Desalination 254 (2010) 154–161

Contents lists available at ScienceDirect

Desalination

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

# Application of response surface methodology (RSM) for optimization of ammoniacal nitrogen removal from semi-aerobic landfill leachate using ion exchange resin

Mohammed J.K. Bashir, Hamidi Abdul Aziz *, Mohd Suffian Yusoff, Mohd. Nordin Adlan

*School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*

ARTICLE INFO

*Article history:*
Received 4 October 2009
Received in revised form 25 November 2009
Accepted 1 December 2009
Available online 6 January 2010

*Keywords:*
Ion exchange resin
Stabilized leachate
Process optimization
Response surface methodology (RSM)
Adsorption
Kinetics

ABSTRACT

Disposal of untreated landfill leachate can be a source of hazard to receiving waters. Hence, treatment of landfill leachate is considered environmentally essential. In this study, optimization of ammoniacal nitrogen ($NH_3$–N) removal from Malaysian semi-aerobic landfill stabilized leachate using synthetic cation ion exchange resin was investigated. An ideal experimental design was carried out based on Central Composite Design (CCD) with response surface methodology (RSM). This RSM was used to evaluate the effects of process variables and their interaction towards the attainment of their optimum conditions. Equilibrium isotherms in this study were analyzed using the Langmuir and Freundlich. Kinetic data were obtained and analyzed using pseudo-first-order and pseudo-second-order equations. Based on statistical analysis, the $NH_3$–N removal model proved to be highly significant with very low probability values (<0.0001). The optimum conditions obtained were 24.6 cm$^3$ resin dosage, 6.00 min contact time, and 147.0 rpm shaking speed. This resulted in 94.2% removal of $NH_3$–N as obtained from the predicted model, which fitted well with the laboratory results (i.e., 92%). The adsorption isotherm data were fitted well to the Langmuir isotherm, and the monolayer adsorption capacity was found as12.56 mg/g.

## 1. Introduction

Sanitary landfilling remains the most prevalent method to dispose municipal solid waste (MSW) as compared to other disposal techniques. Such prevalence can be attributed to its several advantages, such as simple disposal procedure, economically cheap disposal method, and landscape-restoring effect on the holes from mineral workings [1,2]. For such reasons, it has received significant attention over the last few decades. However, the large amount of a high contaminated landfill leachate produced is considered a significant negative aspect of this disposal method [3,4]. Furthermore, disposal of raw landfill leachate can be a source of hazard to receiving water bodies. Accordingly, the treatment of landfill leachate is considered as an essential step prior to its discharge. Generally, landfill leachate is defined as a complex liquid containing a mixture of organic substances (i.e., biodegradable and non-biodegradable carbon) and inorganic materials (i.e., heavy metals, sodium, calcium, sulphate, and ammonia nitrogen) [5–8].

The presence of high concentrations of ammoniacal nitrogen in landfill leachate over a long period of time is one of the main problems usually encountered by landfill operators [6]. According to Chu et al. [9], landfill site can produce leachate with high concentration of $NH_3$–N over 50 years after the stoppage of a filling operation. This high concentration of untreated $NH_3$–N leads to stimulated algal growth, decreased performance of biological treatment systems, accelerated eutrophication, enhanced dissolved oxygen depletion, and increased toxicity of living organisms in surface waters [6,10–12]. Since landfill leachate properties continue to be dangerous and poisonous over long periods, ammoniacal nitrogen removal has become an important concern in leachate treatment over the recent decades. To eliminate $NH_3$–N, several wastewater treatment technologies have been applied, including precipitation [13], nitrification and denitrification [14], electrochemical coagulation [15], anaerobic ammonia removal [16], aerated bioreactor [17], membrane distillation [18], adsorption [6,19] ammonia stripping [20–23], and ion exchange [24].

Ion exchange resins are widely and effectively applied for removing ions and dissolved organic matter from water and wastewater [25–31]. Ion exchange technology was investigated as a polishing step in the treatment of landfill leachate [25]. Primo et al. [25] reported the removal of nitrate from electro-oxidized landfill leachate using two selective anion exchangers i.e., Purolite A 520E and Purolite A 300. The highest exchange capacities of Purolite A 520E and Purolite A 300 were 95.1 and 83.3 mg/g, respectively. According to Heavey [26], treatment rate of 3.4 g ammonia/m$^2$/day was obtained for landfill leachate using peat. About 100% percent of ammonia was removed from initial concentration of 218 mg/L. However, a literature review claims that studies on removal of ammoniacal nitrogen from semi-aerobic landfill stabilized leachate using ion exchange resin remain limited. The same is true with studies concerning optimization of ion exchange treatment process for ammoniacal nitrogen removal

---

* Corresponding author. Tel.: +60 4 5996203; fax: +60 4 5941009.
*E-mail address:* cehamidi@eng.usm.my (H.A. Aziz).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2009.12.002

from leachate using Design Expert software that could statistically design experiments and analyze related data.

This study focuses on stabilized leachate generated from the Pulau Burung semi-aerobic landfill site. The site is one of only three sites of its kind in Malaysia. Pulau Burung landfill site (PBLS) is situated within Byram Forest Reserve at 5° 24′ North Latitude, 100° 24′ East Longitude in Penang, Malaysia, which is around 20 km southeast from the Penang Island [32]. The total landfill site area is 62.4 ha; however, only 33 ha is currently utilized to receive about 1800 tons of solid waste daily [5]. This landfill produces a dark color liquid with pH level more than 7.0 and is classified as stabilized leachate with high concentration of COD, $NH_3$–N, and low BOD/COD ratio [33].

