

Pb(II) Removal from Synthetic Wastewater Using *Kombucha* Scoby and Graphene Oxide/Fe₃O₄

S.M. Mousavi^a, S.A. Hashemi^a, A.M. Amani^a, H. Esmaili^{b,*}, Y. Ghasemi^a, A. Babapoor^c, F. Mojoudi^d and O. Arjomand^e

^aDepartment of Medical Nanotechnology, School of Advanced Medical Sciences and Technologies, Shiraz University of Medical Sciences, Shiraz, Iran. Pharmaceutical Sciences Research Center, Shiraz University of Medical Sciences, Shiraz, Iran

^bDepartment of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran

^cDepartment of Chemical Engineering, University of Mohaghegh Ardabili, P.O. Box: 179, Ardabil, Iran

^dDepartment of Environment, Faculty of Natural Resources, College of Agriculture & Natural Resources, University of Tehran, Karaj, Iran

^eDepartment of Chemical Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

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Kombucha Scoby is a colony consisting of bacteria, yeast and cellulosic pellicle that present fantastic performances in various fields. In addition to the anti-toxicity and antimicrobial specifications of *Kombucha* scoby, this unique colony can be used for waste water treatment and removal of heavy metals. Herein, efficiency of graphene oxide/Fe₃O₄ nanoparticles (GO/Fe₃O₄) and *Kombucha* Scoby in the removal of Pb(II) from synthetic wastewater were examined and compared. The characteristics of GO/Fe₃O₄ nanoparticles were analyzed using FTIR and SEM. Moreover, the effect of significant parameters such as pH (1-7), temperature (10-60 °C) and amount of adsorbent (1-200 g l⁻¹) on the removal of Pb(II) ion from aqueous solution was investigated. The maximum adsorption efficiency was obtained at a temperature of 50 °C and adsorbent amount of 0.3 and 15 g using GO/Fe₃O₄ and *Kombucha* Scoby, respectively. Additionally, pHPZC values of 6.1 and 6.2 were obtained for GO/Fe₃O₄ and *Kombucha* Scoby, respectively. The maximum adsorption efficiencies for GO/Fe₃O₄ and *Kombucha* Scoby were found to be 98.08 and 99.73%, respectively. Likewise, the adsorption isotherm behavior of Pb(II) on adsorbents were investigated using Langmuir and Freundlich models. Achieved results showed that the Langmuir isotherm model is better fitted with experimental data. Furthermore, the maximum adsorption capacities by Langmuir model for GO/Fe₃O₄ nanoparticles and *Kombucha* Scoby were found to be about 114.9 and 126.6 mg/g, respectively. Generally, achieved results revealed that *Kombucha* Scoby, which is a cost affordable colony, can remove Pb(II) ions from water better than GO/Fe₃O₄.

Keywords: Graphene oxide, Magnetic nanoparticles, Pb(II), *Kombucha* Scoby, Adsorption

INTRODUCTION

Heavy metal ions in groundwater can be considered as a serious threat to public health and environmental systems [1]. These ions are not degradable and a vast majority of them have toxic and carcinogenic properties [2,3]. They can be stored within living tissues, and enter into food chains.

*Corresponding author. E-mail: esmaeili.hossein@iaubushehr.ac.ir

Based on the United States Environmental Protection Agency (US EPA) and International Agency for Research on Cancer (IARC), metal ions such as lead (Pb (II)) are considered as human carcinogenic agents. It should also be noted that Pb(II) is a highly stable compound that cannot be easily degraded. In most cases, the toxico-kinetic behavior of Pb(II) ion in humans depends on its binding to the albumin protein [4]. To reduce or remove heavy metals from wastewater, various physical, chemical and biological procedures, such as coagulation, chemical oxidation,

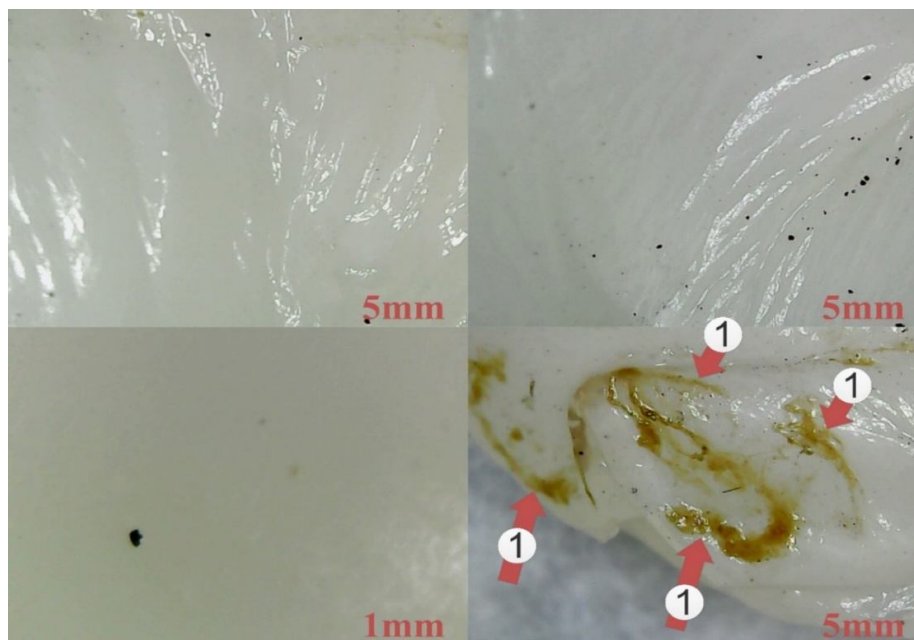


Fig. 1. Optical microscopic images of Kombucha Scoby (Number 1 shows the dead kombucha bacteria).

