Removal of Heavy Metals from Contaminated Waters by Insoluble CMC Bio-Polymer

In this project, insoluble carboxymethyl cellulose adsorbent was used for removal of heavy metals including cadmium and Pb from aqueous environments. The results showed that the maximum removal of Pb and cadmium metal ions by insoluble carboxymethyl cellulose, was observed at reaction time of 24 hours, pH 2, and initial concentration of contaminant 200 ppm. While the temperature increasing did not significantly effect on the removal efficiency of cadmium and Pb ions. Also, insoluble carboxymethyl cellulose whit the same conditions is more capable for removing cadmium ions than Pb ions.

Keywords: Chemical Water Pollution, Pb, cadmium, insoluble carboxymethyl cellulose, Water Purification.

Introduction:

Industrial wastewater, including dyeing industries, electroplating and the battery industry contains dangerous minerals and organic compounds such as aromatic compounds, phenols, heavy metals and dyes, which in some cases have very low concentrations, that often cause cancer and poisoning, so that with the advancement of these industries, the amount of contamination entering the environment also increases (Huang et al., 2011; Alloway,2013).

Heavy metals in the environment are a potential danger, because humans and animals are always exposed to these heavy metals (Godt et al., 2006; Tchounwou et al., 2012; Ahalya et al., 2003).

So far, various types of natural substances have been used as bio-adsorbents to remove metals and other pollutants in environment. Some of these compounds include: various types of bacteria, yeasts, types of aphids, some polysaccharide materials and some polymers that in different conditions for removal of pollutants and heavy metals has been used (Wuana et al., 2011). Among the various bio-adsorbents, natural materials such as cellulosic material and agricultural wastes have attracted a lot of attention due to their abundance, availability and low prices (Khan et al.,2008)

Carboxymethyl cellulose is an anionic polymer in water that is made from cellulose. In fact, this compound is one of cellulose derivatives with carboxymethyl groups

that are attached to some of the hydroxyl group of glucopyranose monomers. It is a combination of cellulose derivatives from the plants cell wall, especially flax's seed and wood. The general formula of this compound is [C6H7O2 (OH) x (OCH2COONa) y] n, where n represents the degree of polymerization, x is equal to x = 1.50 to 2.80 and y is equal to y = 0.2 to 1.50. The sum of the x and y is 3.0, where y represents the degree of succession. In Fig. 1, the chemical structure of sodium carboxymethyl cellulose is shown (Mahurpawar et al., 2011; Järup et al., 2003; Jaishankar et al., 2014; Singh et al., 2011).

Important application of carboxymethyl cellulose is its use as an effective biopolymer absorber for the removal of various pollutants and heavy metals in aquatic environments. So this compound is a biodegradable biopolymer that is a suitable absorbent for the removal of heavy metals, because in addition to the physical absorption properties, the adsorbent has the ability to remove cationic or anionic pollutants, which increases its efficiency (Gupta V., 2009)

Materials and Methods:

Alpha cellulose, monocloroacetic acid, sodium hydroxide and isopropyl used to produce industrial absorbents. Other substances are nitric acid, chloric acid and deionized water.

To prepare an insoluble carboxymethyl cellulose, 90 g of alpha-cellulose (maximum water content of 70%) were immersed in water (37% NaH) and incubated at room temperature (below 30 ° C) for 1 hour. Subsequently, the overflowed cellulose (alkaline cellulose) was filtered using filter paper and then immersed in aqueous 85% alcohol, and slowly added 7 grams of mono-chloroacetic acid dissolved in 10 grams of 99% isopropanol. The mixture was stirred for 90 minutes at 70 ° C to complete the cellulose etherization reaction. Addition of monocloroacetic acid was carried out to pH 6. Then the adsorbent was filtered and dried in oven for 12 hours at 70 ° C. The following formula was used to calculate the removal percentage.

$$R=\frac{(C_0-C_e).100}{C_0} \qquad (1)$$

Where C_0 and C_e are the concentrations of heavy metals in the primary and final states (balance state) in mg / l. In order to achieve the maximum removal of heavy metals by adsorbent, some of the parameters and their optimal amount are in Table1. It should be noted that in all experiments 200 mg of ICMC absorber and syringe separation method were used

