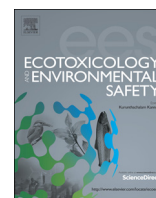




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## Assessment of Ethidium bromide and Ethidium monoazide bromide removal from aqueous matrices by adsorption on cupric oxide nanoparticles

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### ABSTRACT

The present study was undertaken to develop an effective adsorbent and to study the adsorption of Ethidium bromide and Ethidium monoazide bromide from aqueous solution using the CuO nanoparticles. The characteristics of CuO nanoparticles were determined and found to have a surface area 89.59 m<sup>2</sup>/g. Operational parameters such as pH, contact time and adsorbent concentration, initial concentration and temperature were also studied. The amount of removal increases with the increase in pH from one to seven and reaches the maximum when the pH is nine. Adsorption data fitted well with the Langmuir, Freundlich and Florry–Huggins models. The results show that the best fit was achieved with the Langmuir isotherm equation with maximum adsorption capacities of 0.868 and 0.662 mg/g for Ethidium bromide and Ethidium monoazide bromide, respectively. The adsorption process was found to follow pseudo-second-order kinetics. The calculated thermodynamic parameters, namely  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  showed that adsorption of Ethidium bromide and Ethidium monoazide bromide was spontaneous and endothermic under examined conditions.

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### 1. Introduction

Ethidium bromide (EtBr) is an intercalating agent commonly used as a fluorescent tag (nucleic acid stain) in molecular biology laboratories for techniques such as agarose gel electrophoresis (Stevenson et al., 1995). EtBr is a toxic chemical and a potent mutagen (Lunn and Sansone, 1987). EtBr is an intercalating agent which resembles a DNA base pair. Due to its unique structure, it can easily intercalate into DNA strand. Therefore, it is commonly used as nucleic acid fluorescent tag in various techniques of the life science field.

Ethidium monoazide bromide (EMA) is a fluorescent nucleic acid stain with a photoaffinity label. The EMA after photolysis, binds covalently to nucleic acids (Hixon et al., 1975). The EMA has been used to footprint drug binding sites on DNA (Jeppesen and Nielsen, 1989), to modify plasmid DNA (Coffman et al., 1982; Hardwick et al., 1984) and to determine hematopoietic cell phenotype, function and position in the cell cycle (Lund-Johansen et al., 1990).

The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics and catalysis (Lanje et al., 2010;

Bjoerksten et al., 1994; Dow and Huang, 1996; Larsson et al., 1996; Jiang et al., 1998).

Nanoparticles are derived from metals and metal oxides such as Titanium dioxide (Deedar et al., 2009), metal oxide nanomaterials (Hristovski et al., 2007), cupric oxide, nanoiron (hydr)oxide impregnated granulated activated carbon (Hristovski et al., 2009), and synthetic nanostructured Fe (III)–Cr (III) mixed oxide (Basu and Ghosh, 2011). Ghaedi et al. (2011a,b, in press) have used nanoparticles for the treatment of colored effluents such as murexide, reactive orange 12, alizarin red S and morin. Very few literatures are available on heavy metals removal using copper nanoparticles. Among the oxides of transition metals, copper oxide nanoparticles are of special interest because of their efficiency as nanofluids in heat transfer application. Recent studies have shown that nanoparticles adsorbents have a higher adsorption capacity for pollutant than larger particles (Reddy et al., 2013). The use of CuO nanoparticles provides an adsorbent with a higher surface area and therefore, a higher adsorption capacity for removal of EtBr and EMA.

In this study, CuO nanoparticles were examined as potential adsorbent for the removal of Ethidium bromide and Ethidium monoazide bromide from aqueous solution. To achieve this goal, the influence of experimental conditions such as pH, adsorbent dose, temperature and contact time on adsorption behavior was investigated. The isotherm, kinetic, thermodynamic parameters were also evaluated.

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## 2. Material and methods

### 2.1. Material

Ethidium bromide and Ethidium monoazide bromide was supplied by Sigma-Aldrich, United States (maximum purity available). Cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ ) (molecular weight, 170.48 g/mol), glacial acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ) (molecular weight, 60.05 g/mol) and sodium hydroxide (NaOH) (molecular weight, 40.00 g/mol) were supplied by Merck, Germany (maximum purity available). All solutions were prepared with deviations of less than  $\pm 0.1$  percent from the desired concentrations.

### 2.2. Synthesis of CuO nanoparticles

CuO nanopowders were prepared by Sol–Gel method (Etefagh et al., 2013). The aqueous solution of  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  (0.2 M) is prepared in cleaned round bottom flask. 1 ml of glacial acetic acid is added to above aqueous solution and heated to 100 °C with constant stirring. 8 M NaOH is added to above heated solution till pH reaches to seven. The color of the solution turned from blue to black immediately and the large amount of black precipitate is formed immediately. It is centrifuged and washed 3–4 times with deionized water. The obtained precipitate was dried in air for 24 h. This powder is further used for the characterization of CuO nanoparticles. A scanning electron microscope (SEM); JEOL JSM-5600 Digital Scanning Electron Microscope and X-ray diffractometer (XRD) Philips X'Pert were used to characterize the adsorbent for its morphological information. The particle size of the CuO nanoparticles was measured using Transmission Electron Microscope (TEM) (Zeiss EM-900). The Brunauer–Emmett–Teller (BET) surface area ( $S_{\text{BET}}$ ) of the powder was analyzed by nitrogen adsorption in an ASAP2020 surface area and porosity analyzer (Micromeritics, USA). Zeta-potential measurement was performed by ZEN 3600, Malvern.

