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Synthesis of nanostructured ZnO loaded on carbon cloth as high potential adsorbent for copper ion

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ABSTRACT

In this study removal of copper ion from aqueous solution by activated carbon cloth and carbon cloth loaded with nanostructured zinc oxide was investigated. Microwave assisted chemical bath deposition method as a simple and rapid method was used to deposit nanostructured ZnO onto activated carbon cloth. The deposited ZnO was characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. SEM images showed that the structure of deposited ZnO is flower like with size of 2–5 μm. XRD spectrum shows characteristic peaks of zinc oxide with crystalline size of 22 nm. The prepared ZnO-loaded activated carbon cloth was used as adsorbent for removal of copper ion from aqueous solution. The effects of the contact time, initial metal ion concentration, and pH on removal efficiency were examined. Kinetic experimental data were fitted to the pseudo-first-order and pseudo-second-order kinetic models. The equilibrium experimental results were fitted to Langmuir and Freundlich models. The maximum adsorption capacity of the ZnO-loaded carbon cloth is 769 (mg/g) which is much higher than activated carbon cloth.

Keywords: Adsorption; Copper ion; Activated carbon cloth; Nanostructure; Zinc oxide

1. Introduction

Heavy metal ions are released into environment by different industries. Heavy metal ions such as Cu^{2+} can be deleterious for health when exceed permissible level. Although Cu^{2+} has important role in metabolism, heart and blood vessels [1], but its excess intake, can cause hemolysis, intestinal irritation, hepatotoxic, and nephrotoxic effects [2,3]. The accumulation of Cu^{2+} may lead to brain, skin, pancreas, and heart diseases [4]. Copper is a widely used metal in industry including: electroplating, mining and metallurgy, paints and dyes, petroleum refining, explosives, pesticides, iron and steel industries [1,2].

In order to achieve environmental detoxification and remove heavy metals, various techniques including, chemical precipitation [5], membrane filtration [6], electrochemical technologies [7], adsorption, and ion exchange [8], are commonly used. But adsorption is one of the most efficient techniques for removal of heavy metals ions from water [9,10].

Some of materials, such as activated carbons [11,12], chelating materials [13], chitosan [14], sugarcane bagasse [15], and metal oxides [16] have been used to adsorb metal ions from aqueous solution. Compared with traditional materials, nanosize metal oxides have great removal efficiency of heavy metal

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ions in wastewater due to their higher surface areas and much more surface active sites [17,18]. Recently, ZnO gained researcher attention because of photocatalytic activity, chemical stability, and biocompatibility. Furthermore it is nontoxic and inexpensive metal oxide [19,20].

Numerous methods including hydrothermal [21,22], solvothermal [23], chemical vapor deposition [24,25], electrochemical deposition [26,27], and microwave irradiation [28] have been developed for preparation of nanostructured ZnO. Microwave-assisted chemical bath deposition (MACBD) is one of the methods to prepare nanostructured ZnO as a simple and fast technique. This method can produces ZnO nanostructures with various morphologies including rods, flower-like, wires, and sheets [29]. ZnO nanostructures can be grown on any hard or flexible substrate, such as Si, plastic, glass, paper, etc.

Carbonaceous materials such as activated carbon is the most commonly used adsorbent for water treatment [30,31]. They have large specific surface area and different surface functional groups [32,33].

The purpose of the present work is to prepare nanostructured ZnO loaded on carbon cloth as a novel and high potential adsorbent for removal of copper ion from aqueous solution.

2. Materials and methods

Activated carbon cloth (CH-700-15) was supplied from Kuraray chemical Co. Ltd. Japan. Acetic acid was purchased from Panreac Co. The other chemical materials were supplied from Merck Co. including: $CuSO_4 \cdot 5H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$, NaOH, HCl.

Recently MACBD method was used to prepare nanostructred ZnO as powder [29] and as thin film on glass [34]. In this work we used the same method but for preparation of ZnO-loaded activated carbon cloth. Briefly, the precursor solution of zinc acetate dihydrate as the zinc cation source and ammonium hydroxide as the anion precursor was used to synthesize ZnO nanostructure. For this purpose, 1.832 g of zinc acetate dehydrate was dissolved in 50 mL deionized water. Then NH_4OH (5N) was added slowly to the solution under magnetic stirring at constant temperature (30℃). Adding NH_4OH to aqueous solution at first, produced curd white precipitate. More ammonium hydroxide was gradually added until the white precipitate was dissolved and a clear solution resulted.

