Journal of Industrial and Engineering Chemistry 20 (2014) 597–604

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Neuro-evolutionary optimization methodology applied to the synthesis process of ash based adsorbents

Silvia Curteanu, Gabriela Buema, Ciprian George Piuleac, Daniel Mircea Sutiman, Maria Harja *

"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 73 Prof. Dr. Docent D. Mangeron Street, 700050 Iasi, Romania

ARTICLE INFO

Article history:
Received 17 January 2013
Accepted 12 May 2013
Available online 28 May 2013

Keywords:
Adsorption
Stacked neural network
Genetic algorithm
Optimization
Ash

ABSTRACT

Ash and modified ash were investigated as alternative adsorbents for copper ions. Our aim was to establish optimal working conditions for obtaining the new adsorbents, using a neuro-evolutionary optimization methodology. The materials were characterized by SEM, FT-IR, EDAX, XRD, and by the removal percentage. Three multilayer perceptron neural networks were developed and aggregated into a stack to form the model of the process. The neural model was integrated into an optimization procedure solved with a genetic algorithm to obtain the optimum values for the percentage of adsorption. The new adsorbents provide two benefits: environmental protection and energy recovery.

1. Introduction

The artificial intelligence (AI) aims to develop a simulator of human intelligence able to identify and correctly use knowledge to solve a specific problem. The soft computing concept, introduced by Lotfi Zadeh, is an approach from mathematical computation toward the goal of exploiting the tolerance to imprecision, uncertainty, and partial truth in order to gain flexibility, robustness, and low cost solutions with better ties to reality [1,2]. Generally, it is accepted that a phenomenological approach to a chemical system implies a complex quantification procedure for different variables in their interactions. For this reason, it is not always possible to obtain a good and reliable model. Soft computing methods are useful variants of classical techniques of modeling and optimization of engineering processes [3–6]. Neural networks (NNs) as empirical modeling tools [7–10] and genetic algorithms (GAs) as optimization solving methods [11,12] can be successfully applied to chemical processes.

Working as "black boxes", NNs may solve different problems in a situation where complete knowledge is not available, the process is highly non-linear, a classical model is affected by approximations or does not provide accurate results, or multiple constraints need to be met simultaneously. They can be used individually, in different configurations (type, topology, and parameters), or aggregated into homogeneous and heterogeneous stacks (SNNs). Combining NNs into an assembly is a method to improve modeling results, based on the possibility of developing separate models for different sub-spaces of the experimental domains or to include in the stack different neural networks (such as type and number), connected in different ways. The literature presents examples of using stacked neural networks for chemical process modeling [10,13–15].

GAs are multi-objective optimization tools which benefit from a series of advantages compared with gradient-based optimization methods: flexibility, good chances of achieving the global optimum, and the fact that GAs do not need information related to the initial points of the search space. Optimization GA procedures can include phenomenological models or neural networks [16,17]. A hybrid structure SNN–GA created to reproduce a cause–effect relationship and optimize the process parameters could constitute an efficient methodology for complex chemical processes.

In the present work, such a technique was developed and applied to the copper(II) ion adsorption process. The efficiency of the adsorption process was investigated with the goal of removing copper ions using unmodified and modified ashes.

Adsorption is a widely used technique for removing heavy metals, due to its economical and environmental advantages [18].

* Corresponding author. Tel.: +40 0232 278683; fax: +40 0232 271311.
E-mail addresses: silvia_curteanu@yahoo.com (S. Curteanu), buema_gabrielaa@yahoo.com (G. Buema), ciprianpiuleac@yahoo.com (C.G. Piuleac), sutiman@ch.tuiasi.ro (D.M. Sutiman), maria_harja06@yahoo.com (M. Harja).

1226-086X/$ – see front matter © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jiec.2013.05.020

Many adsorbents can be used for adsorption: activated carbon, zeolites, carbonates, and phosphate rocks; additionally, low-cost adsorbents have recently been studied [18]. Activated carbon is currently the most widely used adsorbent, but the use of activated carbon is restricted by its high cost [18]. Low-cost adsorbents synthesized from different wastes are being developed worldwide to replace activated carbon, such as ash and zeolites from ash [19–22].

Ash, a by-product of power plants, contains quartz (SiO_2), calcite, mullite, and kaolinite, and provides a ready source of Al and Si, necessary for zeolite synthesis. Zeolites with a low Si/Al ratio have proven to be excellent sorbents for heavy metal ions, as they have high cation exchange capacities (CEC) and large pore volumes [23,24]. Zeolites are recognized as important sorbents, naturally or prepared synthetically from different wastes. Four methods for zeolite synthesis from ash have been reported in the literature: direct conversion, fusion, microwaves, and ultrasound [25–30]. In all methods, the synthesis conditions are: 2–5 M NaOH solution, temperature of 70–150 °C, and contact time of 12–96 h; these conditions incur high energy consumption [26–30].

