Zhou, L., Huang, Y., Qiu, W., Sun, Z., Liu, Z., & Song, Z. (2017). Adsorption Properties of Nano-MnO₂-Biochar Composites for Copper in Aqueous Solution. *Molecules (Basel, Switzerland)*, 22(1), 173. doi:10.3390/molecules22010173.
- [32] Xiao, X., Chen, B., Chen, Z., Zhu, L., & Schnoor, J. L. (2018). Insight into Multiple and Multilevel Structures of Biochars and Their Potential Environmental Applications: A Critical Review. *Environmental science & technology*, 52(9), 5027–5047. doi: 10.1021/acs.est.7b06487.
- [33] Cha JS, Park SH, Jung S, Ryu C, Jeon J, Shin M, Park Y (2016) Production and utilization of biochar: a review. *J Ind Eng Chem* 40:1–15.