The pH of obtained solution was adjusted to 9.8 by adding CH_3COOH. In this stage the activated carbon cloth was put in to the solution and the beaker was transferred in to the microwave oven (Moulinex, MW 200130, 2450 MHz).

The precursor solution was heated in microwave oven at 700 W for four steps. Each step include 30s irradiation and 10s off. After irradiation the beaker was remained in oven for 10s and then transferred to water bath at room temperature for 10 min. The activated carbon cloth was separated from the solution, then washed with distilled water and finally dried in an oven at 60℃ for 60 min.

All adsorption experiments were carried out at 25.0 ± 0.1℃. Initial solutions with different concentrations of Cu ions were obtained by dissolving copper sulfate in deionized water.

The concentrations of Cu ions in aqueous solution were measured by a UV/visible spectrophotometer (PG Instrument Ltd., London, UK, Model T80) at $\lambda = 600$ nm by complexometric method using Zincon indicator [35]. A pH meter (Corning–140) was used to measure the pH of solution.

For equilibrium experiments, Cu ion solutions with different concentrations (between 20 and 270 ppm) were prepared. Then 0.015 g of adsorbent (ACC, ACC loaded with ZnO nanostructures) was added to 15 mL of the solution and the samples were agitated using shaker (n–Bio TEK, Korea) at 150 rpm for 24 h. Then, adsorbent was separated from the solutions and the residual concentration of Cu ion in the solutions was determined. Adsorption amounts per unit mass of adsorbent (q_e) were calculated by:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of Cu ions in the aqueous solution (mg/L), respectively. V is the volume of the solution (L), and m is the mass of adsorbent (g).

For kinetic studies a series of 15 mL of Cu^{2+} solutions with equal concentrations were contacted with 0.015 g of adsorbent (ACC or ACC loaded with nanostructured ZnO) and the samples were shaken by shaker in a water bath. At different time intervals, the concentration of Cu^{2+} in the solution (C_t) was monitored by UV/visible spectroscopy. The amount adsorbed per unit mass of adsorbent at any time (q_t) was calculated by:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{2}$$

For measuring the point of zero charge pH of adsorbent, the experiment performed using a series of the water solutions with different initial pH value in range of 3–10. The solutions (10 mL) were allowed to contact with known weight of adsorbent (0.025 g) and agitated for 24 h. Then the final pH was measured with a pH meter [36].

The effect of solution pH on the adsorption efficiency was investigated in solutions with similar concentration of Cu^{2+} (300 ppm) but different pH values in range (3–5.5). Then 0.015 g of adsorbent was put in Cu (II) solutions (15 mL) and solutions were agitated for 180 min. The removal percentage ($R\%$) was calculated as:

$$R\% = \frac{C_o - C_e}{C_o} * 100 \tag{3}$$

3. Result and discussion

Both adsorbents were characterized by X-ray diffraction (XRD) (Italstructure ADP2000) and scanning electron microscopy (Cam scan-MV2300) methods. The XRD patterns of the ACC and ZnO-loaded ACC are shown in Fig. 1(a) and (b), respectively.

In Fig. 1(a), three diffraction peaks appeared at $2\theta = 13.8°, 16.8°$, and 25.2° that can be related to the graphitic structures of the activated carbon cloth.

The x–ray diffractograph of ZnO loaded onto ACC is shown in Fig. 1(b). In this XRD pattern the appeared peaks at $2\theta = 31.9°$, 34.6°, 36.4°, 48°, 56.6°, and 63.2° are the characteristic peaks of ZnO [34] and confirm the formation of ZnO on ACC. By using of XRD data and Shearer equation the crystalline size of ZnO was obtained as 22 nm.

