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Research article

Efficient multistep arsenate removal onto magnetite modified fly ash

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ABSTRACT

The modification of the fly ash (FA) by magnetite (M) was performed to obtain FAM adsorbent with improved adsorption efficiency for arsenate removal from water. The novel low cost adsorbents are characterized by liquid nitrogen porosimetry (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD), Mössbauer spectroscopy (MB) and Fourier transform infrared (FTIR) spectroscopy. The optimal conditions and key factors influencing the adsorbent synthesis are assessed using the response surface method (RSM). The adsorption experiment was carried out in a batch system by varying the contact time, temperature, pH, and mass of the adsorbent. The adsorption capacity of the FAM adsorbent for As(V), calculated by Langmuir model, was 19.14 mg g^{-1}. The thermodynamic parameters showed spontaneity of adsorption with low endothermic character. The kinetic data followed the pseudo-second-order kinetic model (PSO), and Weber-Morris model indicated intra-particle diffusion as rate limiting step. Alternative to low desorption capability of the FAM was found by five consecutive adsorption/magnetite precipitation processes which gave exhausted layered adsorbent with 65.78 mg g^{-1} capacity. This research also has shed light on the mechanism of As(V)-ion adsorption, presenting a promising solution for the valorization of a widely abundant industrial waste.

1. Introduction

Heavy metals, as naturally occurring and easily transferable chemical elements, have come under more and more scrutiny of study due to their omnipresence as well as their perceived environmental and human risks (Ahmaruzzaman, 2011; Ma et al., 2016). Among the processes that are currently used for the removal of heavy metal ions from wastewater (*e.g.* chemical precipitation, coagulation, solvent extraction, ion exchange, ultra filtration, membrane filtration biological systems, electrolytic processes, reverse osmosis, oxidation with ozone/hydrogen peroxide, photocatalytic degradation, etc.), the adsorption process is studied in its single application or combined with other techniques (Ahmaruzzaman, 2011; Ahmed and Ahmaruzzaman, 2016; Fu and Wang, 2011; Reddy and Yun, 2016; Visa, 2012). Therein, the appropriate selection and modification of the material may prove to be an economic and effective approach for heavy metal removal (Randelovic et al., 2012).

Waste for waste treatment is a new concept that has been launched in order to intensify the use of adsorption processes in wastewater treatment (Karanac et al., 2018; Visa, 2016). Accordingly, the most abundant solid waste material (by-products) generated from coal combustion is fly ash (FA) (Spadoni et al., 2014). Although a waste product that is otherwise toxic, it possesses good adsorptive properties (Simate et al., 2016; Visa et al., 2012). FA is used for various environmental decontamination purposes: i) as an adsorbent for heavy metals (Ahmaruzzaman, 2011; Koshy and Singh, 2016; Simate et al., 2016) and dye removal (Visa and Chelaru, 2014); ii) as a soil amelioration agent (Simate et al., 2016); iii) in the reduction of carbon emissions (Siriruang et al., 2016; Vargas and Halog, 2015). Many distinct benefits are found in the reuse of FA solid wastes, not least of which is that they are zero cost materials due to their by-product origin (Belviso, 2018). Their utilization allows improved natural resource conservation and thus removes them as an environmental pollutant. Since 2014, the U.S. Environmental Protection Agency (EPA) has reclassified FA as non-hazardous material (Connors, 2015). FA contains high levels of potential toxicants which dictate high responsibility in relation to FA disposal and use/reuse processes. Minimization of the contaminations effect, i.e. impacts on human health and environment, must be main concern of adequate management of FA. Landfilling associate with two problems: air and water pollution, and demand

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consideration of the elements of hazard preventive in storage area and disposal place. Application of engineered composite liner systems, leaching toxicants collection channels/reservoirs, surface and ground water monitoring in a short and long period, and system adaptability. Due to such complex requirements, the development of new idea on FA use is beneficial in appropriate area of human activities.

FA has significant potential in wastewater treatment stemming from the properties of its major chemical components: alumina, silica, ferric oxide, calcium oxide, magnesium oxide, and carbon, as well as from its physical properties, such as porosity, particle size distribution, and surface area (Meawad et al., 2010; Pehlivan et al., 2006; Visa, 2012). As (V) removal by coal fly ash is due to of its high content of calcium minerals and amorphous iron/aluminium hydroxides (Wang and Tsang, 2013).

Developing numerous techniques to remove arsenic from water has proved to be a considerable challenge to environmental science (Budimirović et al., 2017; Lata and Samadder, 2016; Mohan and Pittman, 2007; Taleb et al., 2015, 2016; Velickovic et al., 2013; Veličković et al., 2012). Arsenic causes various adverse health effects. It is a known carcinogen, as well as toxic and mutagen element (Siddiqui and Chaudhry, 2017). The new standards of arsenic in drinking water, according to the United State Environmental Protection Agency and the World Health Organization, is set to 10 μg L^{-1} (WHO, 2017).

