Journal of Water Process Engineering 8 (2015) e81–e91

Contents lists available at ScienceDirect

Journal of Water Process Engineering

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

Nickel removal from aqueous solutions by alginate-based composite beads: Central composite design and artificial neural network modeling

Akeem Adeyemi Oladipo*, Mustafa Gazi

Department of Chemistry, Eastern Mediterranean University, Gazimagusa, TRNC via Mersin 10, Turkey

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form 5 December 2014
Accepted 6 December 2014
Available online 25 December 2014

Keywords:
Bentonite
Acid dye
Artificial neural network
Nickel
Central composite design

ABSTRACT

Alginate-based composite bead (AB) was applied for the removal of Ni(II) ions from solutions in batch and fixed-bed systems. The reuse feasibility of the spent adsorbent was investigated for binding azo dye. Elovich kinetic model and mean adsorption energy (E) (13.2 kJ mol^{-1}) indicated that Ni(II) ions removal followed ion-exchange mechanism. 98.5% removal for Ni(II) was observed at the maximum column operation (viz. 2.0 mL/min flow rate, 100.0 mg/L influent concentration and 9.0 g dose). Artificial neural network (ANN) and central composite design (CCD) models were applied to elucidate the complex adsorption process, and the finding is consistent with the experimental data. Desorption efficiency (DE) was noted to be higher when HCl (DE = 92%) was used as desorbing agent compared to NaOH (DE = 6%) in the first cycle.

1. Introduction

Increasing industrial activity lately has led to the release of heavy metal infected effluent into freshwater systems, which is a serious threat to the environment and biota [1]. Industrial process such as electroplating, leather, textile, galvanization and batteries production have contributed to the occurrence of life-threatening pollutants in drinking water, surface water and even groundwater. Heavy metals and dyes are the most undesired pollutants released into the water bodies since tiny presence of dye can easily be detected by human eyes and, high concentration of heavy metals are undesirable to both human beings and aquatic animals. Nickel, the fifth most abundant element has been reported to be toxic and carcinogenic if accumulated above the World Health Organization (WHO) limit (0.1 mg/L) in drinking water [2].

Research has shown that the toxicology effects of acid dyes are obvious due to their ability to induce sensitization in humans as a result of the dye complex structure [3]. Acid red 25 (AR) is an azo dye extensively used in various industries and exposure to a considerable amount of AR is responsible for life-threatening diseases [4]. There are few reports dealing with the removal of nickel from aqueous media compared with other heavy metals; hence it is necessary to eliminate the threat as efficient as possible.

Adsorption process using adsorbents is regarded as economic, simple and efficient technique for decontamination of wastewater [1–4]. Researchers have suggested the various adsorbent to remove heavy metals/dyes from aqueous solutions [3–7]. However, low performance, high cost and poor regeneration/reutilization of spent adsorbent have led to the search for efficacious adsorbent [8]. Many reports focused on the removal of heavy metals from aqueous media while few researches have been directed to the utilization of the spent adsorbents which normally constitute secondary pollution.

Bentonite has been used in this research due to its ion-exchange capability, availability, excellent surface and structural properties compared to other clays [8–10]. The bentonite's adsorptive features can be attributed to the negative charges on its surface which emanated from the substitutions of metal ions (Al^{3+} and Mg^{2+}) within the clay octahedral sheets making it suitable for adsorption of heavy metals [10]. Even though bentonite exhibits specific selectivity reaction with cations (M^+), its separation from aqueous media and regeneration after spent has limited its industrial application [8].

The surface of the natural bentonite used in this study was modified with HCl to enhance its ion-exchange capability and encapsulated within the matrix of alginate (biopolymer) to improve the overall structural integrity of the adsorbent and for easy separation after use [8,11]. In our previous study [8], AB was utilized

---

* Corresponding author. Tel.: +90 392 630 2136; fax: +90 392 630 3039.
E-mail addresses: akeem.oladipo@emu.edu.tr (A.A. Oladipo), mustafa.gazi@emu.edu.tr (M. Gazi).