The main objectives of the present study include the following:

1. To investigate the efficiency of synthetic cation ion exchange resin (INDION 225 Na) for treating ammoniacal nitrogen from semi-aerobic stabilized leachate.
2. To build up the equation of ammoniacal nitrogen removal efficiency from stabilized leachate with respect to operational conditions (i.e., cation dosage, contact time, and shaking speed using RSM and CCD).
3. To determine the optimum operational condition of studied application.
4. To determine isotherm and kinetic model parameters, in addition to evaluation of suitable models describing the isotherms and kinetics of this cation exchange resin.

## 2. Materials and methods

### 2.1. Cation ion exchange resin

The synthetic cation ion exchange resin used in this study was INDION 225 Na supplied by Ion Exchange (INDIA) Ltd. The selected resin and its physicochemical properties are presented in Table 1. The INDION 225 Na was chosen in the form of $H^+$ due to its known characteristics, such that it can work as a strong acid cation exchanger if used in the form of hydrogen; it is capable for use in hydrogen form (cation resin carry $H^+$ mobile ion) and sodium form (cation resin carry $Na^+$ mobile ion); and it can be applied over wide range of pH levels and temperatures.

According to Letterman [34], cation ion exchange resins are copolymers typically made of styrene and divinyl benzene (DVB). Styrene acts as the backbone or chain, while DVB acts as a crosslinker. Strong acid cation resins function with the sulfuric acid producing a sulfonic functional group ($–SO_3^-$ $H^+$). Sulfonate group ($–SO_3^-$) is a fixed functional group. $H^+$ is mobile exchangeable ion.

### 2.2. Experimental procedures

Method 1060, collection, and preservation of samples [35] were used for sample collection and preservation. Raw stabilized leachate samples at 20 L plastic containers each were collected every month from the aeration pond at PBLS from January to May 2009. All samples were manually collected, and were immediately transferred to the laboratory and kept in a cool room at 4 °C prior to experimental use in order to avoid biological activities and changes in the samples. Table 2 shows some characteristics of the leachate sample.

The studied cation ion exchange resin was rinsed with distilled water to remove adhering dirt, followed by filtration using vacuum pump. For experimental purposes, cationic exchanger was pre-treated using 0.8 N $H_2SO_4$ to convert cationic resin into their $H^+$ form [36].

All experiments were carried out by shaking 100 mL of leachate sample in 300 mL-sized volumetric flask using an orbital shaker (model Bioblock Scientific Agitator 74578). The process variables include contact time, dosage, and shaking speed. After each run, the supernatant was filtered using GC-50 filters (pore size of 0.45 µm; Advantec Toyo Kaisha Ltd., Japan) before measuring $NH_3$–N.

### 2.3. Analytical methods

The concentration of ammoniacal nitrogen ($NH_3$–N) was measured by Nessler Method (Method: 8038) using a Hach's DR2010 spectrophotometer, with the spectrophotometer set at 425 nm wavelength. Removal efficiency of ammoniacal nitrogen was obtained using the following equation:

$$NH_3\text{–}N\ Removal\,(\%) = \frac{C_i - C_f}{C_i} * 100 \qquad (1)$$

where $C_i$ and $C_f$ are the initial and final concentrations of $NH_3$–N (mg $L^{-1}$), respectively.

### 2.4. Experimental design and analysis

Experimental design of the process for optimum removal of $NH_3$–N from semi-aerobic stabilized leachate was carried out using the RSM. The RSM is a collection of mathematical and statistical techniques that are useful for the optimization of chemical reactions and industrial processes, and are commonly used for experimental designs [37–41]. In this study, RSM was used to assess the relationship between response (ammoniacal nitrogen removal, %) and independent variables, as well as to optimize the relevant conditions of variables in order to predict the best value of responses. Central Composite Design (CCD), the most widely used approach of RSM, was employed to determine the effect of operational variables on ammoniacal nitrogen removal efficiencies. According to Guven et al. [40], CCD is an effective design that is ideal for sequential experimentation, as it allows reasonable amount of information to test lack of fit when a sufficient number of experimental values exist. CCD and RSM were established with the help of the Design Expert 6.0.7 software program. The three

**Table 1**
Main physico-chemical properties of the studied resins*.

| Property | INDION 225 Na |
|---|---|
| Type | Strongly acid cation exchange resin |
| Matrix | Crosslinked polystyrene, gel type |
| Functional group | Sulphonic acid ($–SO_3^-$) |
| Ionic form (as supplied) | Sodium form |
| Maximum operating temperature | 120 °C ($H^+$ form)<br>120 °C ($Na^+$ form) |
| Operating pH range | 0–14 |
| Particles size rang | 0.3–1.2 mm |
| Total exchange capacity | 2.0 mEq/mL |
| Appearance | Yellow |

*Properties given by the manufacturer.

**Table 2**
Characteristics of raw leachate from PBLS.

| Parameters | Values |
|---|---|
| COD, mg/L | 2380–2850 |
| BOD, mg/L | 160—40 |
| $NH_3$–N, mg/L | 1820–2200 |
| Color, Pt-Co | 5330–5760 |
| Turbidity, FAU | 128–162 |
| SS, mg/L | 114–131 |
| pH | 8.3–9.10 |
| Conductivity, µS/cm | 22,250–25,060 |
| Iron, mg/L Fe | 1.6–2.3 |
| Zinc, mg/L Zn | 0.2–0.4 |
| Total hardness, mg/L as $CaCO_3$ | 2370 |
| Calcium, mg/L as Ca-$CaCO_3$ | 1900 |
| Magnesium, mg/L as Mg-$CaCO_3$ | 470 |