membrane filtration, electro dialysis, reverse osmosis, chemical precipitation and adsorption have been employed, however, often these methods are not very successful due to their high operating costs and inefficiencies. Among the above-mentioned methods, adsorption process has recently attracted lots of attention. This is a simple and efficient method for removal of heavy metals from water and wastewater with positive features such as high purification effect and no harmful by-products as well as significant properties such as availability and ease of use [5-7]. Therefore, the development of adsorbents with high adsorption capacity, low toxicity and efficient separation has attracted great attention [7,8]. Additionally, in order to remove heavy metals and organic pollutants from water, many attempts have been made to produce useful adsorbents with various chemical compounds and superficial properties [8]. The use of magnetic adsorbents (such as Fe_3O_4 nanoparticles) can be considered as a newly efficient technology in which magnetic nanoparticles are easily separated from sewage using an external magnetic field after adsorption [9]. To improve the magnetic properties of iron oxide, it can be combined with different materials such as clay, CaO, graphene oxide (GO), *etc.*

[9,10]. In addition, some microorganisms such as algae, fungi and bacteria can be considered as an effective adsorbents to attenuate heavy metals [5,6].

The main aim of the present study is to deeply understand the removal percentage of Pb(II) ions from aqueous solution by means of two effective adsorbents such as modified graphene oxide with magnetite nanoparticles (GO/ Fe_3O_4) and *Kombucha* Scoby (KS), and also comparing their performances with each other. To this end, the effect of different parameters such as pH, temperature and adsorbent concentration on the removal of Pb(II) ions from synthetic wastewater is investigated. In fact, *Kombucha* is a fermentation of sweetened tea that provides symbiosis of acetic acid bacteria and yeast species. *Kombucha* Scoby (floating solid part in the liquid media), so called “tea fungus” (*i.e.* symbiotic colony of bacteria and yeast [11]), consists of symbiosis of acetic acid bacteria, various kinds of yeasts, and cellulosic pellicle [12,13]. This unique colony is cost affordable, and can be developed through least funds to develop a highly effective waste water purification system. Besides, the adsorption isotherm models such as Langmuir and Freundlich were investigated to describe the equilibrium behavior of adsorption.

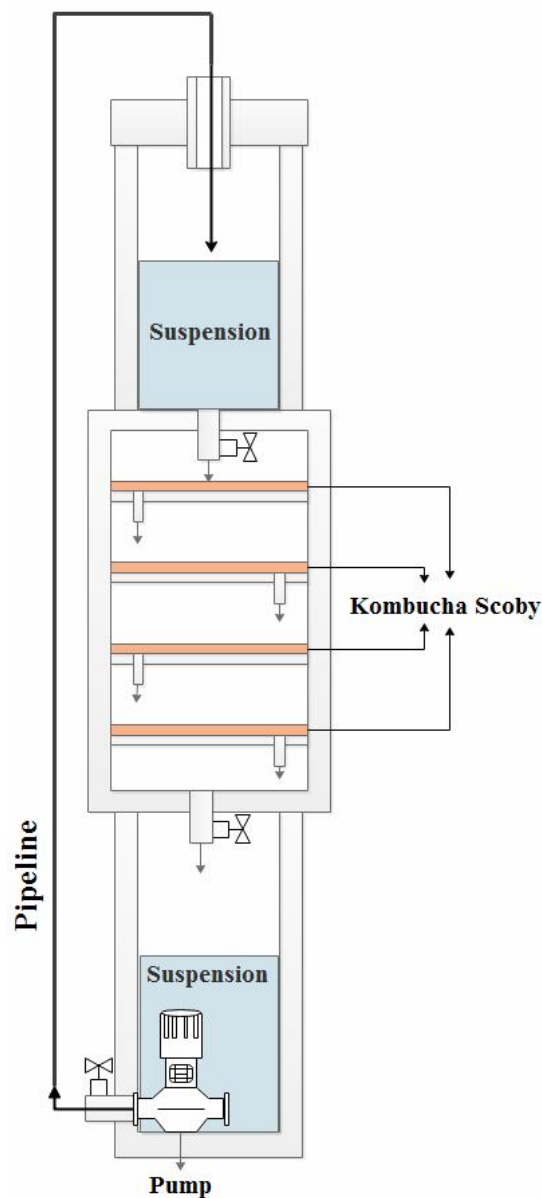


Fig. 2. Schematic of experimental setup for reactor operation.

EXPERIMENTAL

Materials and Methods

Kombucha Scoby was procurement from the Caucasus Mountains. The spectrophotometric measurements were performed with a Cintra 101 spectrophotometer (GBC, Australia). Scanning electron microscope (SEM, TESCAN) and digital pH meter (Metrohm 744) were used in these

experiments. SEM was used to determine the morphology and structure of the adsorbent, and the pH meter was used to measure the pH value of solutions. Materials such as Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), $\text{Pb}(\text{NO}_3)_2$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and graphene were purchased from Merck Co. (Germany). Furthermore, an optical microscope was used to observe Kombucha Scoby. Optical microscopic images of Kombucha Scoby is shown in Fig. 1.

