Arsenic removal from synthetic waste water by CuO nano-flakes synthesized by aqueous precipitation method

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ABSTRACT

Arsenic contamination in the drinking water is a serious issue affecting health of inhabitants of developing countries like India and Bangladesh and needs cost effective solutions. The nanomaterials having large surface area per unit volume could be useful adsorbent for water arsenic decontamination. The CuO nanomaterial synthesized by aqueous precipitation method. The obtained nanomaterial suspension sonicated for 15 min before centrifugation at 5,000 g for 10 min. Thoroughly washed and overnight dried pellets at 60°C characterized by scanning electron microscope revealed nanoflakes structure of the pellets. The copper nanoflakes (CONF) have monoclinic CuO structure in XRD analysis. The kinetics of arsenic adsorption determined by varying arsenic content and dose of adsorbent for a period of 1 h revealed second order adsorption kinetics. The synthesized nano-flakes have potential application for arsenic removal from water well below safe limit.

Keywords: Adsorption; Aqueous precipitation method; Arsenic; Copper oxide; Nanoflakes

1. Introduction

Presence of arsenic in drinking water even in very low concentration leads to adverse health effects in inhabiting human population [1]. Arsenic has been found to be present in both surface water and ground water in several countries across the globe. The surface water is mainly contaminated by arsenic due to the mixing of agriculture run off containing organ arsenic pesticides whereas ground water contamination arises due to the dissolution of arsenic minerals presents in the deep earth crust and percolation of excessively used pesticides. According to World Health Organization, maximum permissible limit of arsenic in drinking water is 10 µg/L. In India, Gangetic belt have been shown to be very high in arsenic content in ground water in India. It is a challenge for the scientific community to provide safe water to all, especially the severely affected poor population in the developing countries [2,3].

There are several methods for removal of arsenic from water e.g., precipitation [4], membrane separation, ion exchange, and adsorption [5–8]. All the methods are associated with some limitations. The precipitation process produces large amounts of toxic sludge posing serious environmental contamination problem [9,10]. Arsenic (V) is efficiently removed by membrane separation process. So, Arsenic (III) should be converted to Arsenic (V) by apply oxidation steps for Arsenic (III) contaminated. However, oxidizing agents adversely deteriorates membranes quality and durability [11]. Again Ion exchange is useful for As (V) removal but suffers limitations like strong competition from

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co-existing anions [12]. In comparison to above mentioned methods adsorption process is easy to operate, cost effective and well suitable for individual homes of the developing countries. The adsorbents tested for the arsenic removal from drinking water include activated alumina, iron oxide, mixed metal oxides, resin, and modified fibers [13–18]. Further, nanosized adsorbent prepared from metal oxides/hydroxides with high surface area per unit volume could enhance arsenic adsorption [19–23].

The present investigation deals with the synthesis of copper oxide nanoflakes by solution combustion method, their characterization and kinetic study for the arsenic adsorption potential.

2. Material and methods

2.1. Chemicals

High purity copper acetate, glacial acetic acid and sodium hydroxide (Merck) were used as such without further purification. Reference arsenic standard solution of 1,000 μg/ml (Accu Standard) was diluted for preparing various initial concentrations for Arsenic in double distilled water as per experimental requirements.

2.2. Preparation of CONF

CONF was synthesized through aqueous precipitation method in two sets simultaneously under same experimental conditions. In brief, the copper acetate monohydrate solution (300 ml, 0.02 M) was taken in a 500 ml flask in and a small quantity of glacial acetic acid (1 ml) was added to avoid hydroxylation of Cu^{2+} ions. The solution was continuously stirred with the help of a magnetic stirrer and aqueous NaOH (1 M) was dropped from a burette in this solution until the appearance of a great quantity of black precipitate [24].

The precipitate generally appears when pH value reaches in between 9 and 11 at room temperature. After appearing of the precipitate, stirring of reaction mixture was continued for the next 20 min at 32°C followed by centrifugation at 5,000 g for 10 min to separate the precipitate in one set. The other set was subjected to the sonication for next 20 min followed by centrifugation to separate precipitate. The precipitate was washed with double distilled water and dried at 60°C overnight.

