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Research paper

Competitive adsorption of Cu^{2+} and Ni^{2+} on *Luffa acutangula* modified Tetraethoxysilane (LAP-TS) from the aqueous solution: Thermodynamic and isotherm studies

Rais Ahmad*, Shaziya Haseeb*

Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India

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ABSTRACT

Luffa Actangula Peels modified with Tetraethoxysilane (LAP-TS) was evaluated for the removal of Cu^{2+} and Ni^{2+} ions from the aqueous solution. The presence of functional groups like –CH and –CO_3, –C–O groups on the surface of the peel and surface morphology were characterized by FTIR, EDX and SEM. The LAP-TS shows equilibrium adsorption capacity of 12 mg g^{-1} at pH 5.0 for Cu^{2+} ion and 12 mg g^{-1} at pH 7.0 for Ni^{2+} ion in 120 min at 303 K temperature. In case of Cu^{2+} ion it is best fitted by Langmuir Isotherm showing monolayer adsorption capacity of 22.056 mg g^{-1} whereas in case of Ni^{2+} it is best fitted by Freundlich Isotherm with multilayer adsorption capacity of 22.716 mg g^{-1} and higher regression coefficient n single metal adsorption system the adsorption efficiency removal of LAP-TS towards Cu^{2+}(95%) were more than Ni^{2+}(80%) ions, whereas in case of binary system it was about 96%, which increases at higher concentration at pH 5.0. The adsorption of Cu^{2+} and Ni^{2+} ions were thermodynamically spontaneous, Endothermic in nature with randomness at solid/liquid solution interface in both the cases. The adsorption of Cu^{2+} and Ni^{2+} follows pseudosecond order kinetics showing chemisorption interaction and intraparticle diffusion is the main rate determining step.

1. Introduction

Veneration of our pristine environment is geometrically diminishing due to human non-adherence to environmental laws in their quest for technological advancement. Pollutants such as heavy metals, dyes, pesticides and pharmaceutical wastes are alien to groundwater and rivers thereby impacting negatively on the ecosystem. Heavy metals have become major surface water and groundwater contaminants. Untreated and uncontrolled discharge of heavy metals containing wastewater into the natural environment is toxic to the flora and fauna of the ecosystem (Ahmad et al., 2010). The toxicity of Cu^{2+} and Ni^{2+} affects the human organism causing several diseases like Wilson disease, gastrointestinal problems, affecting brain and liver and carcinogenic diseases. These metal ions, and their supplementary complexes, could accumulate in the body of fishes and other aquatic organisms, and finally could reach to the human body by bio-accumulation, bio-concentration and bio-magnification through the drink and food chains (Hu et al., 2007).The removal of these toxic metal ions from the wastewater streams is a challenging process. Removal of toxic metal ions from large volumes of waste waters requires a cost effective remediation technology.

Various treatment technologies like ion exchange, flocculation, precipitation, reverse osmosis, coagulation, electro deposition, membrane separation (Mallampati et al., 2015) have been used. All of these technologies have its pros and cons. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Adsorption is the one of the most studied wastewater treatment technologies, which has been effectively applied using a wide range of different materials, including low-cost and highly available biosorbents (Ramirez and Holmes, 2008). Extensive studies have been carried out in recent years with the aims of finding alternative and economically feasible biosorbents for wastewater and water treatment. At a large scale, economic sorbents can be defined as materials which are abundant in nature can be found as a by-product or waste from agro-industry are cheap and normally do not require significant

Abbreviations: LAP-TS, Luffa Actangula peels-Tetraethoxysilane modified; SEM, Scanning Electron Microscopy; FTIR, Fourier Transform Infrared Spectroscopy; EDX, Electron Dispersive X-ray Spectroscopy; AAS, Atomic Absorption Spectroscopy; pHzpc, Point of Zero Charge

* Corresponding authors.
E-mail addresses: rais45@rediffmal.com (R. Ahmad), shaziya.shoaib@gmail.com (S. Haseeb).

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pre-processing. Recent studies on the removal of heavy metals have reported the use of numerous types of biomass/biomaterials. Various agricultural waste like Cashew nut shell, (Kumar et al., 2011) tea factory waste (Malkoc and Nuhoglu, 2005), banana peel (Qi and Aldrich, 2008), Luffa peels and corn fibers (Mallampati et al., 2015), tobacco dust (Hossain et al., 2012), Luffa Cylindrica Fibers modified with Tetraethoxysilane for removal of dye (Demir et al., 2008), Luffa Actangula Peel (Ahmad and Haseeb, 2016). Several mechanisms may govern biosorption of metals that differ qualitatively and quantitatively from species to species, origin, and processing procedure of biomass/biomaterials (Karthikeyan et al., 2007). Biomass/biomaterials comprise several chemical or functional groups such as acetamide, amino, amide, sulfhydryl, sulfate, carboxyl etc. which could attract and sequester the metals from solution (Karthikeyan et al., 2007; Vieira and Volesky, 2010).