Reactor setup and Operation

To perform experiments, anaerobic reactor made of polypropylene (PP) (4 cm in diameter, 63 cm in height and with an operating level of 58 cm) was used. The separation of Pb(II) from synthetic wastewater in the presence of microorganisms was done by a membrane module. A scheme of this bioreactor is shown in Fig. 2.

Preparation of Pb(II) Solution

A preliminary stock solution of lead was prepared at a concentration of 100 mg l⁻¹ by dissolving 0.16 g of Pb(NO₃)₂ in 1000 ml deionized distilled water. Other solutions were prepared by diluting the base solution with double-distilled water. The pH of the working solution was adjusted by 0.1 M NaOH and 0.1 M HCl.

Preparation of Graphene Oxide (GO)

In this study, graphene oxide (GO) was prepared using a multi-step method. In this case, 10 g graphite was initially poured into a flat-bottom flask, and then, 2 l H₂SO₄ was added to the flask and stirred at 500 rpm for 30 min. Then, 60 g KMnO₄ was added to the suspension and stirred at 500 rpm for 1 h while the temperature was maintained at ~5 °C. Thereafter, 110 ml H₃PO₄ was added to the suspension, and then the temperature was smoothly increased to about 50 °C and stirred for 72 h (500 rpm). Then, the solution was poured into a vacuum Erlenmeyer flask and some ice (made by deionized water) was poured into the flask. Afterwards, 10 ml H₂O₂ was poured in the solution very slowly and the vacuum Erlenmeyer flask was filled with deionized water. After that, the solution was kept without stirring for 48 h for further filler sediment. The solution was then filtered, and remaining fillers on the filter were washed with deionized water, and the pH of the solution was then adjusted to 7. Eventually, materials were dried for 1 h at 80 °C in an oven and then placed in humidity reduction chamber for 48 h. A view of GO preparation steps is shown in Fig. 3. More details about the production procedure of GO have been documented in our previous works [14,15].

Preparation of the Modified Graphene Oxide with Fe₃O₄ (GO/Fe₃O₄)

GO nanoparticles were decorated with Fe₃O₄

nanoparticles through a multi-step method. In this case, 320 ml deionized water was poured into a round-bottom flask and its temperature was set to 80 °C. Then, 3.89 g FeSO₄.7H₂O and 4.55 g FeCl₃.6H₂O were poured into the flask and stirred for 1 h. In next step, 0.0844 g GO was ultrasonically mixed in 100 ml of deionized water for 20 min and then poured into the previous suspension. The resulting suspension was stirred for 2 h and then 40 ml NH₃ was slowly added to the suspension. The suspension was then stirred for further 2 h with simultaneous heat (80 °C). In addition, the suspension was filtered and simultaneously washed with deionized water in order to set the pH on 7 and afterward dried in an oven for 1 h at 100 °C. The resulting material was placed in a moisture absorbing chamber for 48 h. A schematic of this multi-step method is shown in Fig. 4.

Batch Adsorption Experiment

Pb(II) adsorption using prepared adsorbents was done within a 250 ml Erlenmeyer flask containing 100 ml lead solution with a certain initial concentration. In this case, the effect of significant parameters like pH, adsorbent dose and temperature on the adsorption efficiency was investigated. In order to investigate the effect of pH, the adsorption process was done at pH ranging between 1-7. After determining the optimal pH, the optimum amount of other parameters was determined. To investigate the effect of temperature on the adsorption efficiency, temperature evaluation in the range of 10-60 °C was performed. The effect of adsorbent dose on the adsorption efficiency of lead was studied over the range of 1-200 g l⁻¹ of adsorbents in 100 ml solution. After performing the related assays, to separate the solid phase (sorbent) from the solution, about 10 ml of solution was centrifuged. The concentration of heavy metal after adsorption was determined by spectrophotometer. Adsorption efficiency (%) is determined by the following equation [16-18]:

$$\text{Removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where, C_o and C_e are the initial concentration (mg l⁻¹) and the equilibrium concentration of Pb(II) ions in solution (mg l⁻¹), respectively.

