



# Equilibrium, thermodynamic and kinetic studies on removal of chromium, copper, zinc and arsenic from aqueous solutions onto fly ash coated by chitosan



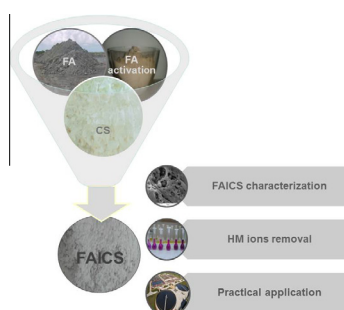
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## HIGHLIGHTS

- The modification of fly ash using chitosan.
- Fly ash coated by chitosan as an adsorbent for the removal of heavy metal ions.
- The adsorbents were characterized using the FTIR, SEM, BET and XRD methods.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 11 January 2015

Received in revised form 17 March 2015

Accepted 18 March 2015

Available online 4 April 2015

### Keywords:

Fly ash  
Chitosan  
Chromium  
Copper  
Zinc  
Arsenic

## ABSTRACT

The objective of this work was to examine the effectiveness of fly ash coated by chitosan (FAICS) as an adsorbent for the removal of heavy metal ions from aqueous solutions. The adsorption isotherms, effect of initial concentration, pH, contact time, temperature and adsorbent dosage were investigated. In this work the characterization of synthesized adsorbents is also presented. The adsorbents were characterized using the FTIR, SEM, BET and XRD methods. The process kinetics was evaluated by the pseudo first order, the pseudo second order and the intraparticle diffusion models. Batch kinetic data from the experimental investigations on the removal of heavy metal ions from aqueous solutions using FAICS have been well described by the pseudo second order model. The adsorption data for Cr(III,VI), Cu(II), Zn(II) and As(V) were fitted well with the Freundlich isotherm model. The adsorption capacities of FAICS(8:1) for Cr(III,VI), Cu(II), Zn(II) and As(V) were equal to 36.22 mg/g, 28.65 mg/g, 55.52 mg/g and 19.10 mg/g, respectively. The thermodynamic parameters such as enthalpy, entropy and free energy of adsorption of metal ion-FAICS systems were determined. It was found that the process is endothermic, favourable and spontaneous in nature. The results showed the highest efficiency in the case of adsorption of Zn(II) onto FAICS(8:1).

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## 1. Introduction

In recent years heavy metal ions have been widely emitted in large quantities into the environment [1]. They come from both

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natural sources such as rocks and from effluents of such industries as metallurgy, electroplating, leather tanning, paints and pigments, textile, steel fabrication [2–5]. It is commonly known that heavy metals are strongly toxic and hazardous for human health. For example arsenic and chromium are at the top of a priority list of hazardous substances [6]. Many methods of heavy metal ions removal from water and waste water are presented in literature,

but it is still necessary to develop new materials and more efficient technologies.

Today much attention is paid to the reuse of fly ash. The literature on various aspects of the use of fly ash is abundant and hence many possibilities how to expand the use of this material are presented [7,8]. For example, fly ash can be used as a cement additive for oil-well casings, a structural filler in concrete and for waste and road base stabilization [9], additive to agricultural soils to neutralize acidity, an absorbent for oil spills, a filler in plastics, for separation of oil-sand tailings [10]. As fly ash contains SiO<sub>2</sub> and a portion of unburnt carbon, one of the applications is the use of fly ash as low-cost adsorbent for removal of dyes and heavy metal ions [11–15].

As follows from the literature data coal fly ash (FA) may be an interesting material for the treatment of waste waters. The studies of the metal ions sorption of this kind of sorbent are well known and described and therefore not presented in the reviewed paper. In many papers, the proposed mechanism assumes [16,17]:

- metal ions sorption on the alumina:  $2\equiv\text{AlO}^- + \text{M}^{2+} \rightleftharpoons (\equiv\text{AlO})_2\text{-M}$
- taking into account that the major component of the fly ash is SiO<sub>2</sub> (pH<sub>PZC</sub> < 2), protonation of the superficial hydroxyl groups (SiOH + H<sup>+</sup> → SiOH<sub>2</sub><sup>+</sup>) takes place at pH < 2. This leads to a positive charge of the fly ash surface. Under these conditions, M(II) sorption corresponding to low pH (pH 2) is caused by the repulsion between the surface charge and metal ions,
- in the pH range 2–5 as a result of superficial hydroxyl groups dissociation, the fly ash surface is negatively charged. The sorption increase with the increasing pH may be due to these negative charges at the active sites on the fly ash surface that would allow metal ions to be chemisorbed:  $-\text{SiO}_2 + \text{H}_2\text{O} \rightleftharpoons -\text{SiO}^- + \text{H}_3\text{O}^+$  (observed when pH of the solution is above the pH of the point of zero charge (pH<sub>PZC</sub> = 3.1) and  $-\text{SiO}^- + \text{M}^{2+} \rightleftharpoons -\text{SiOM}^+$  as well as  $-\text{SiO}^- + \text{MOH}^+ \rightleftharpoons -\text{SiOMOH}$
- precipitation of metal cations on the surface of the adsorbent particles must be also taken into account.