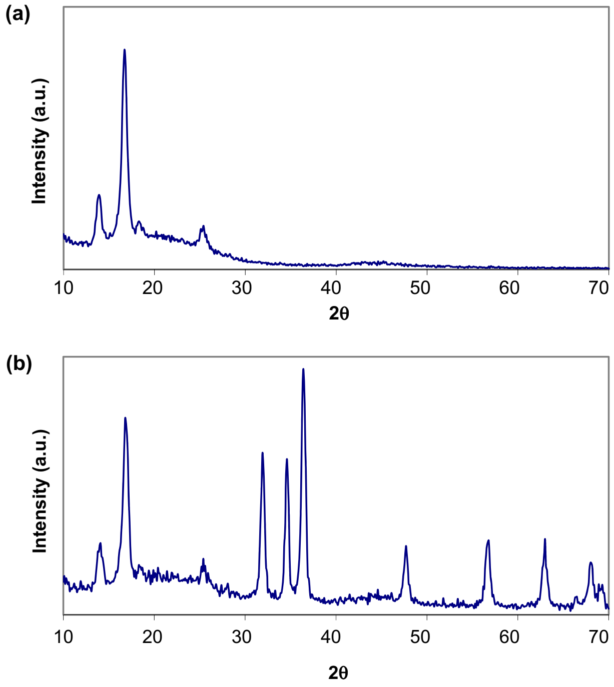

Fig. 1. XRD patterns of (a) ACC and (b) ACC loaded with ZnO.

The morphology of the ZnO loaded onto ACC has been investigated by transmission electron microscopy (SEM). Fig. 2(a) shows the SEM image of ACC that the warps and woofs of cloth are clear. The SEM micrograph at two different scales for ZnO loaded onto ACC has been shown in Fig. 2(b) and (c). The image show that the ZnO deposited onto ACC are flower like of size 2–5 μm with tapered spines petals around a central rod. These results are in agreement with previous reports [29,34].

The equilibrium adsorption of Cu^{2+} on ACC or ACC loaded with ZnO as a function of the equilibrium concentration of Cu ions is shown in Fig. 3. It is observed from the Fig. 3 that adsorbed amounts of Cu^{2+} increases with concentration until the saturation is attained. The results in this figure clearly show that ACC has no affinity for adsorption of Cu^{2+}, while ACC loaded with ZnO has very high affinity for adsorption of copper ion from aqueous solution.

Analysis of equilibrium data and interaction between the adsorbate and adsorbent can be described by adsorption isotherms. In this study Langmuir and Freundlich models were used to correlate the experimental data.

The Langmuir model is applied in cases where monolayer adsorption occurs on homogeneous surface. The linear form of Langmuir model is given by following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{4}$$

where C_e is the equilibrium concentration of Cu^{2+} in solution (mg/L), q_e is the amount of copper ion adsorbed per unit mass of adsorbent (mg/g), and K_L is the Langmuir constant. Freundlich adsorption isotherm is an empirical model and describes adsorption on heterogeneous surface. The linear form of this equation is:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{5}$$

where K_F and n are Freundlich constants that n related to heterogeneity of surface.

The obtained equilibrium data were fitted to the above equations and the results were listed in Table 1.

Based on r^2 values it can be concluded that the adsorption of Cu ions onto ACC was correlated with

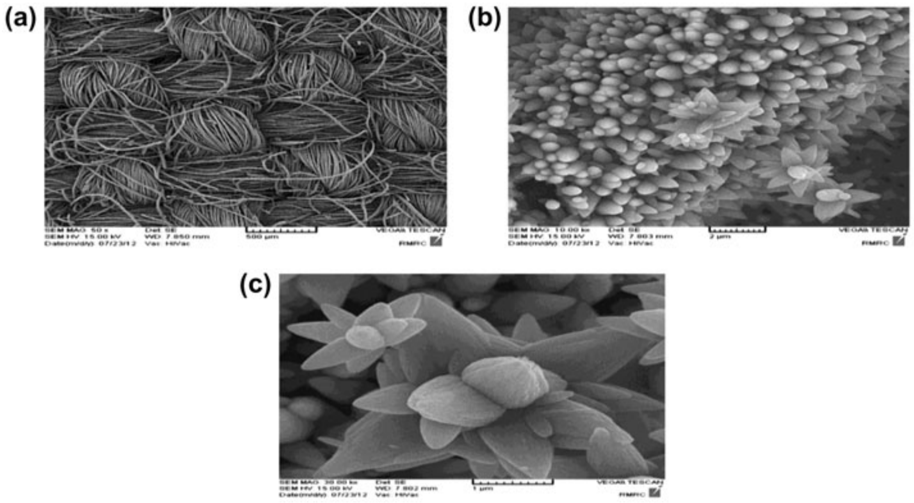

Fig. 2. Scanning electron micrographs of (a) ACC, (b) and (c) ZnO loaded onto ACC with different magnification.