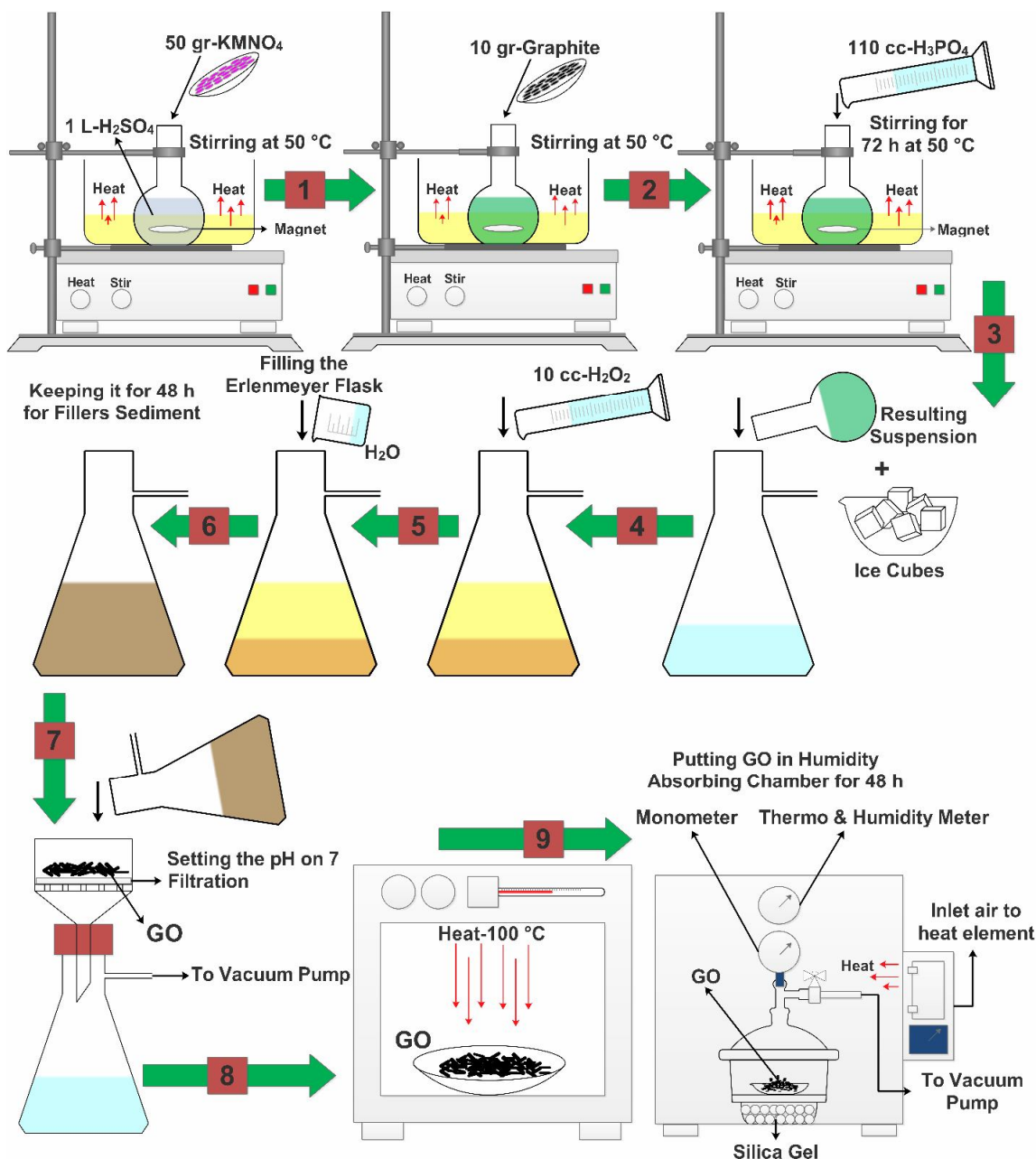


Fig. 3. Schematic of GO preparation steps.

RESULTS AND DISCUSSIONS

Characterization of Adsorbent

The FTIR spectra of Fe_3O_4 and $\text{GO-Fe}_3\text{O}_4$ nanoparticles are presented in Fig. 5. As can be seen in Fig. 5, peaks in the region between $530\text{-}630\text{ cm}^{-1}$, related to the Fe_3O_4

spectrum, correspond to the stretching vibration mode of Fe-O . In this regard, a broad and strong peak at 575 cm^{-1} corresponds to Fe_3O_4 indicating the successful synthesis of Fe_3O_4 nanoparticles [19-21]. Furthermore, peaks at 923 and 1113 cm^{-1} are related to the sp^2 alkene C-H band (disubstituted-E) and stretching vibration of in-plane C-H,