Luffa acutangula or simply called ridged gourd or Turai (in hindi) is a cheap vegetable easily available in India. This vegetable is a rich source of fat, carbohydrate, potassium. Luffa peels contain carotenoids, oleanolic acid and phenolic compounds (Kao et al., 2012) and functional groups such as –OH and –COOH on the surface could act as potential adsorption sites for pollutants. The Luffa Actangula peels are highly fibrous as shown in SEM images, so it can work effectively for the removal of metals ion. The Luffa Actangula peels were used for the removal of the Pb^{2+} ions as reported in the literature (Ahmad and Haseeb, 2016).The Luffa Actangula peel show lesser adsorptive removal efficiency towards Cu^{2+} and Ni^{2+} ions. Luffa Actangula peels adsorptive efficiency was increased with the help of Tetraethoxysilane towards Cu^{2+} and Ni^{2+} ions. Dried and grounded powder of Luffa Actangula peel was treated with tetraethoxy silane Tetraethoxysilane solution and was used for further adsorption studies. Tetraethoxy silane Tetraethoxysilane or commonly called Siloxane with the chemical formula $C_8H_{20}O_4Si$. It is a stable, flammable, incompatible with strong oxidizing agent. The effects of various parameters such as contact time, pH, Point of zero charge, temperature, isotherms, kinetics and thermodynamic studies were analyzed. In order to understand the adsorption mechanism and evaluate the effectiveness of the adsorbent, different adsorption and kinetic models were used to analyze the data in detail.

2. Materials and methods

2.1. Materials

Luffa Actangula Peels were collected from the local markets as a waste, Tetraethoxy silane in liquid form (mol.wt=208.33 g) purchased from Alfa Ceaser, India. Copper Nitrate, Nickel nitrate, HCl, NaOH, KCl Copper Nitrate ($Cu(NO_3)_2.4H_2O$), Nickel nitrate($Ni(NO_3)_2.6H_2O$), Hydrochloric Acid(HCl), Sodium Hydroxide(NaOH), potassium chloride (KCl) was purchased from Merck India (AR Grade).

2.2. Adsorbent preparation

The Luffa Actangula Peels (LAP) was collected as a waste. It was washed with distilled water and dried. The dried material was grinded in a mechanical grinder followed by sieving. The dried adsorbent was converted into 50 (0.297 mm) Mesh BSS particle size.

It was then further washed several times with double distilled water to remove dirt, color and impurities. The dried material was grinded in a mechanical grinder followed by sieving. The dried adsorbent was converted into 50 (0.297 mm) Mesh BSS particle size.

In order to modify the surface,10 g of LAP was treated with 0.5 M (100 mL) of Tetraethoxy silane solution in a conical flask and left for 24 h followed by stirring. Afterwards the adsorbent was filtered and washed several times with double distilled water and the dried powder LAP-TS was used for further adsorption studies.

2.3. Characterization

The photomicrography of the exterior surface of adsorbent was obtained by scanning electron microscopy (JSM-6510LV). The functional groups were characterized by FTIR (Perkin Elmer, U.S.A, model spectrum-BX, range 4000–400 cm^{-1}). The elemental characteristics were obtained by EDX (JSM-6510LV). The adsorption characteristics were determined. The residual metal concentration remained in the solution after treatment were determined by Atomic Absorption Spectroscopy (GBC-902, Australia). The pH was measured by pH meter (Elico L1 120, India)

2.4. Batch adsorption studies

The selective nature of LAP-TS was studied for Cu^{2+}, Ni^{2+}, Cr^{6+} and Pb^{2+}. The maximum adsorption was found in the order of $Cu^{2+} > Ni^{2+} > Pb^{2+} > Cr^{6+}$. On the basis of maximum removal capacity the Cu^{2+} and Ni^{2+} was selected for further studies and shown in Fig. 1

Adsorption studies were carried out in batch process. Solutions of Cu^{2+} and Ni^{2+}(50 mL) of desired concentrations (10–100 mg L^{-1}) were equilibrated with 0.1 g of adsorbent (LAP-TS) in 50 mL capped glass bottle. The mixture was kept at room temperature for 24 h. Samples after equilibration were taken for AAS analysis. The samples were analyzed in triplicates and adsorption capacity values at equilibrium (q_e) were calculated by using the following relationship:

$$q_e = \frac{(c_o - c_e)V}{W} \tag{1}$$

$$\%removal = \frac{(c_o - c_e)100}{c_e} \tag{2}$$

where q_e is the adsorption capacity at equilibrium, c_o is the initial concentration of the adsorbate (mg L^{-1}) and c_e is the concentration of adsorbate at equilibrium (mg L^{-1}), *V* volume of the solution (L) and *W* is the mass of the adsorbent (g).

Binary component adsorption of Cu^{2+}, Ni^{2+} onto LAP-TS was performed by taking 50 mL of solution with concentration of each metal in the range of 20–100 mg L^{-1}. The adsorption experiment in binary system was carried out in pairs with the mass ratio of 1:1

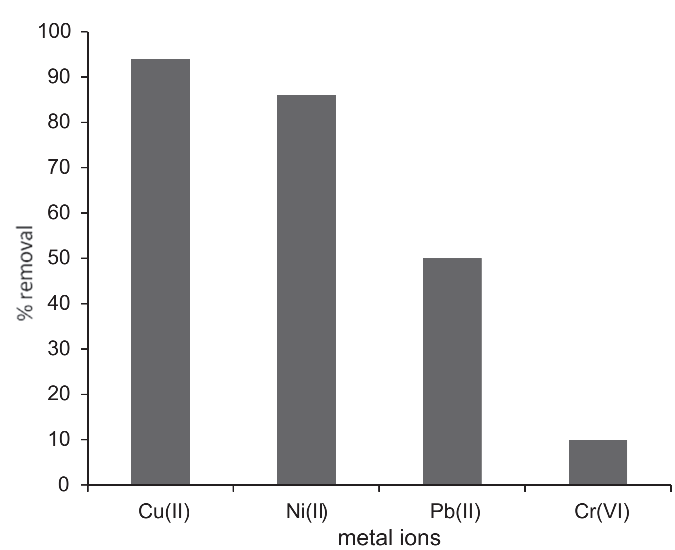

Fig. 1. % removal efficiency of metal ions on LAP-TS.