Table1: parameters and their optimal amount

Step	Optimized level	Variable levels
First	2	pH: 2 4 7
Second	40	Tempreture (c) 25 35 40 60
Third	24	Reaction time (hour) 1 12 24 26
Fourth	syringe	Separation method filter paper syringe

RESULTS:

As the Fig. 2 shows, the carboxymethyl cellulose is very thin and fibrous fibers, which also makes the adsorbent largely porous and thus has a very high effective level for removing pollutants and heavy metals. Also, the coalescence of fibers has led to the creation of porous at absorbent surface, which can be used to capture heavy metal whit specific size. The size of these cavities was calculated in the range of 50 to 80 micrometers. In Fig. 3, the SEM image is also shown with a magnification of 5 micrometers. In which the carboxymethyl cellulose strands are well visible.

In FTIR spectrometric of carboxylated cellulose (Fig. 4), the observed peaks in the 1423, 1608, 2930, and 3420 cm-1 is related to the symmetric and asymmetric tensile vibration of the COO group, the tensile vibration of the aliphatic CH and hydroxyl group (OH). Also, the observed peak in the 1064 cm-1 also is related to the tensile vibration of the C-O bond, which is consistent with published reports (Han R et al., 2010; Bratby J et al., 2006)

Optimization of Initial concentration of heavy metals:

The initial concentration of the heavy metals (cadmium, Pb) solution have a great effect on its removal rate. Therefore, as the results shown in Fig. 5 So, four different concentrations (10, 50, 100 and 200 ppm) were tested at pH = 2, 25 ° C and 24 hours. The results showed that by increasing initial concentration from 10 to 50 ppm, the percentage of removal was increased and reached to highest level (80.50%) at 100 ppm, but by increasing to 200 ppm, removal decreased in cadmium solution (Fig 5.a)

Also results showed that by increasing the initial concentration from 10 to 50 ppm, the percentage of Pb^{+2} removal was increased and reached to its highest value (67%) at 100 ppm, but increasing concentration to 200 ppm caused reduction in adsorption Percentage to 56% (Fig. 5.b)

Base on the results, absorption of metal ions at first large spaces on the surface of the ICMC were available for the metal ion to absorb, And with passage of time, occupation of these sites by ions and their repulsive effects cause to difficult absorbtion, so the rate of absorption is lower (Han R et al., 2010; Bratby J et al., 2006). It is quite clear that the absorption rate depends on the initial concentration of the metal solution. Therefore, the optimum concentration of 100 ppm Cd and Pb solution was considered.

Optimization of pH effect

The initial pH of a heavy metal solution is known to be one of the most important operational parameters that can have a clear effect on the adsorption mechanism of heavy metals and adsorbents (Weidlich C et al ., 2001). The comparison of the pH effect and the percentage of heavy metal removal is shown in Fig. 6. Because there are many carboxylic groups on the ICMC, the initial pH of the metal ion solution will have a significant effect on its action (Malaeb L.,2011). In this study, pH values of 2, 4 and 7 were used to determine the effect of pH. The highest amount of heavy metal removal was observed at pH 2 for Cd and Pb solutions. Therefore, the optimum value for pH was considered to be 2.

Optimization of the temperature effect:

The effect of temperature on the removal of heavy metals by ICMC at various temperatures operating conditions were tested in (100 ppm metal concentration, 24 h contact time and pH = 2). The results are shown in Fig. 7. A slight increase in removal percentage was observed with increasing temperature. Whit increasing temperature, kinetic energy increases the metal ions on the ICMC surface.

