International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2018): 7.426

Kinetic Study for Removal of Cu^{+2} from Waste Water by Chemically Modified Bio-Adsorbents of *Citrus Reticulata*

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Abstract: ***A series of waste of "kinnow" bio-sorbents has been prepared by different chemical modifications for the removal of copper(II) adsorption from waste water. The different bio-sorbents and raw kinnow peels were examined with different parameters like influences of pH, contact time, initial copper concentration. The maximum adsorption capacity of copper was 1.22 mol/kg, using orange peel esterified by 0.6 mol/L citric acid at 80 °C after 0.1 mol/L NaOH saponification. A comparison of different isotherm models revealed that the combination of Langmuir and Freundlich (L–F) isotherm model fitted the experimental data best. Results indicate that the chemically modified kinnow peel can provide an efficient and cost effective technology for eliminating copper from aqueous solution.***

Keywords: *Citrus Reticulata*, Cu^{+2}, pH, Adsorbents, Contact Time, Kinetics isotherms.

1. Introduction

In present time, heavy metal ions become a problem due to their toxic effects to the environment and accumulation throughout the food chain. These ions are discharged by the industries of mining, milling and surface finishing into the environment. There are many methods and technologies are available for the removal of heavy metal ions like chemical reduction, ion exchange, electrochemical treatment, chemicalprecipitation, membrane separation etc. But these methods requires heavy cost, so an efficient and very cost effective treatment method is required to treat large volumes of industrial heavy metal containing wastewaters (Volesky2001; Leusch and Volesky 1995).Biosorption have been considered as cost effective methods for the removal of heavy metal ions. In biosorption, heavy metal ions are removed by biological materials and biomaterials. Biomasses are generated as a waste by-product of large-scaleindustrial processes and vegetable biomass, such as marine algae (Luoet al., 2006), rice husk (Chockalingam and Subramanian 2006), sawdust(Larous et al., 2005), crKP milling waste (Saeed et al., 2005), corncob(Leyva-Ramos et al., 2005), cellulose/chitin beads (Zhou et al., 2005), etc.There are many studies have been reported on the adsorption ofheavy metals like biomaterials derived from the marine algae (Feng andAldrich, 2004); the biosorption of heavy metals by Sphaerotilusnatans(Esposito et al., 2001); the adsorption of lanthanum and cerium on leaf(Sert et al., 2008) and the cKPper adsorption on calcium alginate beads(Veglio et al., 2002).

In our present work, we have investigated in detail the removal ofCu(II) by modified kinnow adsorbents and in this work we consider the adsorption behaviorof Cu(II) ions. Kinnow residue was chosen as biosorbentdue to its special structure, insolubility in water, chemical stability andlocal availability. Cellulose, hemi-cellulose, pectin substances, chlorophyll pigments and other low molecular weight compounds like limonene is present in kinnow.These components contain various functional groups suchas carboxyl, hydroxyl and amido-cyanogen, which play an importantrole in removing the heavy metals (Gross 1977).In this study, a series of kinnow cellulose adsorbents were prepared by means of different chemical modifications to explain the adsorption mechanism. The effects of different chemical modification with NaOH, citric acid, and Fe_3O_4 on thecharacter of the adsorbents were examined under different conditions, including acid concentration, temperature,pH of the solution, contact time, initial copper concentration and solid/liquid ratio on copper removal.

2. Materials and Methods

Biosorbentpreparation "Kinnow" *citrus reticulata*

Kinnow was collected from local market and washed with water, it abbreviated as KP, was dried for 24 h at 50 °C then ground to approximately 0.106mm. Elemental analysis of kinnow was carried out using GmbH Elementar by heating the sample from 25 °C to 1000 °C at a heating rate of 10 °C/min. The results showed that kinnow is composed of 41.5% carbon, 5.5% hydrogen, 51.2% oxygen and 1.8% nitrogen.

Modified with different alkali saponification

1 g of KP was directly stirred with 5 mL of 0.5M HCl solution and stirred for 2 h at 50 °C temperature.After vacuum filtered, washed with distilled water to neutral pH and then was kept for drying in an oven at 55 °C about 24 h, hereafter abbreviated as AKP.

Modified with alkali saponification

1 g of KP was directly stirred with 5 mL of 0.5M NaOH solution and stirred for 2 h at 50 °C temperature.After vacuum filtered, washed with distilled water to neutral pH and then was kept for drying in an oven at 55 °C about 24 h, hereafter abbreviated as BKP.

Modified with citric acid

1 g of KP was directly mixed with 5mL of 0.5M citric acid solution and stirred for 2 h at 50 °C temperature. After vacuum filtered, washed with distilled water to neutral pH and then was kept for drying in an oven at 55 °C about 24 h, hereafter abbreviated as CAKP.

