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Operational parameter impact and back propagation artificial neural network modeling for phosphate adsorption onto acid-activated neutralized red mud

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ABSTRACT

In this research the combination of neutralization activation and acid activation processes was employed to improve the physicochemical characters of red mud. In order to better understand the phosphate adsorption behaviors and further improve the phosphate adsorption performance of acid-activated neutralized red mud (AaN-RM), for the first time the impact of operational parameters on phosphate adsorption onto AaN-RM was systematically investigated, and back propagation artificial neural network (ANN) modeling was conducted. The results demonstrated that phosphate adsorption capacity of AaN-RM decreased with the enhancement of adsorbent dosage and the concentration of the competing ion (carbonate), while it increased with the increase of initial phosphate concentration and contact time. The optimal adsorption temperature and initial solution pH for phosphate adsorption onto AaN-RM were 50 °C and 4.0, respectively. Moreover, a 6-10-1 feed forward ANN structure with trainlm algorithm was successfully constructed for predicting the phosphate removal by AaN-RM. The RMSE and R^2 values for two subsets (training and validation subset, and testing subset) were 3.06 and 2.61, and 0.9932 and 0.9969, respectively. Furthermore, the importance analysis showed that contact time and initial phosphate concentration were the most influential parameters on phosphate removal by AaN-RM, the importance of which reached 24.64% and 22.16%, respectively.

1. Introduction

Phosphorus is a non-renewable macronutrient for the growth of plants and other organisms in the ecosystem [1]. However, the excessive discharge of phosphorus into water bodies may cause detrimental eutrophication, which not only seriously destroy the biodiversity but also threaten the drinking water safety [2]. Therefore, it is necessary to explore effective methods to remove and recover phosphate from municipal and industrial wastewater. Compared with other available technologies, the adsorption method has incomparable advantages due to its inexpensiveness, simplicity of design, ease of operation, and insensitivity to toxic pollutants [3]. Various natural minerals, industrial by-products and synthetic adsorbents have been used in phosphate adsorption systems [4]. Among these available materials, red mud is considered to be a promising alternative [5,6].

Red mud, a waste tailing generated from the alumina producing process, is a hazardous solid waste because of its highly alkaline nature [7]. There are three processes commercially applied for alumina refining, including the sintering process, the Bayer process, and the combination process (Bayer-sintering) [8]. Among them, the Bayer process is a key method used in producing quality alumina worldwide. It was reported that about 90% of bauxite is processed by Bayer technology [9]. Correspondingly, managing the rapidly expanding Bayer red mud, a hazardous solid waste generated in alumina refining from bauxite with Bayer technology, has become more and more important. Up to date, Bayer red mud has got a variety of applications such as adsorbents, catalysts and coagulants [10], and the application of modified red mud in wastewater treatment has become an emerging and promising research field [11–13]. However, most works only employed single activation technology such as acid activation or heat activation to improve the physicochemical characters of red mud [14–15]. Our previous study demonstrated that the combination of neutralization activation and acid activation technologies effectively improved the phosphate adsorption capacity of red mud [16]. In order to better understand the phosphate adsorption behaviors and further improve the phosphate

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adsorption performance of acid-activated neutralized red mud (AaN-RM), the effects of different operational parameters should be systematically investigated.

Nowadays, the application of artificial neural network (ANN) for mapping, regression, modeling, clustering, classification and multivariate data analysis has attracted increasing attention [17,18]. The ANN is a multivariate statistics technique which is commonly used to describe a variety of mathematical objects and processes [19]. The main advantages of ANN include nonlinearity, allowing better fit to the data; noise insensitivity, providing accurate prediction in the presence of uncertain data and measurement errors; high parallelism, which implies fast processing and hardware failure tolerance; learning and adaptability, allowing the system to update (modify) its internal structure in response to changing environment and generalization [20]. Feed forward back propagation network is the most widely used ANN architecture, which is suitable for modeling the whole phosphate adsorption process and evaluating the importance of different operational parameters [21,22].

Therefore, the aims of this study were: (1) investigating the effects of different operational parameters on phosphate adsorption onto AaN-RM; (2) evaluating the potential of back propagation artificial neural network for modeling the phosphate adsorption performance of AaN-RM with different training algorithms; (3) quantifying the importance of different operational parameters on the phosphate adsorption process.