2.3. Characterization of CONF

Prepared CONF was characterized by an X-ray powder diffractometer (XRD) (Rigaku Japan) fitted with a curved crystal monochromatic in diffracted beam operating at 40 kV and 140 MA. Powder X-ray data was collected in 2θ range in between 20° and 80° at a scan rate of 2°/min and scan step 0.02°. The diffraction pattern was indexed by comparisons with the JCPDS files. The XRD pattern of CONF has been presented in Fig. 2.

The SEM analysis of CONF was done using Zeiss EVO 18 scanning electron microscope. An accelerating voltage of 10 kV and magnification of 1,000X was applied. The Fourier transform infrared (FTIR) spectrum of the prepared material was recorded with a NEXUS-870 FTIR spectrometer in the range of 4,000–400 cm^{-1}.

2.4. Arsenic adsorption experiments

The kinetics adsorption on the Arsenic was investigated using different initial arsenic concentrations (10, 20, 30, 40, and 50 μg/mL), with 0.71 g/100 ml of adsorbent and a total solution volume of 100 ml in 250 ml flask at a pH 7 and at 120 rpm. Aliquots (0.5 ml) were withdrawn at regular intervals and the concentration of arsenic was determined by atomic absorption spectrophotometer (Perkin Elmer,
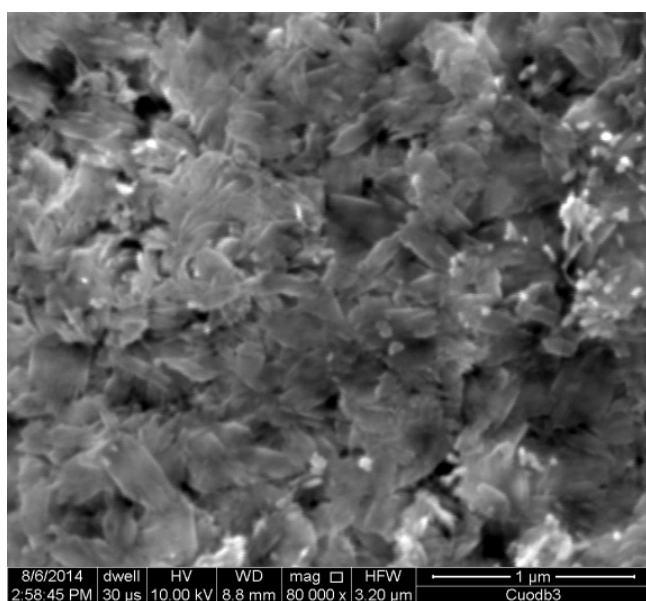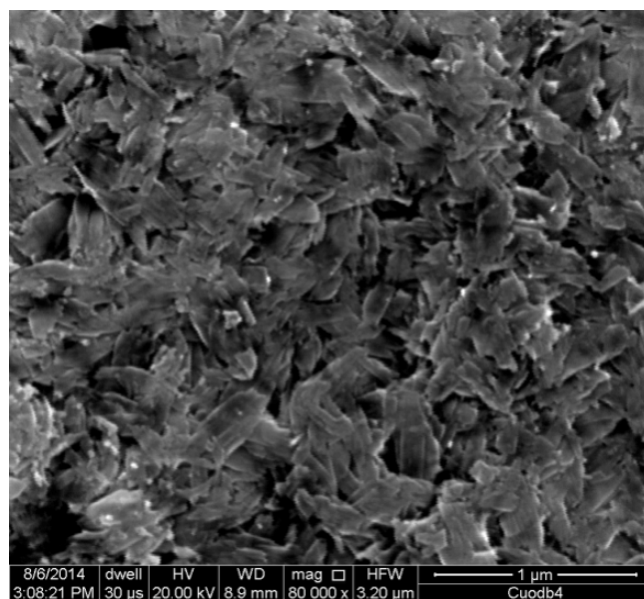
Fig. 1. SEM images of (a) unsonicated, (b) sonicated CONF, respectively.