Optimization of reaction time:

In this study, the effect of reaction time on the removal of cadmium ions from three different time (1, 12, 24 and 36 hours) was performed. The results are shown in Fig. 8. According to the graph, as the reaction time increases, the removal of metal ions also increases regularly. After 24 hours maximal removal reaches 91% and then remains almost constant for Cd (Goldstein J et al., 2012). Therefore, 24 hours was considered as optimal reaction time. Also for Pb after 24 hours the maximum value is 66.8 and then remains almost constant. Therefore,

Conclusion:

Highest removal efficiency occurs when using 200 ppm of contaminant concentration. To achieve the highest percentage of removal of cadmium and Pb, the pH is appropriate in acidic area and is equal to 2. Maximum ion removal Pb and cadmium metal were obtained by insoluble carboxymethyl cellulose biopolymer when used 24 hours for reaction time. The results showed that increasing temperature did not have a significant effect on increasing the efficiency of removal metal ions. And finally, carboxymethyl cellulose absorber in the same conditions is more capable for removing cadmium ions than lead ions.

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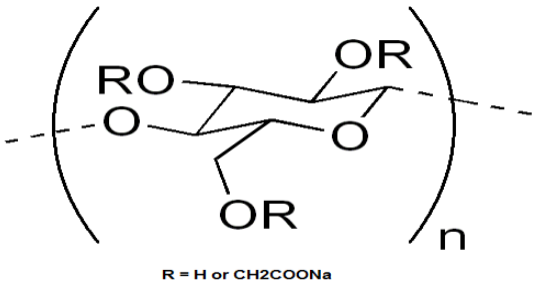


Fig. 1: structure of sodium carboxymethyl cellulose.