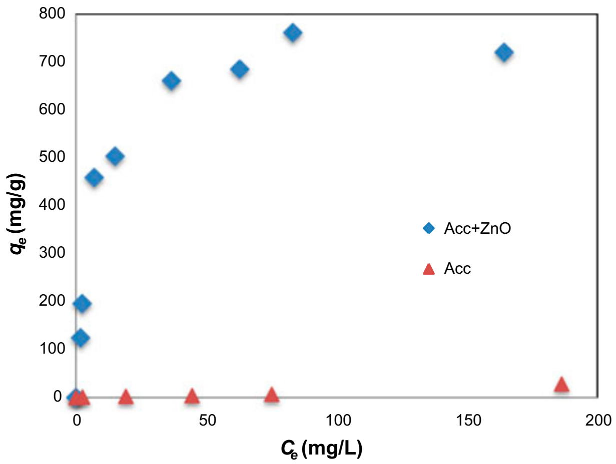

Fig. 3. Equilibrium data for adsorption of Cu^{2+} adsorption on ACC and ACC loaded with ZnO.

Freundlich equation and the equilibrium data of Cu^{2+} adsorption on ZnO loaded onto ACC is fitted better with Langmuir isotherm. This means that the active sites for adsorption of Cu^{2+} on ZnO are homogeneous. These active sites are hydroxyl groups on ZnO surface [34].

The maximum adsorption capacity (q_m) of ZnO loaded onto ACC for copper ion is 769 mg/g. The values of q_m for this adsorbent and other reported adsorbents, are listed in Table 2 for comparison. The adsorbent prepared in this study exhibit higher adsorption capacity compared to other adsorbents.

Kinetic experiments were carried out to obtain the time required for the adsorption of Cu ions from aqueous solution to reach equilibrium. Adsorption kinetic data of Cu^{2+} at different initial concentrations for two adsorbents (ACC and ACC loaded with ZnO nanostructure) are presented in Fig. 4. It is evident from this figure that the removal efficiency of Cu ions increases with time and attained equilibrium after about 120 min. No significant increases in adsorbed Cu^{2+} observed after this time. It is clear that the adsorption of Cu^{2+} increases with its initial concentration. The adsorption rate is higher at the beginning, which is probably due to availability of large number of adsorption sites. Furthermore the rate of adsorption for ZnO/ACC is noticeably higher than for ACC.

Table 1
Obtained Langmuir and Freundlich constants for Cu^{2+} adsorption

	Langmuir isotherm			Freundlich isotherm		
Adsorbent	K_L (L/mg)	q_m (mg/g)	R^2	K_F	$1/n$	R^2
ACC	0.0009	152	0.018	0.983	0.73	0.901
ZnO-ACC	0.163	769	0.997	150	0.37	0.847

Table 2
The maximum adsorption capacity (q_m) of different adsorbents for Cu^{2+}

Adsorbent	Maximum adsorption capacity (mg/g)	References
ZnO (nanoparticles)	137.5	[17]
ZnO (nanoplate)	315.6	[37]
CuO (nanoparticles)	54.10	[17]
Goethite (needle like)	149.25	[38]
Fe_3O_4 (nanoparticles)	14.70	[17]
Hematit (α-Fe_2O_3)	84.46	[16]
Activated carbon prepared from rice husk	112.43	[39]
Chitosan-coated PVC beads	87.92	[40]
Treated rubber (*Hevea brasiliensis*) leaves powder	14.97	[41]
Sugarcane bagasse	114.0	[42]
ZnO loaded onto ACC	769	This work

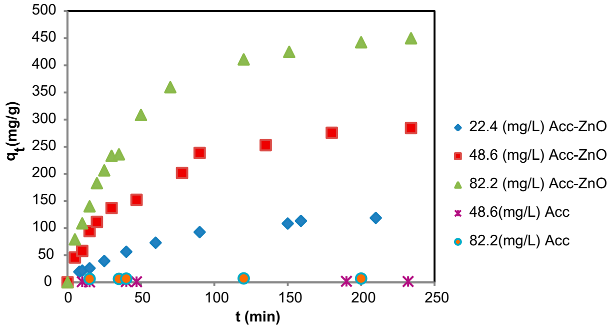

Fig. 4. Effect of contact time on adsorption of Cu ions on two adsorbents: ACC and ACC loaded with ZnO nanostructure.

The kinetic data at different initial concentrations were fitted by the pseudo-first order and second order kinetic models [43].