In this study, the utilization of ash (a hazardous waste) and modified ashes as low-cost adsorbents to remove copper ions from wastewater was investigated. Alkaline attack is a process which has been used before, but our ash (waste from Holboca, Iasi) has not been studied. In parallel with other studies regarding modification by alkaline attack, in this study, the factors which affect the adsorption of copper have been determined. Recommended literature conditions for synthesis include high temperatures and a prolonged curing time, so our aim was to reduce these parameters (establish optimal conditions) for new adsorbents with high removal percentage capacities. The new adsorbents provide two benefits: environmental protection, since this waste will not be disposed of on land, and energy recovery, since it is a low cost adsorbent for wastewater treatment.

The method applied for simulating the process and optimizing the experimental conditions is a neuro-evolutionary technique which includes neural network modeling and genetic algorithm optimization. It is a hybrid technique, developed in an original manner, based on optimized neural network stacks included into an optimization procedure solved with a simple genetic algorithm. The method was efficient, providing accurate results, in agreement with the experimental data used to check the modeling and optimization results.

2. Materials and methods

2.1. Adsorbent synthesis and characterization

Ash was taken from a deposit (Holboca, Iasi) at a power plant burning lignite coal. Detailed information about the ash composition and physicochemical properties has been published elsewhere [20–24]. For the alkali solutions, technical grade (purity > 98%) NaOH was used.

The conditions used for the synthesis of adsorbents are presented in Table 1. After treatment, the synthesized samples were crystallized for 18 h at ambient temperature; after this, they were filtered, washed and dried in an oven at 80 °C for 4 h.

The ash and adsorbent materials were characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), FT-IR analysis, X-ray diffraction (XRD), and the removal percentage of copper ions using the adsorption bath technique.

The chemical and mineralogical characterizations of adsorbents were performed with the following equipment: SEM/EDX for morphological and elementary analysis with a QUANTA 3D – AL99/D8229; FT-IR with Nicolete 6700; XRD with diffractometer X'PERT PRO MRD; Multi-Parameter Consort C831 and Spectrophotometer Buck Scientific for heavy metal detection by atomic spectroscopy.

2.2. Batch adsorption studies

A batch adsorption study was conducted for copper ions, from a copper sulfate solution [31]. The influence of variables such as contact time, amount of adsorbent, initial concentration, and pH of the solution on metal adsorption was investigated experimentally. The initial pH of the metal solution was varied using 0.1 M HCl. The adsorption solution was magnetically stirred at 300 rpm, under controlled temperature (20 °C). All the adsorption experiments were conducted in triplicate and the ion concentration in the solution was determined by atomic adsorption spectrometry at a wavelength of 324.8 nm.

The experiments were performed by following steps:

1. An aqueous solution of copper sulfate with desired copper ion concentration (300, 500, 700 mg/L) was prepared and its pH was adjusted to the desired value (2, 4, or 5).
2. In 200 ml of solution, the adsorbent was added at ratios of 1:25, 1:50, or 1:100.
3. The stirring speed was set to 300 rpm and adsorption was carried out until equilibrium was achieved, i.e., 1400 min.
4. At certain time intervals, samples were collected, filtered, and analyzed by atomic adsorption to establish the content of copper ions.

The removal percentage was determined using the following equation:

$$R\% = \frac{m_0 - m}{m_0} \times 100 \quad (1)$$

where m_0 is the copper mass in solution at the initial moment (mg) and m is the copper mass in solution at the sampling time (mg).

Various factors which affect the adsorption are the type of adsorbent, pH, adsorption time, solid/liquid ratio, and the initial ion concentration in solution.

The adsorption process was carried in the following mode:

Table 1
Conditions of adsorbents synthesis.

Adsorbents	Method of synthesis	NaOH solution (M)	Weight ratio (s/L)	Temperature (°C)	Curing time (h)
A1	Direct activation	2	1/3	70	4
A2	Direct activation	2	1/3	90	4
A3	Direct activation	5	1/5	70	4
A4	Direct activation	5	1/5	90	4
A5	Ultrasound activation	5	1/5	45	1
A6	Ultrasound activation	5	1/5	70	1
A7	Ultrasound activation	5	1/5	70	2