Biosorption experiments

All solutions were prepared from analytical grade reagents in distilled water with 0.1 mol/L NaCl added to control the ionic strength and hexamethylenetetrammine used to buffer the pH. Stock copper solution was prepared by dissolving $CuCl_2$ in 25 mL 0.1 mol/L NaCl and 25 mL hexamethylenetetrammine buffer solution (pH=5.0) and diluting to 250 mL. The pH of each solution was adjusted with 0.1 mol/L NaOH and 0.1 mol/L HCl and measured with a pHs-3C Model acidity meter (Shanghai Precision & Scientific Instrument Co. Ltd. China). Batch adsorption tests were carried out to study the effect of various parameters on the adsorption efficiency of copper by adsorbents. Unless otherwise stated, 25 mg of each adsorbent was placed in 15 mL of copper solution and mixed vigorously in a rotary shaker at room temperature for 24 h to reach equilibrium. The concentration of copper in the filtrate was titrated by standard EDTA solution. All determinations were performed in triplicate and the average was used for this work.

Kinetic study of adsorption of Cu^{+2}

Peel of “Kinnow” *citrus reticulate* was used for removal of metal from aqueous solutions using a batch adsorption process. In each test 20 ml of 0.001mol/Lof Cu(II) solution at pH 7 was taken in 100 mL beaker. The pH of the solution was adjusted using 0.1N HCl or NaOH solutions. After incubation with known amount of adsorbents at predefined time interval the samples were centrifuged for 5 min at 4000 rpm at room temperature. The residual concentration of metal ion was determined by using an UV-VIS spectrophotometer (Systronics) at wave-length of 554 nm in the supernatant. The adsorption amount (Q_e) and the removal percentage ($E\%$) were calculated according to following equation:

$$Q_e = \frac{(C_0 - C_e)V}{W}$$

$$E\% = \frac{(C_0 - C_e)V}{C_0} X\ 100$$

Where $Q_e$is the adsorption amount of metal ion, W is theweight of the adsorbent (g), V is the volume of solution (L), and C_0 and $C_e$are the initial and equilibrium concentrations of Cu^{2+} in solution, respectively (mol/L).

2.1 Adsorption isotherms

To explicate adsorbate-adsorbent interaction the Langmuir (1918), the Freundlich (1906) and the Temkin and Pyzhev (1940) isotherms were used.

2.1.1 Langmuir isotherm

Langmuir isotherm theory is based on the assumption that adsorption takes place on limited number of sites of homogenous surface of adsorbate as a monolayer and there is no interaction between adsorbate and adsorbent except adsorption. Linear expression for the Langmuir adsorption isotherm can be expressed as below:

$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$$

Where C_e and q_e are the concentration of adsorbate in the liquid phase (mg/l) and the equilibrium concentration (mg/g) respectively. Q_{max} and b are the maximum adsorption capacity in monolayer form of the solid phase (mg/g) and the constant energy related to the heat of adsorption respectively. Therefore, the plot of C_e/q_e against C_e should be a straight line. The values of Q_{max} and b were determined from the intercept and the slope of the plot.

A dimensionless parameter, separation factor, R_L, is calculated from the Langmuir isotherm. It can be determined using following equation:

$$R_L = \frac{1}{1 + (bCi)}$$

Where, C_i is the initial concentration of dye. The value of R_L indicates whether an isotherm is irreversible (R_L=0), favorable ($0 < R_L < 1$), linear (R_L =1) or unfavorable ($R_L > 1$) (Gusmão *et al.*, 2013).

2.1.2 Freundlich isotherm

This isotherm (Freundlich, 1906) describes equilibrium on heterogeneous surfaces. This model assumes the multilayer adsorption of the substance on the adsorbent. It can be expressed in its linear form as follows:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$$

Where q_e (mg/g) and C_e (mg/l) are the amount of adsorbate adsorbed on the solid phase at equilibrium and the concentration of adsorbate in the liquid phase at equilibrium respectively. k_f and n are isotherm constants which indicate the capacity and the intensity of the adsorption respectively (Arias and Sen, 2009). The values of k_f and 1/n are calculated from the intercept and slope of the plot of $\ln q_e$ versus ln C_e respectively. Favorability of adsorption can be ascertained, if the value of 1/n falls in the range from 0 to 1.

3. Results and Discussions

Effect of concentration of adsorbenton adsorption

To study the effect of concentration of adsorbent on adsorption Varying concentration (0.01g, 0.02g, 0.05g, 0.10g, 0.25g, 0.50g, 0.75g and 1.0 g) of adsorbents (KP, AKP, BKP, MKP) were added in 20 ml of 0.001mol/Lmetal ionsolution at pH 7 in 100 mL beaker. The suspension was stirred for 60 minutes at 30°C.After that, adsorption of metal ion (mg/g) was determined.