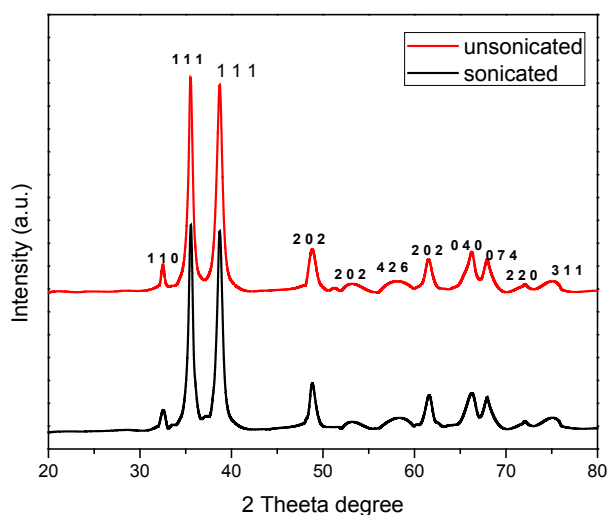Fig. 2. XRD analysis of the dried unsonicated and sonicated CONF, respectively.

Fig. 3. FTIR spectrum of the unsonicated and sonicated CONF.

AAnalyst 800). The adsorption capacity at equilibrium is given by:

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

where C_o and C_e represent the initial and equilibrium arsenic concentrations (µg/L), respectively, V is the volume of the arsenic solution (mL), and m is the amount of adsorbent (g). The variable doses (0.353–3.53 g/L) of adsorbent were immersed in 100 ml and shaken (120 rpm for 4 h) to achieve equilibrium.

3. Results and discussion

3.1. SEM analysis of CONF

The surface scanning of the dried CONF have not shown any visible differences in morphology. SEM micrograph of sonicated and unsonicated CONF are shown in Figs. 1(a) and (b), respectively. The dried CONF have an average width of ~78 nm and length 150 nm with curved and serrate margins as shown in Fig. 1(b).

3.2. Structural analysis of CONF

The XRD pattern of the dried CONF powder is illustrated in Fig. 2. The diffraction peaks at 2θ = 32.612, 35.576, 38.816, 48.812, 53.468, 58.376, 61.70, 66.26, 68.024, 72.428 and 75.272 correspond to the primary diffraction of the (1 1 0), (1 1 1), (1 1 1) (2 0 2), (2 0 2),(4 2 6) (2 0 2) (0 4 0) (0 7 4) (3 1 1) (2 2 0) and (3 1 1) planes of the CuO, respectively.

3.3. FTIR analysis

The FTIR analysis of CONF showed five peaks on different wave numbers like 3,480.1, 2,344.0, 1,502.5, 1,362.2 and 5,19.6 cm⁻¹ in unsonicated CONF. The peaks retained almost similar position in the sonicated CONF with minor shift in
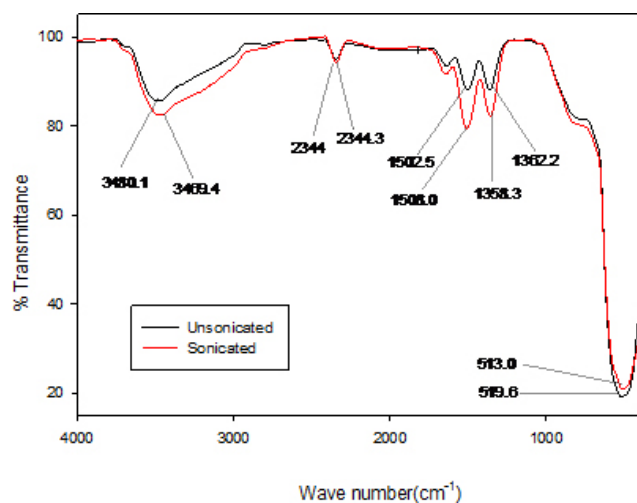

