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Modeling adsorption of copper(II), cobalt(II) and nickel(II) metal ions from aqueous solution onto a new carboxylated sugarcane bagasse. Part II: Optimization of monocomponent fixed-bed column adsorption

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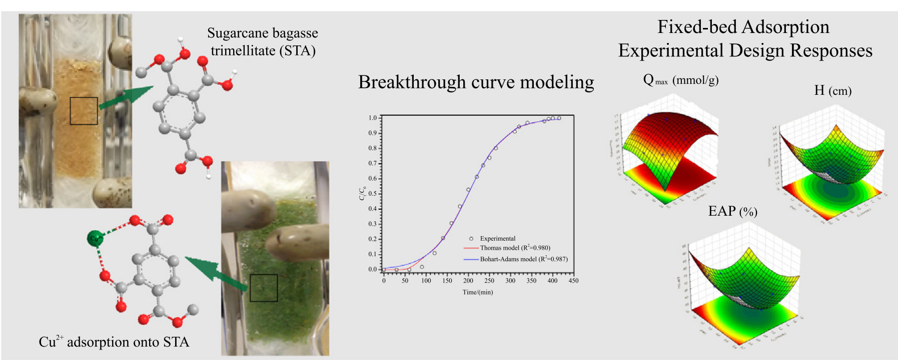
GRAPHICAL ABSTRACT



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ABSTRACT

In the second part of this series of studies, the monocomponent adsorption of Cu^{2+}, Co^{2+} and Ni^{2+} onto STA adsorbent in a fixed-bed column was investigated and optimized using a 2^2 central composite design. The process variables studied were: initial metal ion concentration and spatial time, and the optimized responses were: adsorption capacity of the bed (Q_{max}), efficiency of the adsorption process (*EAP*), and effective use of the bed (*H*). The higher Q_{max} for Cu^{2+}, Co^{2+} and Ni^{2+} were 1.060, 0.800 and 1.029 mmol/g, respectively. The breakthrough curves were modeled by the original Thomas and Bohart-Adams models. The changes in enthalpy ($\Delta_{ads}H^\circ$) of adsorption of the metal ions onto STA were determined by isothermal titration calorimetry (ITC). The values of $\Delta_{ads}H^\circ$ were in the range of 3.0–6.8 kJ/mol, suggesting that the adsorption process involved physisorption. Desorption (E_{des}) and re-adsorption ($E_{re\text{-}ads}$) of metal ions from the STA adsorbent were also investigated in batch mode, and the optimum conditions were applied for three cycles of adsorption/desorption in a fixed bed column. For these cycles, the lowest values of E_{des} and $E_{re\text{-}ads}$ were 95 and 92.3%, respectively, showing that STA is a promising candidate for real applications on a large scale.

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Nomenclature

Abbreviations and symbols

AC	activated carbon
b	Langmuir constant (L/mmol)
C	metal ion concentration (mmol/L)
CCD	central composite design
CTA	carboxylated cellulose derivative
DV	dependent variables
EAP	efficiency of the adsorption process (%)
E_{des}	desorption efficiency (%)
$E_{re\text{-}ads}$	efficiency of re-adsorption (%)
H	effective use of the bed (cm)
$\Delta_{ads}H^{desol}$	enthalpy change associated with the desolvation of adsorption sites on the STA surface and metal ions in the bulk solution (kJ/mol)
$\Delta_{ads}H^{M2+\text{-}STA}$	enthalpy change associated with the formation of the interactions between the STA adsorbent and the metal ions (kJ/mol)
$\Delta_{ads}H^{M2+\text{-}M2+}$	enthalpy change associated with the formation of metal ion-metal ion interactions on the adsorbent surface (kJ/mol)
ITC	isothermal titration calorimetry
$k_{B\text{-}A}$	Bohart-Adams kinetic rate constant (mL/mmol min)
k_{Th}	Thomas kinetic rate constant (mL/mmol min)
Q_{max}	maximum adsorption capacity (mmol/g)
$Q_{max,e}$	maximum adsorption capacity at equilibrium (mmol/g)
$Q_{re\text{-}ads}$	maximum re-adsorption capacity (mmol/g)
$Q_{i,int}$	absorbed or released heat in the reaction cell at the ith injection in the presence of the STA adsorbent (kJ)
$Q_{i,dil}$	absorbed or released heat in the reaction cell at the ith injection in the absence of the STA adsorbent (kJ)
$q_{e,i}$	amount of metal ion adsorbed on the STA adsorbent at ith injection
q_{M2+}	amount of metal ion adsorbed in the bed (mmol)
$RMSE$	root-mean-square error
SB	sugarcane bagasse
STA	trimellitated sugarcane bagasse
t_e	equilibrium time (min)
t_b	breakthrough time (min)
t_s	saturation time (min)
w_{M2+}	total amount of metal ion fed into the bed (mmol)
w_{STA}	weight of STA (g)
w'_{STA}	weight of the STA adsorbent in desorption experiment (g)
$w_{STA,M2+}$	weight of the STA adsorbent loaded with metals (g)
Z	bed height (cm)
ρ_b	bulk density (g/mL)
ε	column void fraction
τ	spatial time (min)
v	interstitial velocity (cm/min)