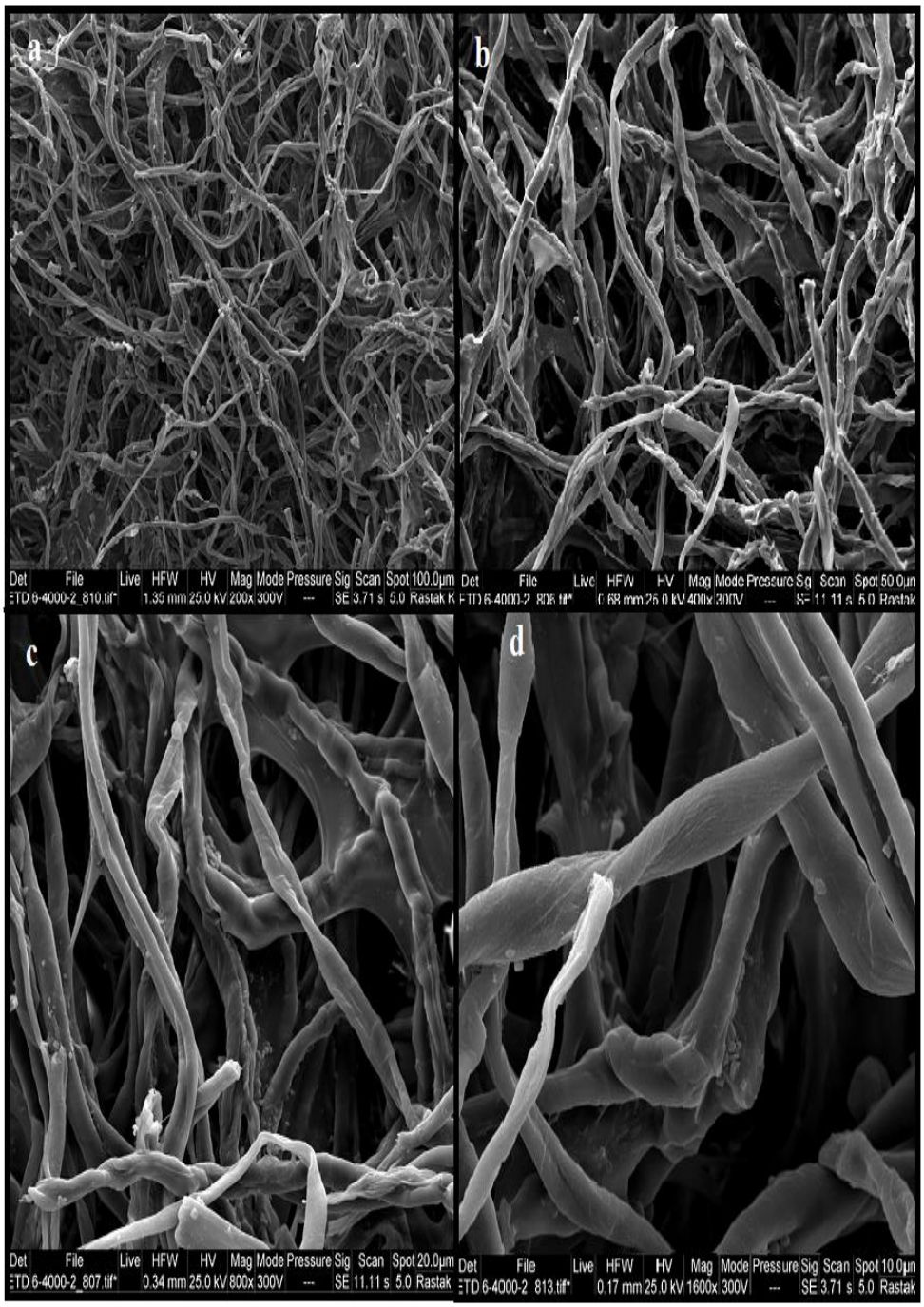


Fig 2:

SEM images with magnification (a) 100 μm (b) 50 μm (c) 20 μm and (d) 10 μm.

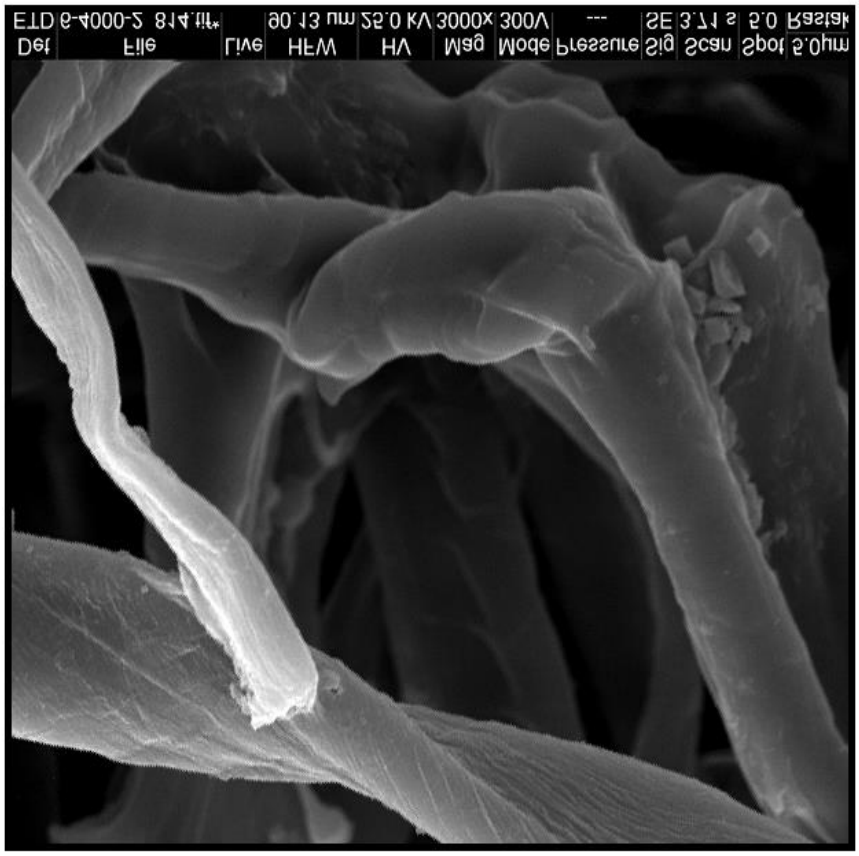


Fig 3: SEM image of insoluble carboxymethyl cellulose with a magnification of 5 μm

