Comparison of three methods modified pine trees on copper absorption from aqueous solutions

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Abstract: In view of water crisis, effective prevention of water resources contamination is increasingly important. Absorption process is as one of the most efficient and application technology water and wastewater treatment in the world. Until now, valuable efforts have been made to develop low-cost adsorbents using agricultural, industrial and urban waste. Sometimes, adsorbent used needs to be modified and preparation. The aim of this study was to compare three different modified pine trees on the removal of copper from aqueous solutions. Also, the effect of copper concentration on absorption efficiency was studied. Pine leaf powder prepared, was modified by three methods using NaCl, Surfactants and Surfactant and NaCl. The test was done in a batch system by building artificial solutions containing copper in the lab. Results showed that adsorbent modified by NaCl had the highest removal efficiency.

[Abdellahi Neisiani S, Soltani Mohammadi A, Boromand Nasab S, Jaafarzadeh N. **Comparison of three methods modified pine trees on copper absorption from aqueous solutions.** *Nat Sci* 2016;14(12):50-52]. ISSN 1545-0740 (print); ISSN 2375-7167 (online). http://www.sciencepub.net/nature. 9. doi:10.7537/marsnsj141216.09.

Keywords: Absorption, Copper, Pine leaf, Modify

1. Introduction

Increasing water consumption and pollution of water resources has become one of the major concerns of the world for healthy water. According to UN predictions, in 2025 about 48 countries, ie 32% of the world's population will suffer from water shortages (Ayati et al., 2006). Rapid industrialization and poor effluent treatment processes in many industries have led to a substantial lowering of water quality that is fed to water bodies. Presence of heavy metals is one of the many factors that lower water quality. The heavy metals cause adverse effects on health, increase environmental toxicity and affect the aesthetic quality of the water. The sources of heavy metals in the environment include metal extraction, metal fabrication, electroplating, surface finishing, paints and pigments, as well as the manufacture of batteries (Parab et al., 2006). As a common heavy metal ion contaminant, copper(II) is widely used in many industries including metal cleaning and plating baths, paper board mills, wood pulp, paints and pigments, fertilizer industry and printed circuit board, etc. Accumulation of copper (II) in human body can cause liver and brain damage, stomach upset and ulcer, skin and heart diseases (Zhong et al., 2014).

Different ways is used to removal heavy metals from water, waste and soil over the years. Current methods of removing heavy metals from aqueous solutions include chemical precipitation, ion exchange, solvent extraction, phytoremediation (extraction plants), ultra-filtration, reverse osmosis, electrolysis and adsorption (Erfani Javdani et al., 2009).

Chemical precipitation is the most prevalent method but not suitable for removing low concentration of heavy metal ions. Absorption processes are promising in this regard as opposed to more conventional chemical precipitation in that, it achieve higher level removal over a wider range of solution conditions. The absorption, with the selection of suitable adsorbents, can be an effective technique for the removal of heavy metals from wastewater (Corapcioglu and Huang, 1987). The use of low-cost adsorbents and accessible have proposed in recent years and scientists approach has been to use this material (Shamohamadi, 2007). World Health Organization (WHO) recommended maximum acceptable concentration of copper in drinking water 1.5 mg/l. Copper pollution in surface water discharge is recommended 1 mg/l and 0.2 mg/l in agriculture and irrigation (Shamohamadi, 2007).

Kalavathy and Miranda (2010) studied copper absorption from aqueous solution using modified and unmodified of Rubber tree. Modification was done in two ways: Using four different levels sodium hydroxide and five different concentrations of phosphoric acid. The modified adsorbent with a ratio of 1:2 phosphoric acid and modified attractive ratio of 1: 1 sodium hydroxide had the highest absorption rate and introduced as the best concentration for modified. Also, adsorbent modified by sodium hydroxide, adsorbent modified and unmodified by phosphoric acid was greatest copper absorption.

Adeogun et al., (2016) in a study of adsorbent made from Sugarcane, used to absorb copper. Studies were conducted on the adsorbent unmodified and

modified by oxalic acid. Modified adsorbent was about 30 percent higher efficiency of adsorbing Unmodified.

2. Material and Methods

2-1. Preparation of adsorbent

Pine leaves were collected then washed, dried in an oven at 70 ° C. Powder prepared were modified by three methods:

2-2. Pine leaves adsorbent modified by NaCl

Pine tree leaf powder were in touch with NaCl 0.2 N for 30 minutes, then it is filtered and washed several times with distilled water to remove excess NaCl until the filtered solution reaches the pH 7±0.2. Then the filtered biomass was dried in an oven at 70°C overnight (Jaafarzadeh Haghighi Fard et al., 2014).

