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Intensified removal of copper from waste water using activated watermelon based biosorbent in the presence of ultrasound

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ABSTRACT

Copper is one of the most toxic heavy metals having significant effects on the living organisms and hence effective removal of copper from waste water is crucial. The current work investigates the application of activated watermelon shell based biosorbent for the removal of copper from aqueous solution. The effect of activation using calcium hydroxide and citric acid as well as the effect of operating parameters like contact time, adsorbent dosage, temperature, pH, initial concentration and ultrasonic power on the extent of removal has been investigated. Experiments performed in the presence of ultrasound to investigate the degree of intensification as compared to the conventional agitation based treatment revealed that the adsorption rate significantly increases in the presence of ultrasound and also the time required for reaching the equilibrium reduces from 60 min in conventional approach to only 20 min in the presence of ultrasound. The extent of adsorption of Cu(II) on adsorbents was found to increase with an increase in the operating pH till an optimum value of 5. The extent of adsorption also increased with a decrease in the initial concentration and particle size as well as with an increase in ultrasonic power till an optimum. Kinetics and isotherm study revealed that all the experimental data was found to best fit the pseudo second order kinetics and Langmuir adsorption isotherm model respectively. Maximum adsorption capacity was found to be 31.25 mg/g for watermelon treated with calcium hydroxide and 27.027 mg/g for watermelon treated with citric acid. Overall present study established that activated watermelon is an environmentally friendly, low cost and highly efficient biosorbent that can be successfully applied for the removal of copper from aqueous solution with intensification benefits based on the ultrasound assisted approach.

1. Introduction

Heavy metal removal from industrial waste as well as natural water sources has become a prime concern over last few decades because of the adverse effects of these heavy metals on ecosystem and living organisms. The industrial effluents from industries like mining, refining ores, fertilizer industries, tanneries, batteries, paper industries etc. contain different types of heavy metals such as Cd, Pb, Ni, Cr, As, Cu, Fe etc. [1]. If these effluent streams are continuously discharged to the ecosystem without proper treatment, it can lead to a significant toxic impact on environment. Heavy metals are non-biodegradable and tend to accumulate in living organisms resulting in several diseases and disorders as well as it can lead to severe ecological hazards. Among all these heavy metals, copper is one of the most common heavy metal observed in the aquatic environment. High intake of copper in the blood system may generate reactive oxygen species and damage the protein, lipids and DNA as well as affect the liver, kidney and pancreas. Copper also affects the marine ecosystem and has been reported to damage the gills, liver, kidneys and the nervous system of fishes as well as change the sexual life [2].

It is imperative to develop a cost effective, efficient and environment friendly method for removal of copper from waste water. Conventional methods like precipitation, coagulation, ion exchange and membrane separation processes (such as ultra filtration, electro dialysis, reverse osmosis, etc.), have been generally employed for the removal of copper from wastewater [3]. However each of these methods shows certain limitations. For example, the chemical precipitation and electroplating treatment produces large quantity of sludge, which has to be treated with great effort significantly altering the economics. Moreover, when copper ion concentration in aqueous solution is over the range of 1–100 mg/L, these methods are ineffective. Ion exchange and membrane based processes are expensive and have limitations at large scale operation.

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In recent years biosorption has shown some promise with advantages as lower cost, ready availability of adsorbents, simple to use and environment friendly. Abandoned agro-wastes are the potential sources for producing biosorbents as an alternative to the high cost adsorbents for heavy metals removal. Different biosorbents have been developed from agro-wastes such as rice husk, seaweed, wood bark, tea-waste, maize corn cob, sugarcane bagasse, sawdust, wool, olive cake, pine needles, almond shells, cactus leaves, banana and orange peel [4–5]. Watermelon shell, an agro waste is discarded all over the world as useless material, also causing waste management problem. It is an abandoned, readily available, low cost, environment friendly bio-material. Considering the above criteria and based on the fact that not much work dealing with watermelon has been reported in the literature, watermelon shell was selected in the present work to synthesize the biosorbent, with subsequent application for removal of copper from water.

Use of ultrasound in adsorption can intensify the rate of removal due to the beneficial cavitational effects obtained by passage of ultrasound through liquid. The physical effects improve the mass transfer due to convection and also result in probable activation of surface. Shock waves have the potential of creating microscopic turbulence within interfacial films surrounding the solid particles leading to significant increase in mass transfer rate. There have been some studies in the past related to the application of ultrasound for intensifying adsorption though with commercial adsorbents. Oualid et al. [6] examined the effects of ultrasound on the adsorption kinetics of p-chlorophenol on granular activated carbon. The obtained results confirmed that low frequency ultrasound enhanced the activity and capacity of the adsorbent and increased the rate of adsorption process.