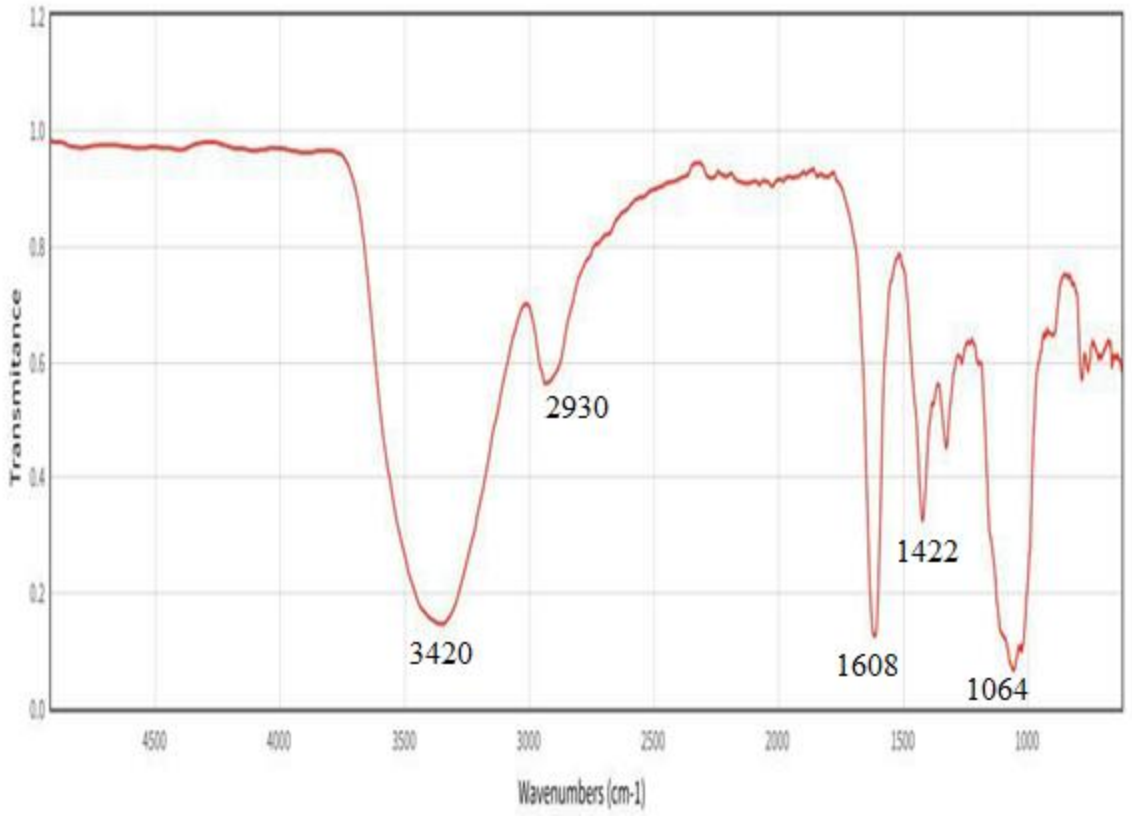
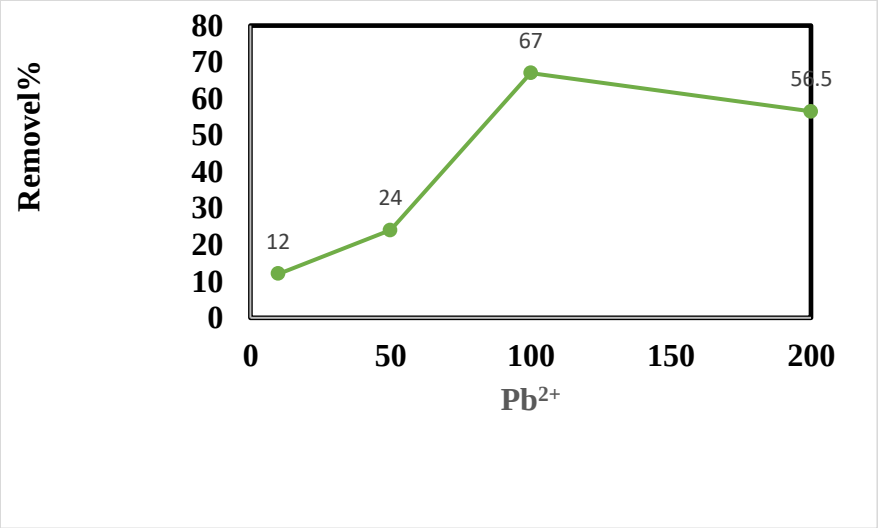
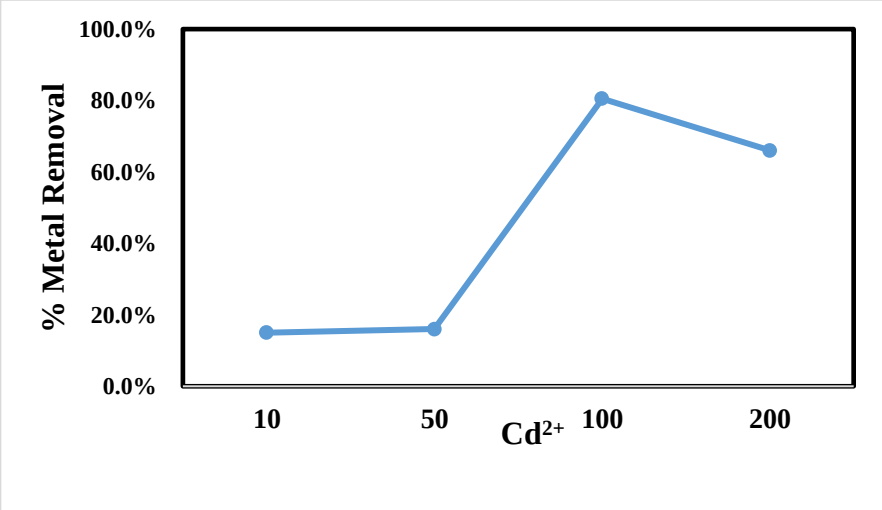


