Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Performance evaluation of activated neem bark for the removal of Zn(II) and Cu(II) along with other metal ions from aqueous solution and synthetic pulp & paper industry effluent using fixed-bed reactor

Utkarsh Maheshwari[a], *Suresh Gupta*[b,*]

[a] *Department of Chemical Engineering Birla Institute of Technology and Science (BITS), Pilani 333031, Rajasthan, India*
[b] *Department of Chemical Engineering Birla Institute of Technology and Science (BITS), Pilani 333031, Rajasthan, India*

ARTICLE INFO

Article history:
Received 11 December 2015
Received in revised form 21 April 2016
Accepted 10 May 2016
Available online 20 May 2016

Keywords:
Zinc
Copper
Yoon model
Column studies
Pulp & paper industry
Multiple metal ions

ABSTRACT

The fixed-bed adsorption experiments are performed for the removal of copper [Cu(II)] and zinc [Zn(II)] by utilizing activated neem bark as an adsorbent. The present study demonstrated the effect of various parameters such as inlet concentration, adsorbent mass and inlet flowrate for the removal of Cu(II) and Zn(II) from aqueous solutions. Various kinetic parameters such as EBRT, stoichiometric capacity, breakthrough time, etc. are evaluated using the experimental data. Yoon–Nelson and Yan model available in the literature are also validated with the experimental data. The developed adsorbent is also tested for the simultaneous removal of multiple metal ions [Cr(VI), Cu(II), Zn(II), Pb(II), Ni(II) and Cd(II)] from the synthetically prepared pulp & paper industrial effluent.

1. Introduction

Water pollution is leading to a new row with an increase in industrialization and utilization of heavy metals in diverse operations. The industries such as textile, pulp & paper, tanning, electroplating, fertilizer production, washing of brass units, etc. are using different heavy metals in their processes. The effluent from these industries are rich in heavy metal ions and are considered as the primary source of water pollution (Gupta and Maheshwari, 2014; Maheshwari, 2013; Maheshwari and Gupta, 2011, 2016b)

The effluent from most of the metal processing industries contain a divalent form of Copper [Cu(II)] and Zinc [Zn(II)]. The effluent from pulp & paper industries contains several heavy metals such as Cr, Cu, Zn, Pb, Ni, Cd, etc. (Thippeswamy et al., 2012). Although, copper and zinc are among the essential nutrients required for the human being for the proper metabolism activity, excessive dosage can lead to the lethal consequences. Cu(II) is having carcinogenic and mutagenic properties, which can lead to a vital condition for lung cancer. This type of problems is very frequent among the personnel working in a vicinity exposed to the Cu(II) containing spray

* Corresponding author. Tel.: +91 1596 515224; fax: +91 1596 244183.
E-mail addresses: utkarsh@pilani.bits-pilani.ac.in, utkarshmaheshwari13@gmail.com (U. Maheshwari), sureshg@pilani.bits-pilani.ac.in (S. Gupta).
http://dx.doi.org/10.1016/j.psep.2016.05.009
0957-5820/

Abbreviation

AAS	Atomic Absorption Spectrophotometer (AA-7000, Shimadzu)
A_c	area underneath the curve (C_{ad} vs t)
a_i	Yan model parameters
C_{ad}	adsorbed concentration, $mg\,L^{-1}$
C_0	initial inlet concentration, $mg\,L^{-1}$
C_e	exit concentration, $mg\,L^{-1}$
EBRT	empty bed residence time, s
$K_{YN,i}$	rate constant of i^{th} component for Yoon–Nelson model, h^{-1}
m_t	total amount of metal fed to the column, g
nANB	nano-porous activated neem bark
Q	flowrate, $ml\,min^{-1}$
$q_{0,i}$	Yan model parameters
q_t	total amount of metal adsorbed in time t, $mg\,g^{-1}$
Ra	adsorbent exhaustion rate
S	total percentage removal of metal
t	sampling time, h
t_b	breakpoint time, h
t_f	final time, h
t_t	equivalent time corresponding to the stoichiometric capacity of the fixed-bed column, h
W	amount of adsorbent utilized
y	fraction of unused bed length

Greek symbol

τ_i	time corresponding to the 50% of i^{th} adsorbate breakthrough, h

(Liang et al., 2010). The high intake of Zn(II) can lead to nausea, loss of appetite and irritability (Naiya et al., 2009). The specified allowable limit provided by United States Environmental Protection Agency (US-EPA) for the presence of Cu(II) and Zn(II) in safe potable water is 1.0 and 5 $mg\,L^{-1}$ respectively (USEPA, 2009). Similarly, the permissible limit for Cr, Cd, Ni and Pb in potable water is 0.1, 0.005, 0.1 and 0.015 $mg\,L^{-1}$ respectively (USEPA, 2009).