The aim of the present study was to investigate the effect of ultrasound on the rate of adsorption of copper from aqueous solutions using biosorbents which have been activated using different treatments based on the use of acids and bases. The work also compares the efficacy of the modified biosorbents with the natural biosorbent and also the efficacy of the ultrasound assisted process with the conventional approach based on the use of orbital shakers. Considering the relevance of the sonochemical effects, the effect of ultrasonic power dissipation on the adsorption rate has also been investigated. To the best of our knowledge such a detailed investigation for the intensified adsorption using combination of ultrasound with activated biosorbents has not been presented and hence this forms the novelty of the present work.

2. Materials and methods

2.1. Materials

Watermelon shells were collected from local market in Mumbai. All the chemicals used as ($Cu(NO_3)_2{\cdot}3H_2O$, $Ca(OH)_2$, citric acid, NaOH, HCl, oxalic acid, lithium hydroxide) were obtained from S D Fine-Chem. Limited (SDFCL), Mumbai.

2.2. Adsorbent preparation

2.2.1. Preparation of saponified watermelon shell (SWS)

Watermelon shells were washed using distilled water repeatedly in order to remove the soluble impurities and dust particles. Watermelon shells were then cut into small pieces and 100 g of obtained watermelon particles was mixed with 5 g of calcium hydroxide and crushed into fine powder. $Ca(OH)_2$ facilitates the saponification and bleaches out the chlorophyll substances as well as removes other low molecular weight compounds that are not useful for adsorption. Suspension was maintained in beaker using agitation at room temperature. The suspension was filtered after 12 h and washed repeatedly with distilled water till pH of 7 was obtained. The separated particles were then dried in an oven at 100 °C overnight. The obtained dried powder was crushed and sieved and particles less than 300 μm were collected, and used for adsorption tests [7].

2.2.2. Preparation of acidified watermelon shell (AWS)

Watermelon shells were allowed to dry under the sun for 48 h. Shells were then heated in the oven at 120 °C overnight. Dried shells were then powdered in the mechanical grinder and sieved to get particles of size less than 300 μm. The powder was then blended with stock solution of 0.1 M citric acid solution in the proportion of 1.0 g of powder to 7.0 ml acid. The suspension was filtered after 12 h and washed repeatedly with distilled water till neutral pH condition was obtained [8]. After filtration the process was similar as described for SWS adsorbent.

2.3. Preparation of metal solution

Stock solution was prepared by dissolving salt of Cu(II) in deionised water. For the preparation of 1000 mg/L solution, 3.810 g of $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in 1000 ml of deionised water. All working solutions of varying concentrations ranging from 10 to 50 mg/L were obtained from this stock solution by successive dilution. The pH of the solution was adjusted to required value by adding either 0.01 M HCl or 0.01 M NaOH as per the requirement. The resulting stock solutions were stored in air tight bottle.

2.4. Batch studies and method of analysis

Batch studies were used to quantify the extent of removal of Cu (II) from aqueous solution. Adsorption experiments were carried out using 200 ml of copper solution of desired concentration in 250 ml capacity flasks. At predetermined time interval, samples were withdrawn and adsorbent was separated by centrifugation at 4000 rpm for 10 min. Residual Cu(II) concentration in the supernatant was analyzed using cuprethol (mixture of 1.5 ml diethanol amine in 100 ml methanol and 1 ml carbon disulfide in 100 ml methanol) reagent using UV–vis spectrophotometer measurement at wavelength of 434 nm and also initially by using ion chromatography (using PAR as eluent and mixture of lithium hydroxide and oxalic acid as solvent) at 530 nm wavelength in order to confirm that the results based on spectroscopic measurements are correct.

The amount of Cu(II) adsorbed per unit of SWS or AWS (mg copper per g SWS or AWS) at equilibrium was calculated according to a mass balance on the copper concentration as per following equation.

$$Q_e = (Ci - Ce)\frac{V}{M}$$

where Ci and Ce are the initial and equilibrium concentration of copper in the solution respectively, V is the volume of solution (L) and M is the mass of adsorbent (g). Q_e represents the adsorption capacity of adsorbent in mg/g.

Percentage removal of copper in the solution was calculated using following equation.

$$\text{Percentage removal }(\%) = \frac{Ci - C}{Ci} \times 100$$

The effect of different parameters such as contact time, pH, temperature, presence of ultrasound as well as ultrasonic power and adsorbent dosage on the extent of removal of copper has been investigated in the present work.