2. Materials and methods

2.1. Materials

The Bayer red mud was provided by Shandong Aluminum Industry Corporation (Zibo, China), and the preparation method of AaN-RM can be found in [16]. The phosphate and carbonate solutions were prepared by potassium dihydrogen phosphate and sodium carbonate, respectively. All chemicals were of analytical grade (Merck Co., Germany).

2.2. Characterization of AaN-RM

The surface micro-morphology of AaN-RM was analyzed with electron dispersive X-ray analysis (Oxford X-Max, Oxford Instruments, UK), which was coupled with an electronic detector (LEO 1530, LEO, Germany). With N_2 adsorption/desorption isotherms at 77 K, the Brunauer–Emmett–Teller (BET) surface area and total pore volume of the samples were determined (ASAP 2020 V3.04 H, Micromeritics, USA). The chemical composition of AaN-RM was determined by X-ray fluorescence spectrometer (S4 Explorer, Bruker, Germany). The XRD patterns of AaN-RM were detected using an X-ray diffractometer (XRD-6000, Shimadzu, Japan) with Cu Kα radiation at 40 kV and 30 mA, and recorded in a 2θ range of 10–70° at a scan speed range of 0.02°/s. The point of zero charge (pH_{pzc}) of AaN-RM was estimated by batch equilibrium techniques described by Chutia et al. [23].

Table 1
Choice of operational parameters for optimization and ANN analysis.

ANN structure	Operational parameters	Range
Input parameters	Adsorbent dosage (mg/g)	0.3–0.8
	Initial solution pH	2.0–6.0
	Adsorption temperature (°C)	20–70
	Initial phosphate concentration (mg/L)	20–200
	Contact time (min)	0–20
	Competing ion (carbonate) (mg/L)	0–206.8
Output parameters	Phosphate adsorption capacity (mg/g)	31.34–192.62
Total number of data points		33

Table 2
ANN training parameters.

Parameter	Value
Maximum number of epochs	1000
Learning rate	0.1
Momentum constant	0.5
Error goal	0.0001

2.3. Adsorption studies

A series of phosphate solutions with different pH values were prepared with 1 mol/L and 0.1 mol/L HCl or NaOH solution. As shown in Table 1, the influences of different operational parameters on the phosphate adsorption performance of AaN-RM were investigated in beaker flasks. The parameters included adsorbent dosage, initial solution pH, adsorption temperature, initial phosphate concentration, contact time and competing ion. The beaker flasks were shaken at 100 rmp for 20 min. The samples were taken at predetermined time intervals, centrifuged at 3000 rmp for 1 min, and then the supernatant was taken to analyze the phosphate concentration.

The phosphate adsorbed by per unit of adsorbent was calculated by Eq. (1):

$$q = \frac{(C_i - C_f)\cdot V}{m} \tag{1}$$

where q is the phosphate adsorption capacity per unit of AaN-RM (mg/g, as PO_4^{3-}), C_i and C_f are the initial and final phosphate concentration (mg/L), respectively, V is the solution volume (L), and m is the mass of adsorbent (g).

The pH value was measured with a multimeter (model Multiline P4, WTW, Germany). The phosphate concentration was determined via the spectrophotometric method DIN-EN-ISO-15681-1 with a QuikChem 8500 flow injection analysis system (Lachat Instruments, USA). All experiments were conducted in triplicate and the average values were used for data analysis.

2.4. ANN modeling

In this research a three-layer feed-forward neural network with back propagation learning was constructed for the modeling of phosphate adsorption onto AaN-RM with MATLAB 10.0. A tangent sigmoid transfer function (tansig) at the hidden layer and a linear transfer function (purelin) at the output layer were selected. Meanwhile, three kinds of training algorithms including training BFGS quasi-Newton

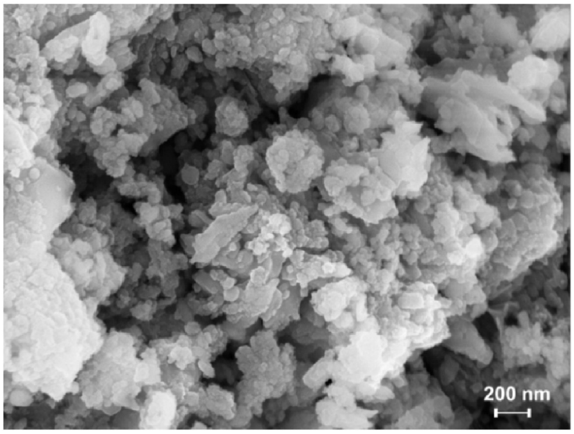

Fig. 1. SEM image of AaN-RM.