2-3. Pine leaves adsorbent modified by Surfactant

Solution of surfactant hexa decyl trimethyl ammonium bromide (HDTMA-Br) prepared at a concentration of 10 mM and was combined with 2 g of adsorbent powder, mixed for 24 hours at 150 RPM put on shaker and then filtered adsorbent and remaining of solid material was washed several times with distilled water and dried in an oven (Nezam Zadeh and Esmaelian, 2008).

2-4. Pine leaves adsorbent modified by Surfactant and NaCl

10 g adsorbent was used in a solution of 2 M NaCl, on vibrate at a speed of 150 RPM for 24 hours, then filtered and washed several times with distilled water and dried. 5 g of dried powder with 100 ml solution of 20 mM surfactant was mixed for 24. Then the mixture was placed in a centrifuge, the remaining solid washed several times with distilled water and dried in an oven (Vosoughi Niri et al., 2015).

To prepare a solution containing the heavy metal used from copper sulfate five water (CuSO4.5H2O). Copper stock solution (concentration of 1000 mg per liter) was prepared by dissolving the required amount of CuSO4.5H2O in distilled water and concentrations of 2, 5 and 10 mg per liter of copper sulfate solution was prepared by dilution of the solution. HCl and NaOH was used to adjust the pH of the solution.

2-5. Sorption experiments

The value of 1 g/lit of modified adsorbent pine leaves was poured in solution containing copper ions at concentrations of 2, 5 and 10 mg/lit. pH solution was adjusted to value of 6. Prepared mixture was used for 90 minutes on the shaker at speed of 150 RPM. At the end of the absorption process, the solution passed through the filter paper to separate adsorbent from solution. The concentration of Cu pre-test and post-adsorption by modified adsorbents pine tree leaves was measured using flame atomic absorption. With initial concentration and final concentration of metal in solution, absorption was calculated.

To calculate the efficiency and the amount of absorbed copper ions were used from equation 1 and 2:

$$E_a = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

$$q = \frac{C_i - C_o}{m} V \quad (2)$$

where, Ea is absorption efficieny (%), q is the absorption of dissolved per unit mass of adsorbent (mg g-1), Ci and Co are initial and final Cu(II) concentrations (mg L-1), respectively, V is the sample volume (lit) and M is the amount of adsorbent (g).

3. Results and Discussions

Between different modified methods, is a better way that in addition to absorption more, lower cost and initial preparation be easier. According to figure 1 and table 1, the adsorbent modified by NaCl, by surfactants and NaCl and adsorbent modified by surfactant had a high absorption efficiency, respectively. Figure 1 shows absorption efficiency for different input concentrations of copper by absorbent modified of pine trees.

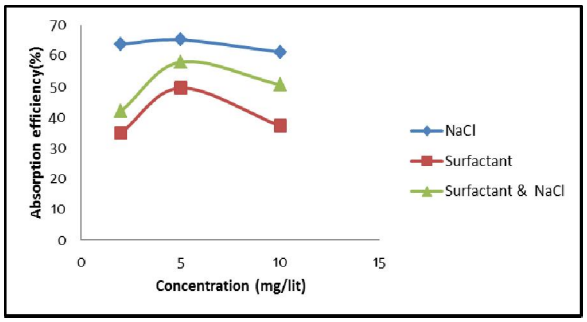

Figure 1. Copper absorption efficiency at different concentrations for different methods of modified pine tree leaves

Table 1, Efficiency values and copper absorption capacity by adsorbents modified with pine tree leaves

Modified by NaCl		Modified by Surfactants		by Surfactant & NaCl		Initial concentration(mg/lit)
Ea(%)	q (mg/g)	Ea(%)	q (mg/g)	Ea(%)	q (mg/g)	
63.69	1.39	34.91	0.76	41.89	0.91	2
65.07	4.24	49.39	3.22	57.87	3.77	5
61.09	5.36	37.06	3.25	50.44	4.43	10

In testing the effect of initial concentration of metals on absorption efficiency, at concentration of 5 mg /lit, because the amount of adsorbent is fixed, high specific surface area and absorption position, metal ions can interact with position absorption on the surface of adsorbent and therefore the absorption efficiency goes up. At concentrations above 5 mg/lit, due to saturation of absorption position, the absorption efficiency is decreased. At lower concentrations of 5 mg/ lit, the ratio of metal ions to absorb the available locations is low. As a result, the amount removed would be independent of the initial concentration. Usually, in the form of increased concentration of pollutants in different adsorption, absorption is increased and decreased the absorption efficiency but the changes were different in the various pollutants. The results were consistent with the results of Mustapha et al. (2014).

4. Conclution

The aim of this study was to compare three different modified pine trees in order to use cheap and available biological adsorbent for the removal of heavy metal copper ions from aqueous environments. Based on the results, use of NaCl, due to the initial preparation easier and more efficient absorption of copper is introduced as the best way to modified.

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