Fig 4: FTIR image from ICMC

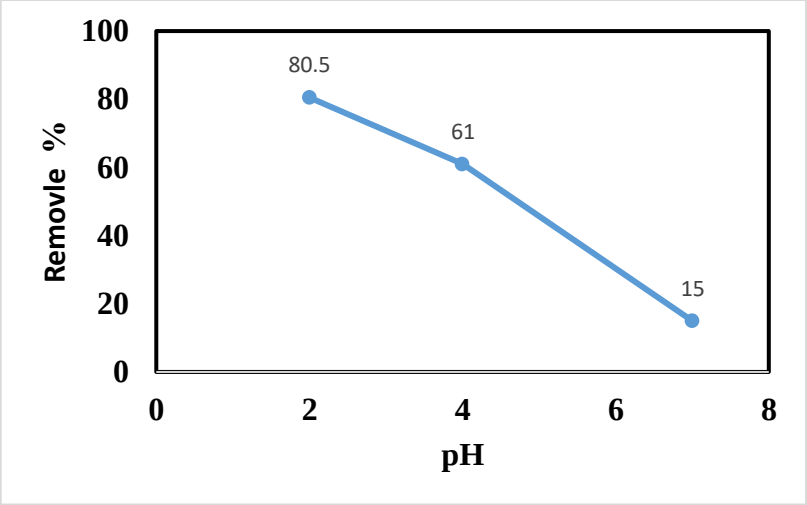


(a)

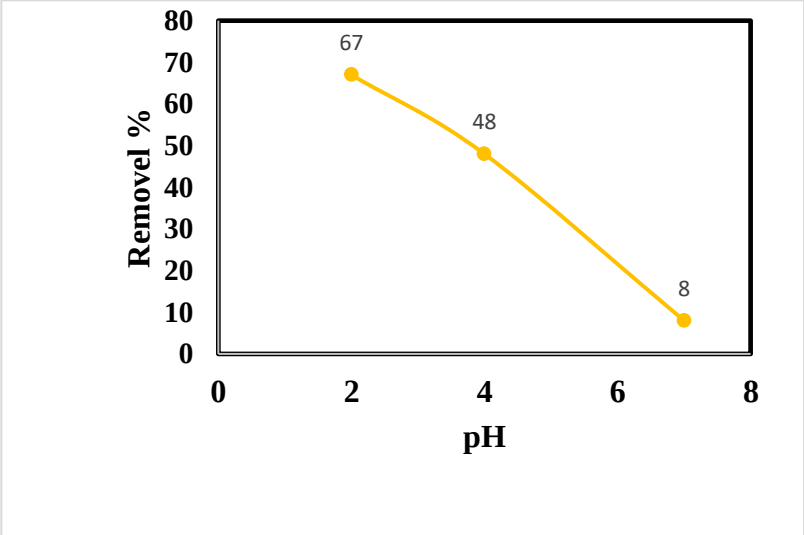


(b)