The negative impact of these metals present in the effluent streams led to a need for proper treatment technique before it get discharged to the external water bodies such as lakes, ponds, rivers, etc. The effluents from industries must contain pollutants in their permissible limit, failing to which can lead to severe environmental regulations breach.

There are various techniques available for the removal of heavy metals from industrial wastewaters. These range from electrolysis (Khattab et al., 2013), ion exchange (Shek et al., 2009), polymer inclusion membrane (Kaya et al., 2016), solvent extraction (Zhang and Zhu, 2012), chemical precipitation (Kim et al., 2008), membrane separation (Salahi et al., 2013), adsorption (Gangadhar et al., 2012; Maheshwari and Gupta, 2016a; Olgun and Atar, 2011), etc. Out of all the available methods, adsorption is proven to be a more reliable method (Atar et al., 2012; Bhargavi et al., 2015; Maheshwari and Gupta, 2015). The basic advantage of adsorption on other techniques is its cost effectiveness and ability to handle large volume & multiple metal ion solutions. Adsorption is much more effective for the simultaneous removal of multiple pollutants (Maheshwari and Gupta, 2016b).

A low-cost adsorbent, capable for the removal of multiple metal ions may be an added advantage to the process. A number of researchers are working for the development of the adsorbents using different low-cost resources such as rice husk (Mohan and Sreelakshmi, 2008), tamarind seeds (Gupta and Babu, 2009b), wheat bran (Kaya et al., 2014), fly ash (Gupta and Babu, 2010b), sawdust (Larous and Meniai, 2012), tree bark (Salem and Awwad, 2014), tea factory waste (Wasewar, 2010), cashew nut shell (SenthilKumar et al., 2011), tomato waste (Yargıç et al., 2015), etc. as a potential alternative to the commercially available adsorbents. Many of the reported studies are limited to batch mode for the pollutant removal from wastewater streams. Most of the adsorbents are tested for the treatment of the single metal ion rich effluent streams. However, in the real situation, the industrial wastewater contains multiple metal ions. Hence, there is a need to develop an adsorbent from a low-cost material which can be efficiently employed for the removal of multiple metal ions from industrial effluent. The low-cost adsorbent being nanoporous may provide the high surface area which results in the increase in active sites for the adsorption process to occur.

The present work deals with the exploitation of the developed adsorbent (activated neem bark) for the remediation of Cu(II) and Zn(II) from aqueous solutions in a fixed-bed column. Continuous experiments are conducted to study the effect of inlet concentration, adsorbent dosage (column height) and the inlet flowrate on the removal of Cu(II) and Zn(II). The Yoon–Nelson and Yan model are utilized to determine different kinetic parameters using the experimental data. Furthermore, the developed adsorbent is utilized for the treatment of synthetically prepared pulp & paper industry effluent containing Cr(VI), Cu(II), Zn(II), Pb(II), Ni(II) and Cd(II) as per the composition reported in the literature.

2. Materials and methods

The neem bark is gathered from the Birla Institute of Technology and Science (BITS), Pilani region. The bark is washed, crushed and screened out to obtain the required particle size ($d_p \approx 1.2$ mm) particles. The specified particles are treated chemically with H_2SO_4 (98%) (1:1 weight%) and later kept for drying at 70 °C for 24 h. Further, the dried neem bark is washed with purified water for the removal of any free acid on the surface. The activated neem bark has already been characterized and reported in one of the earlier studies and is termed as nANB (Maheshwari and Gupta, 2015).

Stock solutions of 1000 $mg\,L^{-1}$ for various metals are prepared using stoichiometric amount of different salts (Table 1). The stock solutions are further diluted to the desirable concentrations using distilled water. A fixed-bed glass column, 1 inch in diameter is utilized for the continuous studies. The column is properly packed with the nANB. A pictographic depiction of the column is given in Fig. 1.

The effect of inlet concentration (50 and 100 $mg\,L^{-1}$) on the Cu(II) and Zn(II) removal is evaluated by performing continuous experiments, keeping the adsorbent dosage and inlet flowrate constant at 75 gm and 10 $ml\,min^{-1}$ respectively. The effect of adsorbent dosage on the removal of Cu(II) and Zn(II) is studied by varying the adsorbent dosage as 25, 50, 75, 100, 125, 150 and 175 gm while maintaining the flowrate at 10 $ml\,min^{-1}$ and inlet concentration constant at 50 $mg\,L^{-1}$ respectively. The effect of flowrate is assessed by keeping the inlet concentration and adsorbent dosage at 50 $mg\,L^{-1}$ and 75 g while varying