The literature reports studies on fly ash exploitation in adsorption of heavy metals from aqueous solutions with the influence of the following parameters: chemical composition of fly ash, pH (the factor deciding about the form of metal ions occurrence and the charge of ash particles), temperature of process, phase contact time and amount of fly ash [12,18–21].

Only several investigations have been reported on using fly ash coated chitosan for removal of heavy metal ions. For example, it was also found that removal capacity at equilibrium for the experiment carried out with fly ash (100 g/dm<sup>3</sup>) at pH 5 and for an initial Cu(II) concentration of 500 mg/dm<sup>3</sup> was around 3.2 mg/g. This value is much less than that obtained for the fly ash modified by chitosan.

Wen et al. [22] reported the chitosan–fly ash composite as a good biosorbent for treatment of Cr(VI). Xie et al. [23] investigated chitosan modified zeolite for its capability of sequestering cationic, anionic and organic pollutants (humic acid) from waters. Removal of humic acid from aqueous solution onto the chitosan–zeolite composite was also described by Lin [24]. He states that fly ash coated chitosan is a potential adsorbent for effective heavy metal ions removal.

Chitosan is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution [25]. It is known as an excellent biosorbent for metal ions in acidic or near neutral solutions [26–30]. It is characterized by

both large sorption capacity owing to the position of –OH and –NH<sub>2</sub> groups and high hydrophilicity due to a large number of hydroxyl groups of glucose units and the presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups) [31]. These properties as well as reactivity and biodegradability of chitosan depend on the amount of protonated amino groups in the chain of polymer [32]. What is more chitosan is insoluble in water and organic solvents but is soluble in acids such as acetic, phosphoric, nitric, hydrochloric, perchloric except sulphuric acid [33,34]. It is capable of various morphological structures formation (films, fibres, hydrogels, membranes, nanoparticles, microspheres) [28,35]. When the molecular mass increases, some physicochemical and biological properties of chitosan in solutions change, which determines the bioactivity of the material. Density of chitosan, solubility in water and biodegradability decrease while viscosity increases with the increasing molecular mass [36].

Many waste waters are highly acidic which is a problem for using chitosan, which is highly soluble in such media [37]. It is necessary to stabilize the chitosan in the acid medium especially in dynamic systems. The modification of fly ash using chitosan can be a solution to this problem. This process also allows to increase adsorption capacity and improve the selectivity towards metal ions. It can be carried out after activation of fly ash. The activation of fly ash develops porosity and surface and can be accomplished for example by using high temperature [38,39].

Because of nontoxicity, both chitosan and fly ash are environmentally friendly. What is more, in view of that fact they are obtained from wastes these materials are low-cost. For these reasons the use of these adsorbents for removal of heavy metal ions from waters and waste waters is an excellent solution to the environmental problems – cleaning waters and waste waters as well as exploiting waste products. It is known that the adsorption process conditions such as pH, temperature, contact time, adsorbent dosage are essential. This paper presents the results of the investigations on the above listed parameters for adsorption of Cr(III,VI), Cu(II), Zn(II) and As(V) on fly ash (FAI) which was activated at high temperature (FAI-573) and coated with a various amount of chitosan (FAICS).

## 2. Material and methods

### 2.1. Materials and their characterization

Fly ash (denoted as FAI) was supplied by the Heat and Power Generating Plant in Poland. Chitosan (denoted as CS) in the form of powder was supplied by Sigma–Aldrich. Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, CuSO<sub>4</sub>·5H<sub>2</sub>O, ZnCl<sub>2</sub>, Na<sub>2</sub>HAsO<sub>4</sub> were used as a source of metal ions. The working stock solution was prepared by dissolving these salts in deionized water. The pH of the solutions was adjusted by adding a small amount of 0.1 M NaOH and 0.1 M H<sub>2</sub>SO<sub>4</sub>. Additionally, NaCl and acetic acid were purchased from POCH (Poland). All the reagents used were of analytical grade.

The results of analysis of chemical composition of fly ash are summarized in Table 1. It shows that the basic components of fly ash are aluminium determined as Al<sub>2</sub>O<sub>3</sub> and silicon determined as SiO<sub>2</sub>. The sum of them are 77.20–80.90% of dry weight of waste. It can be observed that fly ash contains quite large amounts of iron as Fe<sub>2</sub>O<sub>3</sub>, calcium determined as CaO, magnesium determined as MgO, potassium determined as K<sub>2</sub>O, titanium determined as TiO<sub>2</sub> and sulphur. According to the American Society for Testing Materials (ASTM) [40] the material used in this studies is classified as class F because it contained less than 10% CaO and larger than 70% of the three main components (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) combined. Contents of trace elements in fly ash is shown in Table 2.

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