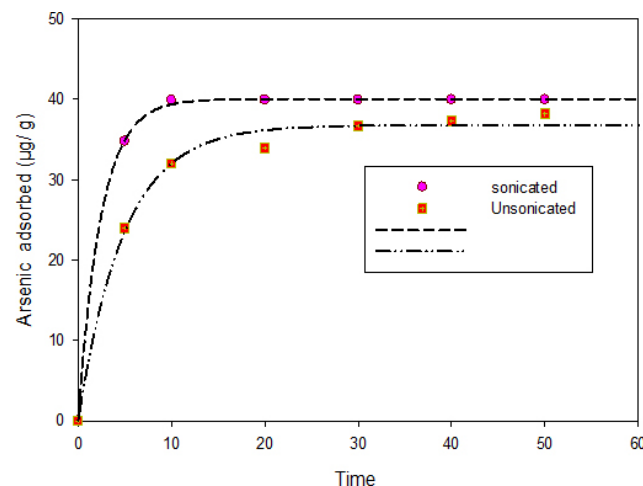
Fig. 4. Kinetics of arsenic removal by the CONF at initial concentrations: 40 mg/L, for adsorbent dose: 3.35 g/500 ml, pH: 7 ± 0.2, temperature: 32°C.

their position 3,469.4, 2,344.3, 1,508.0, 1,358.3, and 5,13.0 cm⁻¹, respectively (Fig. 3). There are reports regarding similar peaks of FTIR of copper nano particles at 3,442, 1,631, 1,019, and 517 cm⁻¹ corresponding to functional groups such as hydroxyl (O-H), ether (C-O), O-C-O, Cu-O, and group respectively [25]. A strong and broad band in 3,600–3,100 cm⁻¹ region is assigned to O–H bond stretching.

3.4. Kinetics of adsorption

The adsorption kinetics of arsenic on the CONF at various initial concentrations was investigated. Fig. 4 shows the change of adsorbed arsenic as a function of contact time. The adsorption of Arsenic was quick in the sonicated CONF compared to unsonicated CONF and needed less time to reach equilibrium. Over 90% of the equilibrium adsorption capacity of sonicated CONF was achieved within 10 min, while about 1 h was needed for to reach 80% of the equilibrium adsorption capacity of unsonicated CONF.

To further quantify the changes of arsenic adsorption with time on the CONF, the pseudo-first-order and pseudo-second-order kinetic models were used to simulate the kinetics (Figs. 5 and 6). The kinetics parameters were obtained by fitting the experimental data and are summarized in Table 1. According to the values of regression coefficients (R^2), the experimental data fitted the pseudo-second-order model better than the pseudo-first-order model for As. The rate constant (k_2) of the pseudo-second-order equation
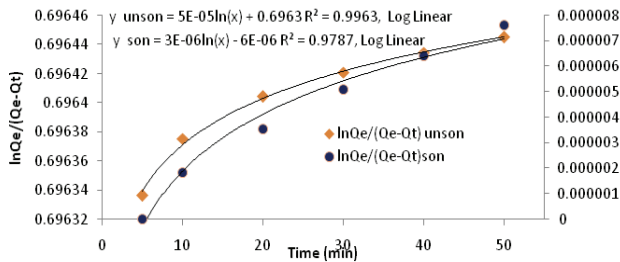
decreased with increasing initial arsenic concentration, indicating that arsenic adsorption might be more favorable at low solute concentration. Meanwhile, the values of sonicated CONF k_2 were higher than those of Unsonicated CONF under the same experimental conditions, confirming better As removal by the former compared to the latter.

Note that k_1 is the adsorption rate constant for pseudo-first order reaction (1/min); k_2 is the rate constant for pseudo-second order reaction (g/(mg min)). Q_e and Q_t are the amounts of solute adsorbed at equilibrium and at any time t (mg/g), respectively.

$C_{initial}$ is the initial concentration of arsenic (mg/L); $Q_{e,max}$ represents the maximum adsorption capacity of arsenic (mg/g); $Q_{e,0.01}$ (mg/g) is the adsorption capacity of arsenic at the arsenic equilibrium concentration of 0.01 mg/L. The effect of varying pH of water on the arsenic removal is presentd in Fig. 7.