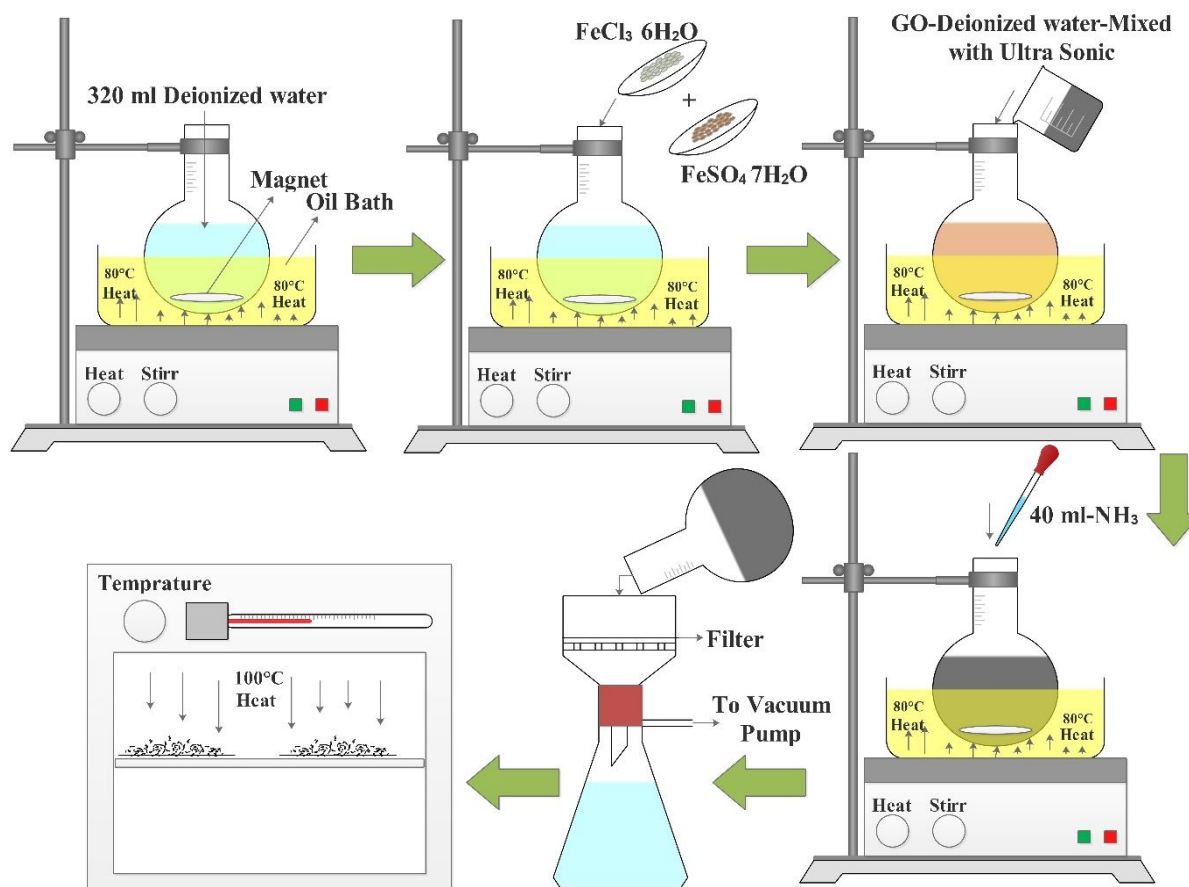


Fig. 4. Schematic of GO-Fe₃O₄ preparation.

respectively. Besides, peak with wavenumber 1627 cm⁻¹ belongs to the FeOO- [20], while peaks in region between ~2838-2921 cm⁻¹ are assigned to the C-H stretching vibration (sp³ stretching of hexyl aliphatic side). Weak peaks in region between 3500-3700 cm⁻¹ are attributed to the amine N-H functional groups. Furthermore, a broad and strong peak at 3424 cm⁻¹ corresponds to the hydroxyl functional group (-OH) [20]. Evaluation of GO-Fe₃O₄ spectrum confirms the successful decoration of GO with Fe₃O₄ nanoparticles. In this matter, appearance of a strong peak at 584 cm⁻¹, known as the finger print of Fe₃O₄ nanoparticles [19-21], along with the peak at 1628 cm⁻¹, corresponding to the FeOO- [20], justifies the successful decoration of GO with Fe₃O₄ nanoparticles. Moreover, peaks at 945 and 3416 cm⁻¹ correspond to the sp² alkene C-H bond and hydroxyl functional group, respectively. Appearance of Fe₃O₄ finger prints (577 and 1627 cm⁻¹)

along with disappearance of the peaks corresponding to the carboxyl and epoxide functional groups, and decrease in the intensity of hydroxyl functional group in the GO-Fe₃O₄ spectrum compared to that in Fe₃O₄ spectrum, justify the successful decoration of GO with Fe₃O₄ nanoparticles. In fact, decrease in the intensity of hydroxyl functional group and disappearance of carboxyl and epoxide functional groups clarify the interaction between functional groups of GO and Fe₃O₄.

The SEM image of GO-Fe₃O₄ nanoparticles is also shown in Fig. 6, providing information about size and morphology of the developed nanoparticles. It can be observed that the adsorbent has heterogeneous surfaces with abundant pores and active sites for adsorption of Pb(II) ions.

Point of Zero Charge (PZC)

PZC could directly lead to a qualitative assessment of

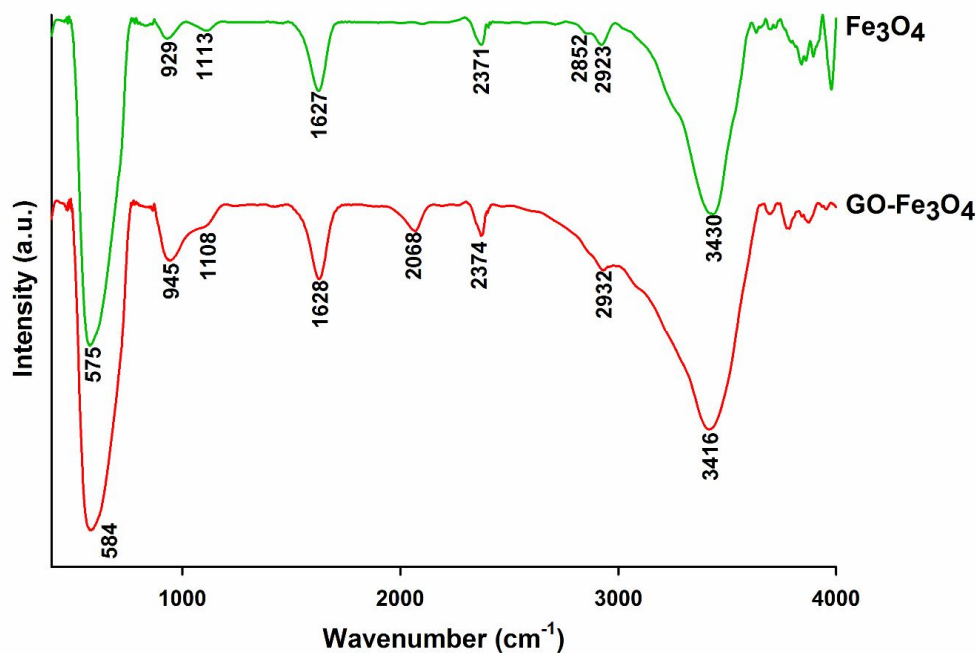


Fig. 5. FTIR spectra of Fe_3O_4 and $\text{GO-Fe}_3\text{O}_4$ nanoparticles.