Fig. 5: Optimization of the initial concentration for Pb (a) and Cd (b) solution (test conditions: 25 ° C, pH = 2 and reaction time 24 hours).

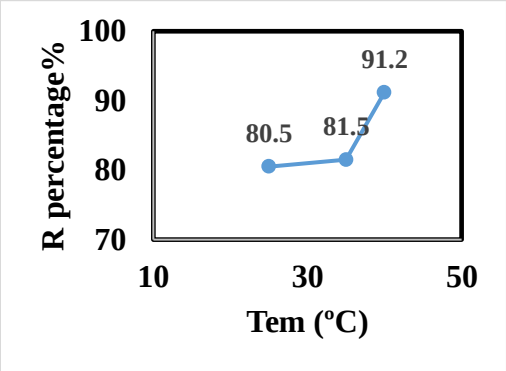


(a)

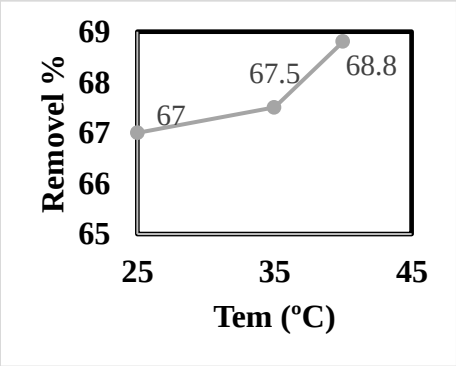


(b)

Fig 6: pH optimization for Cd (a) and Pb (b) (test conditions: 25 ° C, 100 ppm contaminant and reaction time 24 hours).

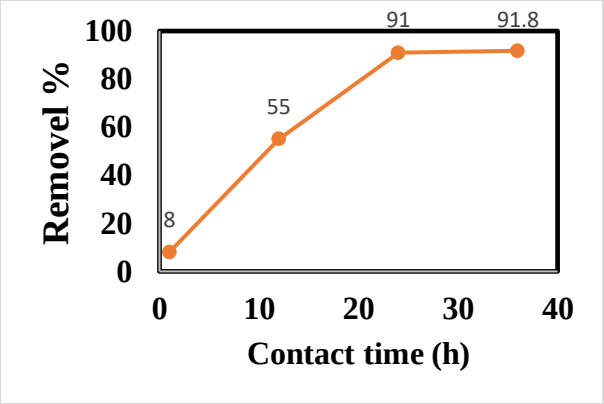


(a)

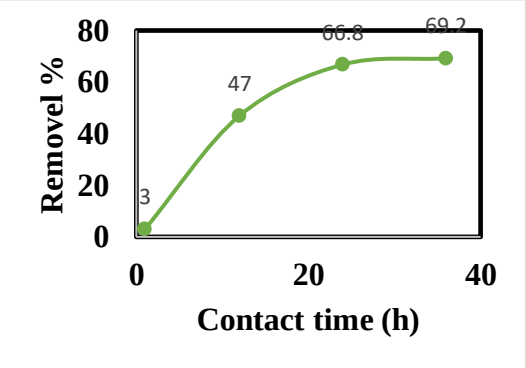


(b)

Fig 7. Temperature optimization for Cd (a) and Pb (b) (Test conditions: Cd and Pb solution concentration: 100 ppm, pH = 2 and contact duration 24 hours).



(a)



(b)

Fig. 8. Optimization for reaction time for Cd (a) and Pb (b) (test conditions: cd and Pb solution concentration: 100 ppm, pH 2 and temperature 40 ° C).