The pseudo-first-order equation is based on the assumption that the adsorption rate is proportional to the number of vacant sites. The rate equation of pseudo-first-order equation is [43]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

where q_e is the amount of Cu ions adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}) and k_1 is the pseudo-first-order rate constant (min^{-1}) while the other parameters were explained previously. The integrated and linear form of pseudo-first-order equation is given as:

$$\ln\left(1 - \frac{q_t}{q_e}\right) = -k_1 t \tag{7}$$

Another useful kinetic model for adsorption is pseudo-second-order model. Based on the pseudo-second-order equation the adsorption rate is linearly related to the square of the number unoccupied sites. The rate equation of pseudo-second-order equation is [43]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

This equation is integrated and transformed in its linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where k_2 is the pseudo-second-order rate constant.

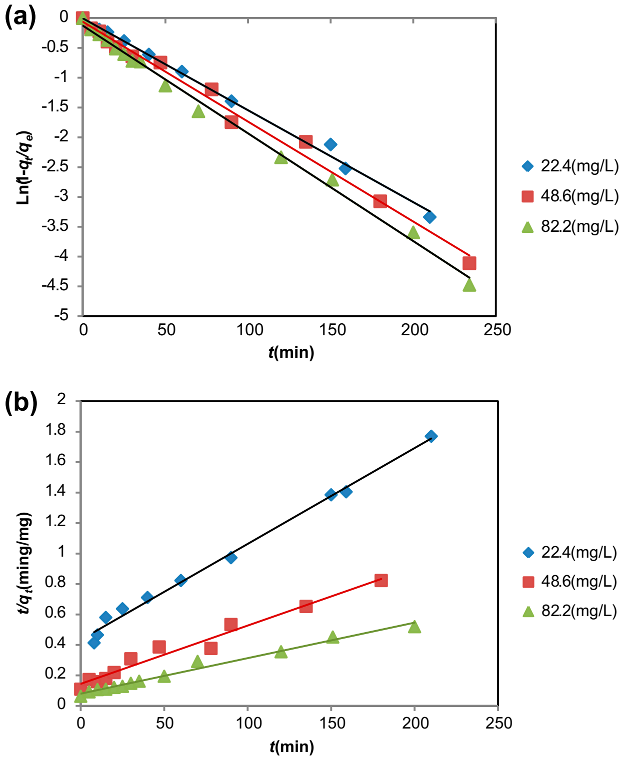

Fig. 5. The linear plots of (a) pseudo-first-order and (b) pseudo-second-order models for Cu^{2+} adsorption onto ZnO/ACC at different initial concentrations.

Table 3
The pseudo-first-order kinetics model constant for two adsorbents

ZnO-ACC				ACC0			
C_o (mg/L)	q_e (mg/g)	k_1 (min^{-1})	r^2	C_o (mg/L)	q_e (mg/g)	k_1 (min^{-1})	r^2
22.4	123.0	0.015	0.995				
48.6	289.0	0.016	0.990	48.6	2.5	0.003	0.683
82.2	455.0	0.018	0.995	82.2	10.0	0.001	0.456

Table 4
The pseudo-second-order kinetics model constant for two adsorbents

ZnO-ACC				ACC			
C_o (mg/L)	q_e (mg/g)	k_2 (g/mg min)	r^2	C_o (mg/L)	q_e (mg/g)	k_2 (g/mg min)	r^2
22.4	158.7	0.00009	0.992				
48.6	263.2	0.0001	0.971	48.6	1.7	0.0265	0.996
82.2	434.8	0.00007	0.985	82.2	7.0	0.0893	0.998

The linear plots of pseudo-first-order and pseudo-second-order models for copper ion adsorption onto ZnO/ACC at different initial concentrations are shown in Fig. 5.

The result of fitting for two adsorbents based on pseudo-first-order and pseudo-second-order kinetic models are listed in Tables 3 and 4, respectively. Based on the obtained correlation coefficients (r^2), the experimental data for ACC at different initial concentration of Cu ions follow pseudo-second–order kinetic model and for ACC loaded with ZnO follow pseudo-first-order kinetic model.

Determination of the point of zero charge pH (pHPZC) is important to describe mechanism and influence of surface properties of the adsorbent. The surface of adsorbent is neutral at pH_{PZC}. In this study the point of zero charge for two adsorbent are determined from Fig. 6(a) and (b) where the final pH is plotted vs. the initial solution pH. From this curve, the pH_{PZC} values of ACC and ZnO loaded onto ACC are about 6.7 and 7.1, respectively.

It is well known that solution pH has strong influence on the adsorption of metal ions [41]. In this section the effect of pH on the adsorption of Cu ions by the prepared adsorbent was studied. The changes in the removal percentage as a function of solution pH are presented in Fig. 7.