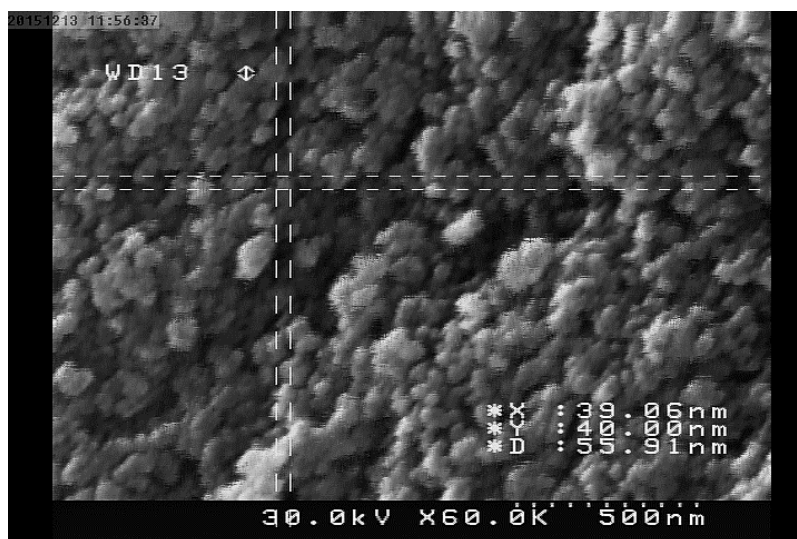


Fig. 6. SEM image of $\text{GO-Fe}_3\text{O}_4$.

the type of interactions (attraction or interaction) between *Kombucha* Scoby as a colony and $\text{GO-Fe}_3\text{O}_4$ if we know the type of charges on their surfaces. Unfortunately, it is experimentally difficult to directly measure the charges on the surface. Instead, indirect methods are available such as

estimation of PZC from electrochemical impedance spectroscopy measurement. PZC is an expedient marker of surface charges, that is critically relevant to adsorption of an electrolyte. It denotes the potential when the surface carries zero charges. Normally, when electrode potential is larger

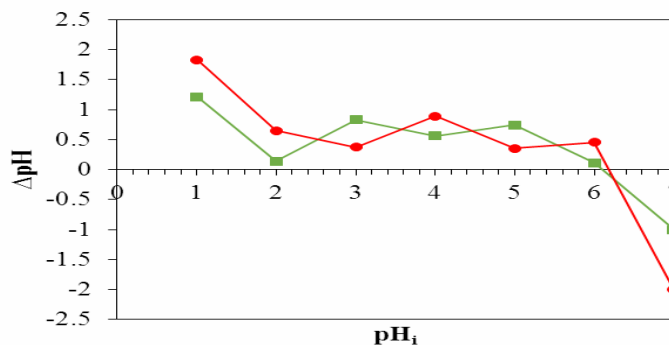


Fig. 7. pH_{ZPC} of GO-Fe₃O₄ (■) and *Kombucha* Scoby (●), and effect of initial pH on the sorption of Pb(II).

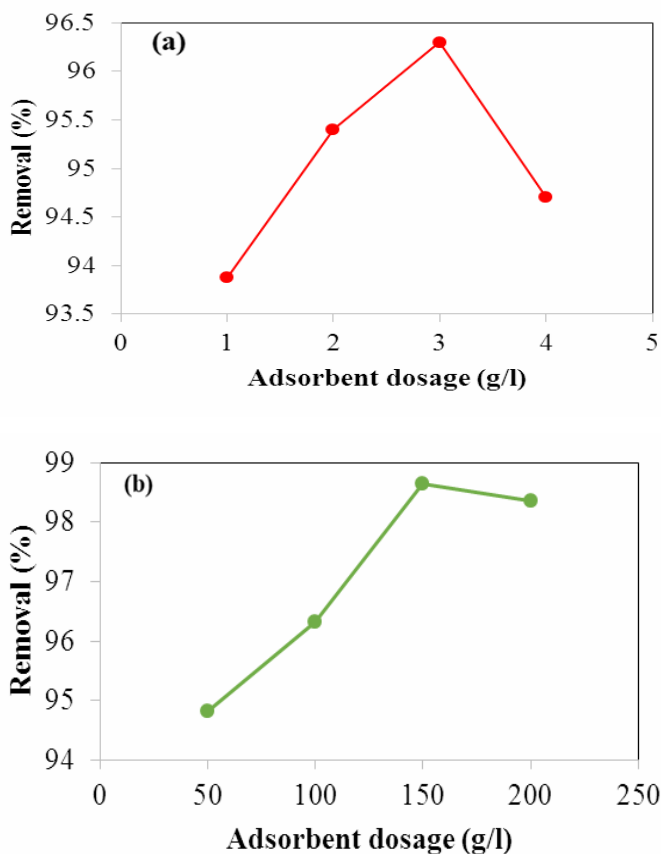


Fig. 8. The effect of the adsorbent dose on the Pb(II) sorption onto (a) GO-Fe₃O₄ and (b) *Kombucha* Scoby.

than PZC, the electrode carries positive charges and when it is smaller than PZC, the electrode carries negative charges. The pH value of the solution, affects the surface charge of the adsorbent and the uptake behavior and efficiency of

adsorbent [22,23]. The difference between the initial and final pH values ($pH = pH_f - pH_i$) was plotted against the pH_i in Fig. 7. The pH_{ZPC} was noted as the pH in which the initial pH and the final pH are equal [24]. The degree of Pb(II)