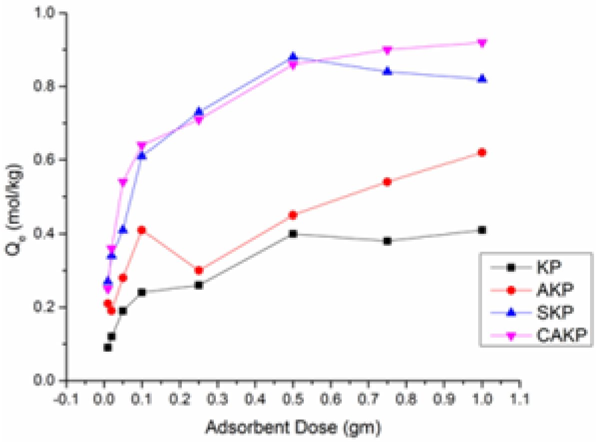

Figure 1: Adsorption of Cu^{2+} at different adsorbent dose by chemically modified biosorbents and raw kinnowpeels (initial copper concentration=0.001 mol/L; s/l ratio=1.6 g/L).

Effect of contact time on adsorption

To study effect of contact time on adsorption, 0.02 g of each chemically modified adsorbent (KP, AKP, BKP, MKP) was added in 10 ml of 0.001mol/Lmetal ion solution at pH 7 in 100 mL beaker. The suspension was stirred for different time interval (10, 20, 30, 40, 50, 60, 70, 80, 90, 100 minutes) at 120 rpm on orbital shaker at 30°C.After that, adsorption of metal ion (mg/g) was determined.

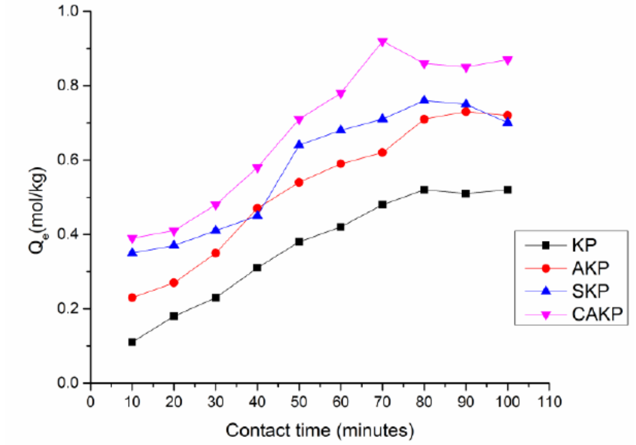

Figure 2: Adsorption of Cu^{2+} at contact time by chemically modified biosorbents and raw orange peels (initial copper concentration=0.001 mol/L; s/l ratio=1.6 g/L).

Effect of pH on metal ion bio sorption:

The effects of initial pH on adsorption of 0.001 mol/L Cu(II) by different adsorbents at room temperature are shown in Fig.1. It is clear that the amount of adsorbed copper increased with the increase in pH as similarly reported by Reddad (2002 a,b). At pHb2.5, because the surface active sites of the adsorbent were protonated, the competition of Cu2+ and H+ for the same surface active sites resulted in very low copper uptake. When the pH was 4.5–5.5, the maximum adsorptionwas obtained for all the adsorbents. With pH further increasing, the Cu^{2+} uptake decreased due to the formation of soluble hydroxyl complexes and the precipitation of copper hydroxide.

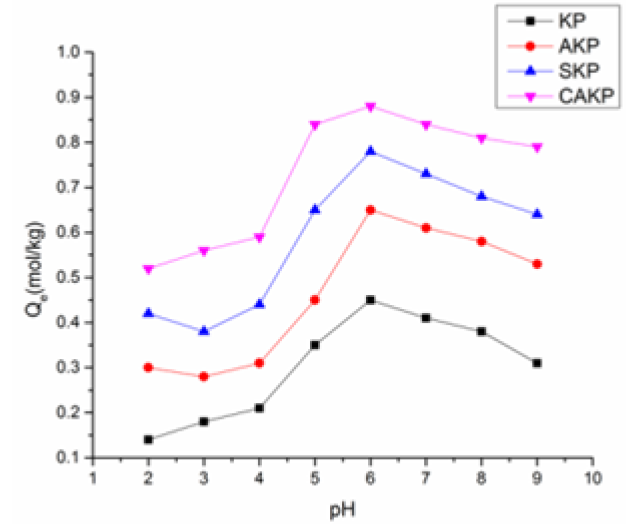

Figure 3: Adsorption of Cu^{2+} at different pH by chemically modified biosorbents and raw orange peels (initial copper concentration=0.001 mol/L; s/l ratio=1.6 g/L).

4. Conclusion

We have synthesized chemically modified adsorbents for removal of copper(II) from industrial waste water as well as aqueous solution. We studied the synthesized adsorbent with different parameters like contact time, adsorbent time and pH of water. It is found that chemically modified adsorbents performed well than non-modified adsorbenst.

5. Acknowledgement

Authors are thankful to SGV University, Jaipur for providing infrastructure facility to conduct the present research work.

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