Fig. 5. Adsorption of arsenic by the CONF for kinetic models.

Fig. 6. Adsorption of arsenic by the CONF for kinetic.
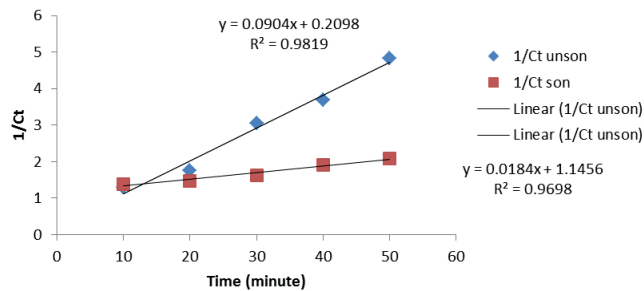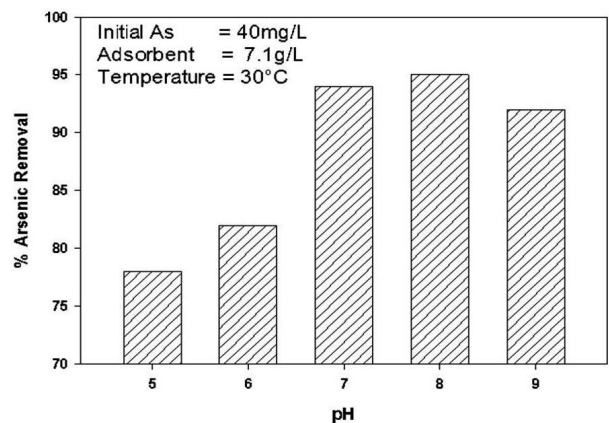
Fig. 7. Arsenic removal (%) at various pH of waste water contaminated with arsenic.

Table 1
Kinetics parameters for arsenic adsorption on the CONF

Treatment	Initial concentration	First order kinetics $\ln(Q_e - Q_t) = \ln Q_e - k_1 t$			Second order kinetics $\dfrac{t}{Q_t} = \dfrac{1}{k_2 Q_{e2}} + \dfrac{t}{Q_e}$		
		k_1 min^{-1}	Q_e (mg g^{-1})	R^2	k_2 (g/mg min)	Q_e (mg g^{-1})	R^2
Sonicated	40 mg/L				0.0013	5.65	0.978
Unsonicated	40 mg/L	0.0030	5.62	0.996	–	–	–

Table 2
Comparison of different granular adsorbents used for arsenic removal from water

Adsorbent	$C_{initial}$ (mg/L)	$q_{e,max}$ (mg/g)	$q_{e,0.01}$ (mg/g)	pH	Reference
TiO$_2$: granular	80	41.4	<3.0	7.0	[26]
Polyaluminum granulate	280	14.85	<0.07	7.5	[27]
Fe oxide coated sponge	5	4.05	<0.5	6.5–7.3	[28]
MICB	50	35.7	<4.02	6.8	[29]
CONF Unsonicated	40	5.66	< 0.54	6.3–7	Present study
CONF Sonicated	40	5.55	< 0.50	6.2–7	Present study

Arsenic concentration in contaminated natural waters is usually low. So, it will be more reasonable to evaluate adsorption performance of As (V) at low equilibrium arsenic concentration. At low equilibrium arsenic concentration, the adsorption data could better fit to the Langmuir model. At equilibrium arsenic concentration of 0.01 mg/L for the standard for drinking water, the adsorption capacities for arsenic were about 4.02 mg/g for As (V) [29]. The comparison of adsorption capacity of the CONF with other materials at low equilibrium arsenic concentration was tabulated (Table 2).

4. Conclusion

This study demonstrates that copper oxide nanoflakes can be used as an effective adsorbent for arsenic in water. We observed, maximum adsorption capacity of about 5.66 mg/g using CONF that was well explained by Langmuir model. The adsorption kinetics followed pseudo-second order kinetic model. The material produced by simple method needs further investigation for its use as an adsorbent for public community.

Acknowledgement

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