Subscripts

0	initial
ads	metal ions adsorbed
des	metal ions desorbed
e	equilibrium
exp	experimental
t	time
t_b	breakthrough point
t_s	saturation point

1. Introduction

Strategies to mitigate the negative effects of various industrial activities on the environment have been discussed in several studies [1–6] due to the increasing number of environmental problems. The pollution caused by metal ions is one of the major environmental concerns because of their toxicity, accumulation in the food chain and persistence in nature [7]. Industries such as electroplating, battery manufacture, mining operations and paint and pigment production are some of the main sources of metal ions [8].

Various technologies have been used for treating metal-contaminated effluents, such as adsorption, biological systems, chemical precipitation, ion-exchange, reverse osmosis, solvent extraction and ultrafiltration [9]. Among them, adsorption is a promising technique because it can be used to treat very diluted effluents with a high removal efficiency, allowing attainment of high standards of water quality, as imposed by public health authorities. In addition, the adsorption process is easy to operate and there is a wide range of adsorbents available, including several materials from renewable sources [8].

The development of the use of adsorbent materials from lignocellulose biomass, such as sugarcane bagasse, has been successfully performed [10–13] and offers an alternative to the traditional treatment processes using activated carbon (AC), first applied in metallurgy for gold recovery [14] and which, nowadays, are widely used for treating industrial and domestic wastewaters [15]. However, the successful commercial application of an adsorbent depends both on its specificity for target pollutants and on its recyclability [16]. For this, specific chemical modifications can be made to improve the adsorbent performance; and in this sense, the use of lignocellulose biomass is favored in comparison to AC due to its chemical composition with great availability of hydroxyl groups on its surface, which can be converted into a variety of functional groups of interest with improved properties [17].

The adsorption process can be performed in batch or continuous mode. The batch mode presents some limitations that are less convenient for industrial applications, such as the capacity to treat small volumes of wastewater, the requirement of an additional separation step for the particle discharge from the reactor before proceeding to the regeneration of the adsorbent, and the concentration of the pollutant in the treated effluent is not always sufficiently low for the permissible limits for discharge. Meanwhile, continuous adsorbers ensure very low outlet concentrations until the breakthrough point and can be easily regenerated and repeatedly applied [18].

Various parameters can affect the process efficiency in a packed column, such as the nature of adsorbate and adsorbent, bed height, adsorbate inlet concentration, influent pH and inlet flow rate [19]. In most studies published in the literature, these effects are evaluated individually, which does not contribute to the understanding of how simultaneous changes in the process variables affect the desired process response. In that situation, multivariate statistical tools are useful for establishing relationships between variables and desired responses; also allowing a significant cost reduction by means of the reduction in the experimental efforts [19–21].

In the first part of this series of studies [17], the synthesis of a new adsorbent material (STA) prepared from the functionalization of sugarcane bagasse with trimellitic anhydride was described in