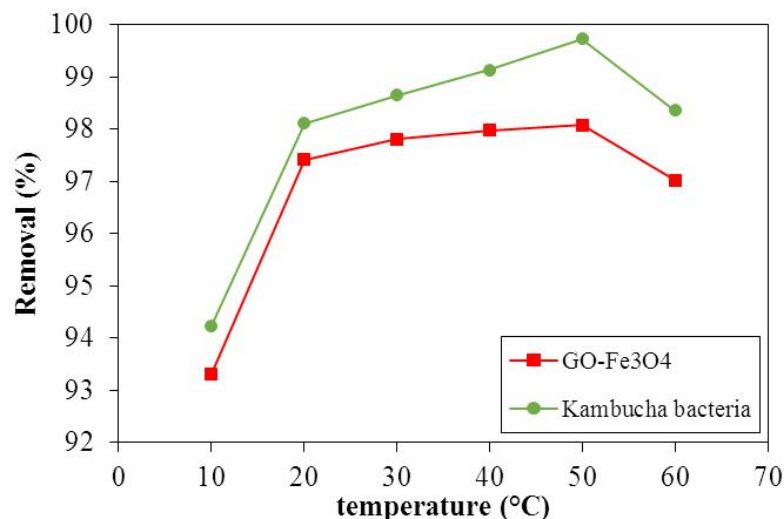


Fig. 9. The effect of the temperature on the sorption of Pb(II) onto GO-Fe₃O₄ and *Kombucha* Scoby.

adsorption onto the adsorbent surface is influenced by the pH zero-point charge (pH_{pzc}) of the adsorbents. As can be seen from the results, the pH_{pzc} of GO-Fe₃O₄ and *Kombucha* Scoby were 6.1 and 6.2, respectively. When the pH value was less than 6.1, the surface of the GO-Fe₃O₄ was positively charged and repelled the cationic Pb(II) molecules at the surface of the adsorbent. This caused competition between protons and cations that resulted in the low adsorption. When the pH was greater than 6.1, negative charges were dominant on the surface of the GO-Fe₃O₄ that facilitated the adsorption of the Pb(II) cations through electrostatic attraction. Based on the results, decrease in the pH led to the increase of removal efficiency; might be due to the increase in the H⁺ ions of the solution (pH < pH_{pzc}) and in positive ions on the adsorbent surface [25].

Effect of Adsorbent Dosage on the Removal Rate of Pb(II) Ions

The effect of adsorbent dosage on the removal of Pb(II) ions is studied by changing the adsorbent dosage without any changes in other parameters. Figure 8 shows that removal efficiency was increased by increase in the adsorbent dose. This phenomenon is due to an increase in the available binding sites on the surface of the adsorbent for adsorption of Pb(II) ions [26]. The removal efficiency of Pb(II) ions increased dramatically from 93.88% to 96.3% and from 94.82% to 98.65% when the GO-Fe₃O₄ dosage

increased from 1 to 3 g l⁻¹ and *Kombucha* Scoby changed from 50 to 150 g l⁻¹, respectively. On the other hand, the efficiency decreased with further increase in the adsorbents dosage. According to the results, the optimum adsorbent dose for GO-Fe₃O₄ and *Kombucha* are 3 and 150 g l⁻¹, respectively. Based on the results, the percentages of metal ion removed by the *Kombucha* were higher than those removed by GO-Fe₃O₄, indicating that *Kombucha* is a better adsorbent because it is cheaper than GO-Fe₃O₄ and has higher efficiency.

Effect of Temperature

The effect of temperature on the adsorption capacity of GO-Fe₃O₄ and *Kombucha* Scoby for the removal of Pb(II) ions from an aqueous solution was studied at pH 6.0 and the results are shown in Fig. 9. As can be seen in this figure, increase in the temperature from 10 to 50 °C leads to increase in the removal efficiency of GO-Fe₃O₄ and *Kombucha* about 98.08% and 99.73%, respectively. This is due to the fact that higher temperature increases the interaction between Pb(II) and adsorbent. Likewise, it indicates the endothermic nature of the adsorption process [27]. In general, the adsorption process involves two successive processes, namely fast diffusion and slow complexation [28]. When the temperature is more than 50 °C, the adsorption capacity decreases, due to the instability of Pb(II) adsorption complex in high temperature.