Novel adsorbents based on ferric oxides have been widely investigated for their As(V) (Iconaru et al., 2016; Su, 2017; Taleb et al., 2016; Zhang et al., 2010a) and As (III) removal properties (Sindhu D. and K.C. 2017) due to their large surface area, selectivity, chemical stability, and ability to reduce the mobility of elements (Izquierdo and Querol, 2012). Among them magnetite (M) modified materials have been proven to be economical, effective and easy for operation (Li et al., 2009), due to their magnetic properties which allow them to be easily separated from aqueous solutions.

The aim of this study has been to remove As(V) ions onto a novel, waste-origin, synthesized material - magnetite modified fly ash - thereby attempting to add a new value to the products that otherwise only serve as industrial waste. In accordance to beneficial use of iron oxide for surface modification, in this work the optimized procedure for magnetite precipitation on waste FA was developed. Except of efficient As(V) removal by FAM, the main environmental treat, i.e. heavy metal leaching from FA and exhausted FAM/As(V), was solved by multistep adsorption/magnetite (re)impregnation methodology. Results of implementation of this methodology provides couple main outcomes such as: i) development of optimized method for FA modification to obtain FAM adsorbent; ii) application of the FAM in a processes of As(V) removal; iii) the enhancement of exploitation and reuse of the studied materials by preforming multistep adsorption/(re)impregnation by magnetite, iv) the reduction of waste materials generation/disposal (initially, the waste product and, afterwards, the exhausted adsorbent), and, consequently, v) the abatement of the risk posed by the presence of arsenic ions in aqueous solutions.

2. Materials and methods

2.1. Materials and chemicals

The FA used in this investigation was obtained from the Thermal Power Plant (TPP) Kostolac. According to ASTM (the American Society for Testing and Materials) standards, the FA pertains to the F class (Komljenovic et al., 2010; Lakusic, 2015). The FA was dried at 105 °C for 24 h and the samples were homogenized prior to the modification process.

All the chemicals used in this study were analytical grade: iron(II)-sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Merck), sodium hydrogencarbonate ($NaHCO_3$) (Zorka Pharma), xylene (Sigma Aldrich), potassium nitrate (KNO_3) (Sigma Aldrich), potassium hydroxide (KOH) (Sigma Aldrich). The As(V) stock solution was made of deionized water (DIW - resistivity less than 18 MΩ cm) using $Na_2HAsO_4 \cdot 7H_2O$ (Carlo-Erba). Adjusting the pH values was carried out by using chemicals of an analytical grade NaOH and HNO_3 (Merck, Darmstadt, Germany).

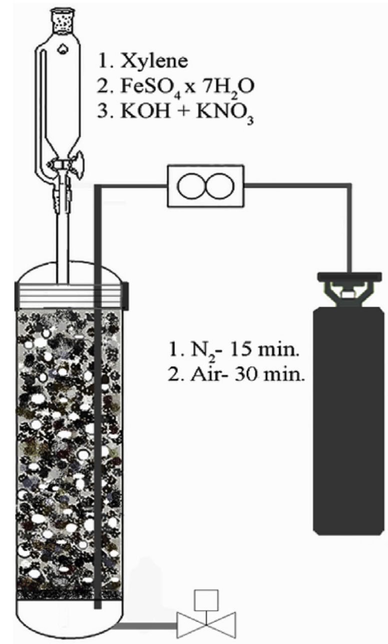

Fig. 1. The schematic presentation of the adsorbent synthesis in a solvent/non-solvent (water/xylene) system applied for controllable precipitation of M onto the FA.

2.2. Optimization methods applied for adsorbent synthesis

The synthesis of the FAM adsorbent was conducted through three distinct phases according to the method set out by below and in accordance to Taleb et al. (2016). The schematic presentation of adsorbent synthesis is given on Fig. 1. In the course of optimization procedure two parameter was varied: quantity of KOH used for pH control (pH change was adjusted in the range from 6 to 10 in first precipitation step, while from 7 to 9 in second and thirds ones), and concentration of $FeSO_4 \cdot 7H_2O$ was varied in the range 0.5–2 mol L^{-1}. The main criterion for selection of optimal synthesis was adsorption capacity (Table 1). Response surface methodology (RSM) method was applied for optimization of adsorbent synthesis (Supplementary material).

Table 1
The experimental plan two factors Optimal (custom) Design of the adsorption capacity of FAM in relation to the concentration $FeSO_4$ and pH_i values in the reaction mixture.

Run	C_{FeSO4}, mol L^{-1}	pH	Response, q_e, mg g^{-1}
1	1.25	8.25	13.2
2	1.85	8.50	18.6
3	0.50	10.00	7.9
4	1.25	8.25	13.2
5	0.50	8.00	7.4
6	1.25	8.00	13.2
7	2.00	10.00	14.0
8	2.00	8.00	16.6
9	1.85	8.50	18.6
10	1.25	8.00	13.2
11	0.50	6.00	6.4
12	1.25	9.00	12.8
13	1.25	9.00	12.8
14	1.25	6.00	8.0
15	2.00	6.00	8.1
16	1.25	10.00	12