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Trimesic acid coated alumina: An efficient multi-cyclic adsorbent for toxic Cu(II)

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Abstract

Biodegradable and eco-friendly organic acid, benzene-1,3,5-tri-carboxylic acid (trimesic acid), coated on commercial basic alumina, was used as adsorbent to remove toxic Cu(II) ion from aqueous solution. Adsorbent preparation was optimized and was characterized by SEM, EDX, FT-IR, and powder XRD pattern. Effect of various regulating parameters like reaction pH, adsorbent dose and initial Cu(II) concentration was studied in detail. Adsorption isotherms followed the Langmuir isotherm model and adsorption was thermodynamically favourable. Maximum adsorption capacity (Q_m) for Cu(II) ion has been achieved as 10.80 mg/g. Detail kinetic study revealed that it followed second-order rate. Desorption of Cu(II) ion and re-usability of the adsorbent was also studied.

Keywords: Trimesic acid; Basic alumina; Adsorption isotherm; Adsorption kinetics; Desorption; Cu(II) removal

1. Introduction

Aquatic pollution by heavy metals is a rising concern at hazardous waste sites around the world. Several heavy metals like cadmium, chromium, copper, lead, mercury, nickel, zinc, etc. are included on the U.S. Environmental Protection Agency's (EPA) list of priority pollutants [1]. Cu^{2+} ion is one of the ubiquitous and frequently found toxic metals in surface water. The potential sources of Cu^{2+} ions are, essentially, pulp, paper and wood preservative-employing mills, industrial waste streams of metal cleaning and plating baths, fertilizer industry, etc. [2]. Cu^{2+} has high affinity for N and S donor containing ligands [3]. Hence, enzymes, whose activities depend on sulhydryl and amino groups [4], are strongly inhibited by Cu^{2+} ions. More over it also has several toxic effects on human [5]. Considering deleterious affects of heavy metals on living systems, strict regulation had been placed on their concentration in potable water supplies and effluent discharges by various agencies through out the world. Hence, the need of efficient techniques to reduce the heavy metal content in the aqueous waste streams is highly important. In addition, there is continuous increase in demand of most of the known metals as their availability decreases continuously. This also strengthens the need of effective waste processing method, so that the water can be recycled and the metals can also be reused.

Adsorption is considered to be an effective and versatile method for reduction of Cu^{2+} ions in wastewater. When adsorption is combined with appropriate desorption step, it solves the problem of sludge disposal [6,7]. Several enhanced adsorbents like activated carbon [8], inorganic colloids [9], functionalized silica [10], polyurethane foams [11], and low cost adsorbent like chitosan [12], zeolites [13], fly ash [13], cellulose [14], saw dust [15], TiO_2 [16], waste iron oxide [17], etc. were used in Cu^{2+} adsorption previously.

The purpose of present article is to study the use of alumina supported by benzene-1,3,5-tricarboxylic acid (trimesic acid, TMA) as an adsorbent materials for the adsorption of toxic Cu^{2+} ion. Trimesic acid has proved to be widely used class of ligands in metal-organic framework research. Due to its rigidity and strong co-ordination ability of three equally spaced carboxylate groups, metal centres can strongly bind with organic

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ligands. The co-ordination behaviour of TMA with Cu^{2+} ion has been reported earlier [18]. It has also been found that TMA acts as a multidentate ligand for various divalent and trivalent metal ions [19]. TMA can exhibit different types of binding mode, resulting various 3D structure [18–20]. Moreover, no such studies were found before where aromatic carboxylated acids like TMA were used as an adsorbent for divalent toxic cations. Hence we are interested to use this aromatic acid as an adsorbent for divalent toxic Cu^{2+} ions from wastewater.

Inorganic oxides such as alumina, iron oxide and silica can be used as solid support for coating of the adsorbent. In the present work, TMA was coated onto the surface of basic alumina as solid support. It is well studied that carboxylic acids are strongly adsorbed on the surface of basic alumina, with adsorption energies much larger than those of other organic compounds [21]. A very common procedure to deposit an organic coating on inorganic oxide is to dissolve the acid in a proper organic solvent and mixed with inorganic oxide particles for a period of time, followed by evaporation of the solvent [22].