### 2.3. Equilibrium studies

The ability of CuO nanoparticles for removal of EtBr and EMA from aqueous solutions was determined under batch mode conditions. 100 ml samples of EtBr or EMA solutions with different initial concentrations (0.1–0.6 mg/L) and different pH (1–13) were mixed with CuO nanoparticles at different adsorbent doses (0.5–3.0 g/L). The mixtures were added to 100 ml Erlenmeyer flasks, and the flasks were shaken at 120 rpm and 25, 35 and 45 °C for different contact times (2–16 min). At the end of contact time, the samples were filtered and the residual concentrations of EtBr and EMA in the filtrate were analyzed by a UV–vis Spectrophotometer (Shimadzu UV-160A) at maximum wave lengths of 285 and 260 nm for EtBr and EMA, respectively. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by Fakhri (in press-a):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where  $C_0$  and  $C_e$  are the EtBr and EMA concentrations in mg/L initially and at a given time  $t$ ,  $V$  is the volume of solution (L) and  $W$  is the mass of the adsorbent (g).

### 2.4. Kinetic and equilibrium models

In this study, batch kinetic experimental data for adsorbed EtBr and EMA onto CuO nanoparticles were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion. These models are listed as follows:

- (i) The pseudo-first-order kinetic model (Doğan et al., 2009a,b; Fakhri, in press-b):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

where  $q_e$  and  $q_t$  are the EtBr and EMA adsorption capacity (mg/g) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  is the rate constant of the pseudo-first-order ( $\text{min}^{-1}$ ).

- (ii) The pseudo-second-order kinetic model (Doğan et al., 2009a,b; Fakhri in press-b):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $k_2$  is the rate constant of the pseudo-second-order (g/mg min).

The equilibrium experimental data were analyzed using Langmuir, Freundlich and Florry–Huggins isotherm models. These isotherms are listed as below:

- (i) Langmuir isotherm model (Langmuir, 1918; Fakhri and Adami, in press-a):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

where  $C_e$  is the concentration of EtBr and EMA at equilibrium (mg/L),  $q_e$  is the amount of EtBr and EMA adsorbed by the CuO nanoparticles at equilibrium

(mg/g),  $q_m$  is the theoretical maximum adsorption capacity corresponding to monolayer coverage (mg/g), and  $K_L$  is the Langmuir isotherm constant (L/mg).

- (ii) Freundlich isotherm model (Freundlich, 1906; Fakhri and Adami, in press-b):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where  $q_e$  is the EtBr and EMA concentration on CuO nanoparticles at equilibrium (mg/g),  $C_e$  is the concentration of EtBr and EMA in solution at equilibrium (mg/L), and  $K_F$  and  $1/n$  are constants.

- (iii) The Florry–Huggins model (Horsfall and Spiff, 2005; Fakhri, in press-c):

$$\log \frac{\theta}{C_e} = \log K_{\text{FH}} + n_{\text{FH}} \log(1 - \theta) \quad (6)$$

where  $\theta$  is the degree of surface coverage,  $n_{\text{FH}}$  is the number of EtBr and EMA occupying adsorption sites,  $K_{\text{FH}}$  is equilibrium constant of adsorption and  $C_e$  is equilibrium EtBr and EMA concentrations.

## 3. Results and discussion

### 3.1. Characterization of the CuO nanoparticles

Fig. 1(A) shows the SEM image of as prepared CuO nanoparticles. It shows that the CuO nanoparticles are in rectangular shape. Fig. 1(B) shows the XRD pattern of prepared CuO nanoparticles. Reflection peaks at  $2\theta = 35.4^\circ$ ,  $38.7^\circ$ ,  $58.3^\circ$ ,  $65.7^\circ$  and  $68.0^\circ$  are indexed as [002], [111], [202], [022] and [220] planes of CuO phase with cubic symmetry. Higher intensity at  $2\theta = 35.4^\circ$  and  $38.7^\circ$  respectively indicates that mixed phase has major proportion of CuO with highly oriented crystalline CuO phase.

Fig. 1(D) shows TEM micrograph of CuO nanoparticles. The actual size of nanoparticles is estimated from TEM micrograph. Most of the nanoparticles have size around less than 100 nm and which is in correlation with the SEM image. The TEM graph also showed that the copper oxide nanoparticles are consists of agglomerated particles with a regular morphology. The differential size distribution histogram was shown in Fig. 1(C). The size distribution indicated that that of copper oxide nanoparticles which had several particles that were around less than 100 nm.

Fig. 1(E) shows the nitrogen adsorption and desorption isotherm for the CuO nanoparticles. There are hysteresis loops that appear at high pressure in the isotherm of CuO nanoparticles, which is presumably due to interparticular spacing between agglomerated CuO nanoparticles. Table 1 summarizes the specific surface area using the Brunauer–Emmet–Teller (BET) method.

The Zeta potential change of the prepared CuO nanoparticles with different pH values is tested, as shown in Fig. 1(F). As observed from Fig. 1(F), the pH value of CuO nanoparticles at the isoelectric point is 9.2. Therefore, it is proved that the CuO nanoparticles prepared by this study meet the basic condition of suspension stability.

### 3.2. Effect of contact time and temperature

The effect of contact time between EtBr and EMA with 1.5 g/L of CuO nanoparticles was studied for solutions where the concentration was 0.3 mg/L. The experiments were performed at 25, 35, and 45 °C. We observed the adsorption of a middle quantity of EtBr and EMA onto the CuO nanoparticles after a very short contact time (Fig. 2). The temperature of the solution is considered as another critical factor which may affect the adsorption process greatly. Also, if the removal efficiency of a certain pollutant from aqueous solution is temperature dependent, which is the case most of the time, it might affect the suitability of the adsorbent as increasing the temperature mostly consumes fuel and time. Generally, the adsorption depends on the temperature in two different ways. High temperature, generally increases the rate of diffusion of the

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