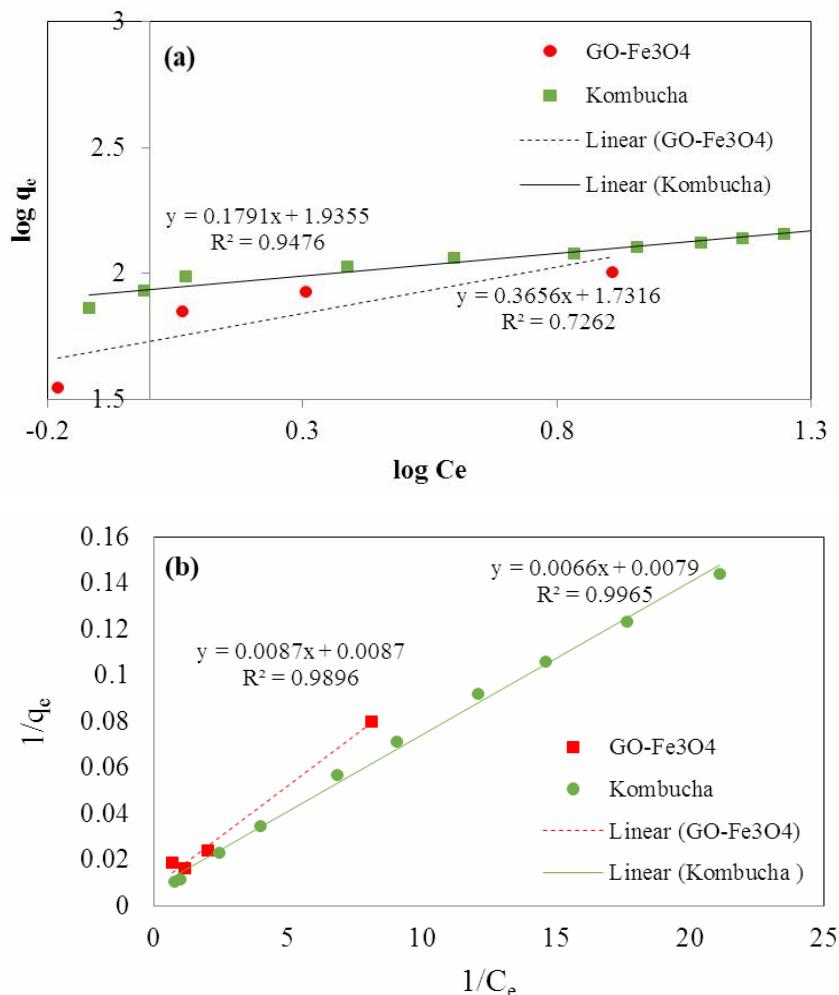


Fig. 10. Pb(II) adsorption using GO-Fe₃O₄ and *Kombucha* Scoby by Freundlich (a) and Langmuir (b) models.

Therefore, 50 °C was chosen as the optimum temperature for adsorption, and *Kombucha* Scoby proved to be a better adsorbent than GO-Fe₃O₄ due to cheaper and better performance.

Adsorption Isotherms

Adsorption isotherms display the interaction pathway of adsorbate with adsorbents [29]. Adsorption isotherms data were modeled using Langmuir and Freundlich models. Freundlich model assumes that the adsorbate uptake occurs on a heterogeneous surface of the adsorbent. Besides, the Langmuir model describes the monolayer sorption process onto the adsorbent surface [30]. The linearized form of the Freundlich model is given as follows [31]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where, K_F and n are the model constants showing the relationship between adsorption capacity and adsorption intensity, respectively [24]. The plot of $\ln q_e$ vs. $\ln C_e$ was employed to determine K_F and n from the intercept and the slope, respectively, according to Fig. 10. The value of $1/n$ represents the isotherm type, that is irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) and unfavorable ($1/n > 1$) [23]. The linear form of the Langmuir model [32] can be seen in equation 3 and the results are plotted in Fig. 10,

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (3)$$

Table 1. Constants and Parameters of Different Isotherm Models Using Kombucha Bacteria and GO-Fe₃O₄

Model	Parameter	Kombucha	GO-Fe ₃ O ₄
Freundlich	K _F	86.2	53.9
	n	5.58	2.74
	R ²	0.9476	0.7262
Langmuir	q _m	126.6	114.9
	k _L	1.197	1
	R ²	0.9965	0.9896

where, q_e , C_e , K_L and q_m are the amount of adsorbed ion in equilibrium state per gram of adsorbent (mg g^{-1}), the equilibrium concentration of metal ions in solution (mg l^{-1}), the equilibrium constant related to the affinity of binding sites (l mg^{-1}) and the maximum amount of the ions per mass of adsorbent (mg g^{-1}), respectively [30]. The plot of $1/q_e$ against $1/C_e$ was applied to determine q_m and K_L from the intercept and the slope, respectively. Constants and parameters of Langmuir and Freundlich isotherm models using Kombucha Scoby and GO-Fe₃O₄ are tabulated in Table 1.

According to Fig. 10 and Table 1, the R² values for Kombucha Scoby were 0.996 and 0.947 and for GO-Fe₃O₄ adsorbent were 0.989 and 0.726 using the Langmuir and Freundlich isotherm models, respectively. The Langmuir isotherm model shows a higher correlation coefficient compared to the Freundlich isotherm model, suggesting that the Langmuir model has a close fitting to the experimental data. The maximum adsorption capacity (q_m) were found to be 126.6 and 114.9 mg g^{-1} for Kombucha and GO-Fe₃O₄, respectively, indicating more sorption of Pb(II) ions onto Kombucha Scoby.

CONCLUSIONS

In this study, Kombucha Scoby and GO/Fe₃O₄ were applied for Pb(II) ion removal from aqueous solution. In this case, the effect of pH, dosage of adsorbents and temperature were investigated. The sorption of Pb(II) ions

and the capacity of adsorption raised by increase in the pH, amount of adsorbents, and temperature. The sorption rate of Pb(II) onto the adsorbents was rapid and Pb(II) was eliminated by 50% within the first 15 min. The maximum removal efficiencies were obtained to be 98.08% and 99.73% for GO-Fe₃O₄ and Kombucha Scoby, respectively. The equilibrium investigation of adsorption process was done and the results showed the experimental data were well fitted with the Langmuir isotherm model due to the higher correlation coefficient. The maximum adsorption capacity was higher for Kombucha Scoby (126.6 mg g^{-1}) than that for GO-Fe₃O₄ (114.9 mg g^{-1}), therefore, the Kombucha bacteria has an excellent potential in the removal of Pb(II) from wastewater, even better than magnetic GO.

Conflict of Interests Statement: The authors declare that there is no conflict of interests.

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