This article reports the synthesis and characterization of the trimesic acid coated alumina and its adsorptive properties of toxic Cu^{2+} ion from aqueous phase. This study provides the insight into Cu^{2+} ion adsorption from aqueous solutions in terms of equilibrium, kinetics, isotherm and thermodynamic parameters. It also provides the optimizing conditions in terms of various system parameters such as initial ion concentration, time, pH, temperature and adsorbent dose for Cu^{2+} ion adsorption. Besides, recovery of metal ion, and regeneration of adsorbents were conducted which is very important to assess the practical utility of the adsorbent.

2. Materials and methods

2.1. Materials

Analytical grade copper sulfate ($CuSO_4{\cdot}5H_2O$) from CDH analytical reagent was used as a source of Cu^{2+} ion. Benzene-1,3,5-tricarboxylic acid (98%) was purchased from Alfa Aesar. Basic aluminium oxide active (Al_2O_3) from Loba Chemie Pvt. Ltd. was used as a supporting material for the organic acid coating.

2.2. Analytical measurement

The Cu^{2+} concentration was measured in atomic absorption spectrophotometer (Spectra AA Varian, model 55B). After addition of adsorbent, the metal solution was stirred in a temperature controlled shaking incubator at a fixed rpm (Labtech Co. Ltd., Model No. LSI-3016R). FT-IR spectra were recorded at 4 cm^{-1} resolution with 10 scan with a Perkin–Elmer spectrum one FT-IR spectrometer from 4000 to 450 cm^{-1}. A background spectrum was measured for pure KBr. To confirm the crystalline nature of the adsorbent sample PXRD data were recorded with Seifert powder X-ray diffractometer (XRD 3003TT) with CuK_α source ($\lambda = 1.54$ Å). Scanning electron micrograph (SEM) images of samples glued on an aluminum stub and gold sputtered were obtained by means of a LEO-1430 VP electron microscope.

2.3. Coating of trimesic acid onto basic alumina surface

Initially 100 mg of TMA per gm of alumina was used for coating experiments; later the amount of TMA was also varied to study its effect on Cu^{2+} adsorption. In a typical preparation, 500 mg (∼24 mM) of TMA was dissolved in 100 ml of methanol followed by continuous addition of 5 g of basic alumina in portion wise with continuous stirring. The solution pH was maintained at ∼2.5, which was close to the pK_a^1 value of TMA [23]. After addition of alumina the solution was stirred continuously for 6 h. Resulting mixture was vacuum-filtered and washed with cold water to remove unadsorbed acids. Adsorbent was air dried before adsorption studies.

2.4. Adsorption experiments

Adsorption experiments were carried out in batch mode. 500 mg/L stock solution of $CuSO_4$ was prepared and diluted to 50 ml of desired concentration and poured into 100 ml specimen tube respectively. After addition of different doses of adsorbent (20 to 100 g/L), specimen tubes were kept in a temperature controlled shaker for proper mixing. Kinetic experiments were performed by adding fixed dose of adsorbent (100 g/L) in known concentration of Cu^{2+} solution. The samples were taken out at regular interval and centrifuged to obtain suitable aliquots for analysis of Cu^{2+} concentration. Rate constants of kinetic models were also calculated from the conventional rate equations. Reaction pH, dose of TMA coated alumina, amount of TMA per gm of alumina in coating, duration of mixing and initial Cu^{2+} concentration were the variables in this study. Solution pH was adjusted by adding 1 M NaOH and 1 M HCl, and once optimised, rest of experiments were performed in the optimized pH.

Isotherm experiments were performed with different initial Cu^{2+} concentration solution (50–250 mg/L) by adding a constant dose of adsorbent of 15 g/L. Initial pH of the solution was adjusted to ∼5.0 as optimized and mixed until equilibrium reaches. Adsorption capacity or the q_e value (mg/g) for Cu^{2+} was calculated as follows:

$$q_e\ (\mathrm{mg/g}) = \frac{\text{initial solute concentration (mg/L)}}{\text{adsorbent dose (g/L)}} - \frac{\text{equilibrium solute concentration (mg/L)}}{\text{adsorbent dose (g/L)}}. \quad (1)$$

Control experiments were carried out in each case with only Cu^{2+} solutions, to validate the adsorption phenomenon. The detail sets of experiments are shown in Table 1. All the adsorption experiments were performed in duplicate for data consistency.

2.5. Desorption and re-adsorption study

Once equilibrium reaches in sorption process, the adsorbent (containing adsorbed Cu^{2+}) was separated by centrifugation and air dried. After drying, the adsorbent was treated with 0.2–1 M HCl and H_2SO_4 solution separately to study the desorption phenomena of Cu^{2+} ion from the adsorbent. On completion of