It can be observed that in strong acidic solutions the removal percentage decreases, because of competition between H^+(aq) and Cu^{2+}(aq) and also repulsion between positive surface charge and Cu^{2+}. This decrease can be explained based on complexation

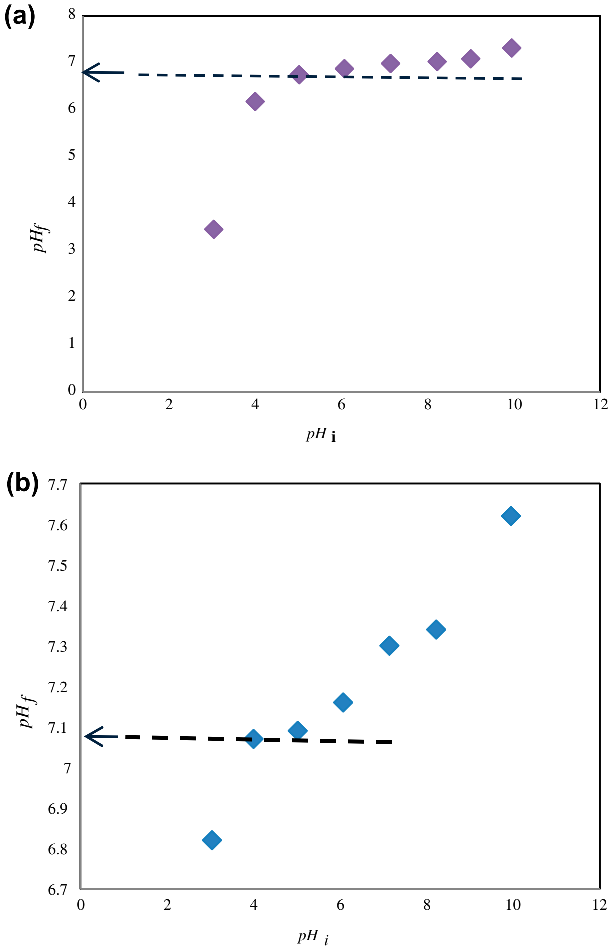

Fig. 6. Plot of final pH as a function of the initial solution pH for (a) ACC and (b) ACC loaded with ZnO.

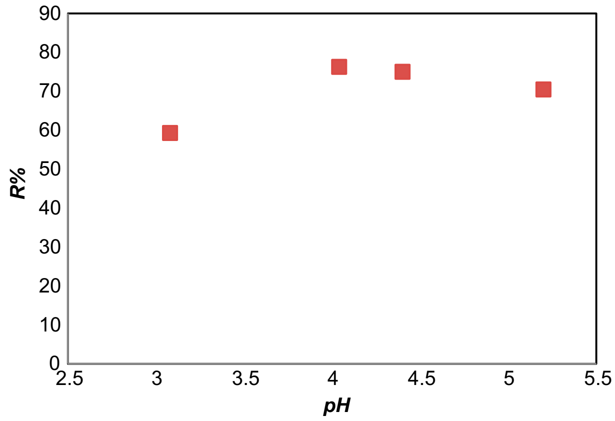

Fig. 7. Effect of pH on removal percentage of Cu ions from aqueous solution with ZnO loaded onto ACC.

mechanism too [34]. The active sites of ZnO in the presence of H2O are hydroxyl groups [37] and therefore based on complexation mechanism, the following mechanism can be suggested for copper ion adsorption by ZnO:

$$\text{Zn-OH} + \text{Cu}^{2+} \rightleftarrows \text{Zn-OCu}^{+} + \text{H}^{+}$$

Therefore by increasing of H^+ concentration (decreasing pH) the equilibrium shifts to the left side and adsorption of Cu^{2+} decreases.

4. Conclusion

In this work nanostructured flower-like ZnO was deposited onto activated carbon cloth which is then used as adsorbent for removal of Cu ions from aqueous solution. The main advantages of this synthesis method are simplicity, low cost, and rapid preparation.

Characterization of adsorbent using SEM and XRD methods show that pure ZnO loaded onto ACC is flower-like, with size of 2–5 μm and crystalline size of 22 nm.

The maximum adsorption capacity for copper ion is 769 mg/g which is among the highest reported values.

The present study shows that by loading of activated carbon cloth with ZnO, the very poor adsorbent (ACC) for Cu^{2+}, is converted to an excellent adsorbent.

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