http://dx.doi.org/10.1016/j.jwpe.2014.12.002
2214-7144/

Nomenclature

b	related to heat of adsorption
B_T	Temkin adsorption constant (kJ/mol)
C	intraparticle diffusion model constant
k_1	pseudo-first order kinetic rate constant (1/min)
k_2	pseudo-second order kinetic rate constant (g/mg min)
K_L	Langmuir adsorption constant (L/g)
K_F	Freundlich adsorption constant (L/g)
K_T	Temkin model constant (L/mg)
k_{AB}	Adams–Bohart kinetic constant (mL/min mg)
k_p	intraparticle rate constant (mg/g min)
k_{Th}	Thomas rate constant (mL/min mg)
k_{YN}	Yoon–Nelson model rate constant (1/min)
M	mass of adsorbent (g)
n	Freundlich constant
N_0	maximum volumetric uptake capacity (mg/L)
q_e	amount of dye adsorbed onto AB at equilibrium (mg/g)
$q_{e,\mathrm{exp}}$	experimental amount of dye adsorbed at equilibrium (mg/g)
q_m	maximum adsorption capacity for adsorbent (mg/g)
q_T	theoretical saturated adsorption capacity in Thomas model (mg/g)
R	ideal gas constant (8.314 J/mol K)
R^2	correlation coefficient
T	absolute temperature (K)
t	time (min)
U_0	linear flow rate (cm/min)
V	volume of solution (L)
ΔG°	free energy change (kJ/mol)
ΔH°	enthalpy change (kJ/mol)
ΔS°	entropy change (J/mol K)
Z	bed height (cm)

Greek letters

ε	Polanyi potential
α	rate of chemisorption at zero coverage (mg/g min)
τ	time required for 50% adsorbate breakthrough (min)
$\lambda_{\max}$	maximum wavelength

to remove crystal violet (CV) dye from solutions in batch mode, its high adsorption capacity and regeneration potential makes it attractive for heavy metal elimination.

The objectives of the present study were to examine the adsorptive potential of AB for nickel removal from aqueous solutions in batch and column modes, and the reuse feasibility of spent adsorbent to treat dye containing wastewaters. Specific focus was on the application of statistical approach to predict and elucidate interactive effects of combined variables on the complex adsorption process using artificial neural network (AAN) and central composite design (CCD), respectively.

2. Materials and methods

2.1. Reagents

Alginic acid, HCl, NaOH, $CaCl_2$, acid red 25 and commercial grade bentonite were purchased from Sigma–Aldrich and utilized without further purification. The Ni(II) feed solution was obtained by dissolving known quantities of analytical grade $NiSO_4{\cdot}6(H_2O)$ in distilled water. All reagents used were of spectral and analytical grade purity.

2.2. Preparation of composite beads (AB)

The detailed preparation of the composite beads was reported in previous work [8]. Briefly, 2.0 g of acid activated bentonite was dispersed in distilled water in a 250 mL flask, a known quantity of alginate solution was added, and the mixture stirred for 180 min at room temperature. The homogenous mixture was dropped into a flask containing $CaCl_2$ (3%, w/v) solution to produce composite beads (AB). Collected beads were washed thoroughly, dried and stored in a desiccator for later use.

2.3. Adsorption studies

Standard stock solution of AR was obtained by dissolving known amounts of AR in a flask of 500 mL double distilled water to give 500 mg/L dye concentration. The working solutions prepared by diluting the stock solutions accurately. The pH of the solutions were adjusted with 0.1 N NaOH or 0.1 N HCl, and UV/VIS Spectrophotometer (Beijing, T80+) was employed for qualitative estimation of Ni(II) and AR from the simulated wastewater.

In batch mode, effect of various parameters (i.e., initial Ni(II) concentration, adsorbent dose, pH and contact time) on Ni(II) uptake were investigated. A known amount of AB was added to 50 mL solution of Ni(II) in 100 mL Erlenmeyer flask agitated under constant speed (200 rpm) until equilibrium was achieved and the effect of contact time examined at various equilibrium times. The Ni(II) removal percent (R) and uptake capacity (q_e) were estimated respectively using the following equations:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)}{M} V \tag{2}$$

The experimental results from batch operations were fed into ANN-based model to estimate the predictive performance of AB.

Column operations were performed using glass columns (length: 43.0 cm, internal diameter: 1.0 cm). The column was packed with varying amount of AB to obtain desired bed heights (3.0–9.0 cm) between glass wool supporting layers. Operation of the fixed-bed columns was halted when the effluent Ni(II) concentration exceeded 95.9% of its influent concentration. The entire experiments were conducted in triplicate with experimental error limit ±2.0%, and average values were reported for each mode. The physical properties of AB and CCD experimental design are summarized in Table 1. The characterization of the adsorbent using various techniques was reported in previous work [8] and $\mathrm{pH_{zpc}}$ shown in Fig. 1a.

The fixed-bed adsorption process for nickel was described further by feed-forward neural network (ANN) model. ANN, a biologically inspired network algorithm has attracted increasing attention recently. The basic ANN architecture consists of neuron-like units, organized in layers. Every unit in a layer is interconnected and each connection may have a different weight or strength. The input layer receives data and passes through the weighted network, layer to layer (hidden), until it arrives at the outputs based on the summation of weighted inputs. No feedback between layers and that is why they are referred to as feed-forward neural networks [8,11].

3. Results and discussion

3.1. Batch studies

3.1.1. Effect of pH and contact time

The effect of pH (3.0–8.0) on nickel uptake at initial concentration of 100 mg/L and 1.0 g AB is represented in Fig. 1b. At lower pH