Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

ISSN: 0972-6268	Vol. 15	No. 4	pp. 1369-1372	2016

Original Research Paper

Assessing the Ability of *Populus* sp. Sawdust in Removal of Heavy Metals Pb(II), Ni(II) and Cr(III) from Wastewaters

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 29-09-2015
Accepted: 10-12-2015

Key Words:
Heavy metals
Wastewater
Sawdust
Populus sp.

ABSTRACT

In this paper we study the ion adsorption of heavy metals Pb(II), Ni(II) and Cr(III) from wastewaters by poplar tree (*Populus sp.*) sawdust. For this purpose, first the wastewaters containing heavy metals were prepared in laboratory, and then by adding the sawdust to the medium, the ion adsorption by the particles of sawdust were investigated in different pH, contact times, and concentrations in wastewater. Our findings showed that with the increase of the pH value of synthetic wastewater, ion adsorption by sawdust particles was increased where in pH=5, it reached its maximum value. The highest rate of adsorption was observed in 200 mg/L concentration. Also, the adsorption rate was dependent on the type of metal. According to obtained results, the increase in the contact time raises the ion adsorption where the optimal contact time was 90 min.

INTRODUCTION

Heavy metals are components of earth's crust, and can be used widely in industries such as cable production, laboratory, paint, electric industries, and rubber manufacturing, but since they do not degrade, they have brought many environmental problems. Existing heavy metals in industrial/urban wastewaters and secondary sludge are highly toxic to plants and animals; they have concentrated in the food chain and have created health hazards for humans (Alloway 1995). Heavy metals are entered into water and soil, contaminate surface water, groundwater and soil, and cause disruption of the ecosystems entered into them; therefore, it is necessary to control and reduce pollution in the environment in such cases. Common processes to remove these elements from industrial wastewater, such as reverse osmosis, ion exchange, chemical deposition, electrolysis, membrane filtration, oxidation, adsorption etc. are very expensive; hence, recently, the use of by-products and agricultural waste such as bark of trees, sawdust, peanut shells, pistachio, rice, bran, and corn sticks, in order to absorb heavy metals from wastewater, has been very efficient and cost-effective (Rao et al. 2010). These biologic waste materials are abundant and available in one hand, and on the other hand, they do not have a specific use.

From a few decades ago the adsorption of heavy metals by biomasses has been introduced, and recently many studies have been conducted on it (Marshall & Champagne 1995). Biomasses can include bacteria, fungi, algae, yeast, and agricultural waste materials such as sawdust. A number of investigations have shown that heavy metals will bind to sawdust and other agricultural products (Dean et al. 1972, Randall et al. 1974 and 1976, Randall 1977, Raji & Anirudhan 1997 and 1998, Ajmal et al. 1998, Bryant et al. 1992, Weider 1990). Many studies conducted on the removal of heavy metals from wastewaters, and different techniques have been suggested. Yu et al. (2001) used sawdust adsorption for the removal of copper and lead from aqueous solutions and concluded that sawdust may also be suitable for other heavy metals. Bulut & Tez (2007) found that the sawdust of walnut could be a good adsorbent for the metal ions from aqueous solutions. Kadirvelu et al. (2003) used activated carbons prepared from the agricultural solid wastes, silk cotton hull, coconut tree sawdust, sago waste, maize cob and banana pith to eliminate heavy metals and dyes from aqueous solution and found good results. Shukla et al. (2002) stated that sawdust is one of the most appealing materials for removing pollutants, such as, dyes, salts and heavy metals. Research data has shown that sawdust treated with a special material or chemical can be significantly effective to the removal of a particular element and that treated sawdust had a higher capacity for ion removal.

Shukla & Sakhardande (1992) reported a study on the removal of divalent Cu, Pb, Hg, Fe, Zn, Ni and trivalent Fe using untreated sawdust and sawdust treated with a reactive monochlorotriazine type of dye. According to Shukla & Sakhardande (1991) cheap cellulose-containing materials, such as bamboo pulp and sawdust, have the capacity to adsorb heavy metal ions. Taty-Costodes et al. (2003) used sawdust of *Pinus sylvestris* to remove Cd(II) and Pb(II) ions, from aqueous solutions and concluded that the sawdust of *P. sylvestris* could be a good adsorbent for the metal ions coming from aqueous solutions. Considering the above mentioned materials, in this study we tried to investigate the ability of *Populus* sp. sawdust in removal of heavy metals Pb(II), Ni(II) and Cr(III) from synthetic wastewaters.

MATERIALS AND METHODS

Adsorbent: The sawdust used in this study was prepared from poplar trees (*Populus* sp.). In order to fix the particle size of sawdust, 200 g of sawdust particles were passed from 1mm sieve. The sieved sawdust was dried at 60°C temperature in the oven for 24hrs. It was used directly for adsorption experiments without any treatment.

Wastewater: We used synthetic wastewaters prepared in laboratory. For making wastewater, each containing one of the heavy metal ions of copper, nickel and chromium, we used water-soluble salts of these metals from Merck Company which were $Ni(NO_3)_2.6H_2O$, $Cr(NO_3)_3.9H_2O$ and $Pb(NO_3)_2.6H_2O$. As a result, wastewaters with pH = 1 to pH = 6, concentration of 100 ppm, and volume of 200 mL were prepared in six separated beakers for each salt. In order to set pH in the interested area, sodium hydroxide (NaOH) and 1 N hydrochloric acid (HCI) solutions were employed. In this study, percentage of dried material to synthetic wastewater was considered as 1%. This percentage was maintained in all phases of the experiment

General procedure: 2g of dried crude sawdust was added to each plate, and the mixture of synthetic wastewater and sawdust with certain acidity was placed on magnetic mixer for 90 min. Finally, the mixture of synthetic wastewater after passing filter paper and sawdust was separated using Whatman filter paper No.4 and a hopper, and using atomic absorption spectrometry, final concentration of existing heavy metal ion in the synthetic wastewater was measured; and pH rate of metal adsorption in one unit of sawdust mass was calculated by pH meter. Since the most glass containers can absorb metals, in order to determine its value or absorbed metal by filter paper, a control was considered for each step, such that all experimental steps were conducted without adding adsorbent (sawdust).

Through these steps, it was found that in which environment the adsorption rate of each heavy metal ion was in high level for pH. By determining that pH ratio, for each salt of wastewaters with concentrations of 100, 200, 400, 600 and 800 ppm and volume of 200 mL, five separate beakers were prepared, and the effect of increasing heavy metal ion concentration on their adsorption rate by sawdust as well as saturation capacity of each gram of dried sawdust was investigated. In addition, for assessing the effect of increasing residence time (contact time of sawdust particles with metal ions in the synthetic wastewater) on adsorption rate of heavy metal ions by sawdust particles for each salt, six plates of synthetic solution with concentration of 0ppm and volume of 200 mL was prepared, and examined with contact times of 10, 20, 30, 60, 90 and 120 min. In the end, the values obtained from tests were imported into EXCEL software, and absorption curve of these ions was drawn.

RESULTS

In order to determine the amount of metal deposited on filter paper, or absorbed by glass containers, control samples were used and their analysis showed that the amount of metal absorbed from synthetic wastewaters by filter paper

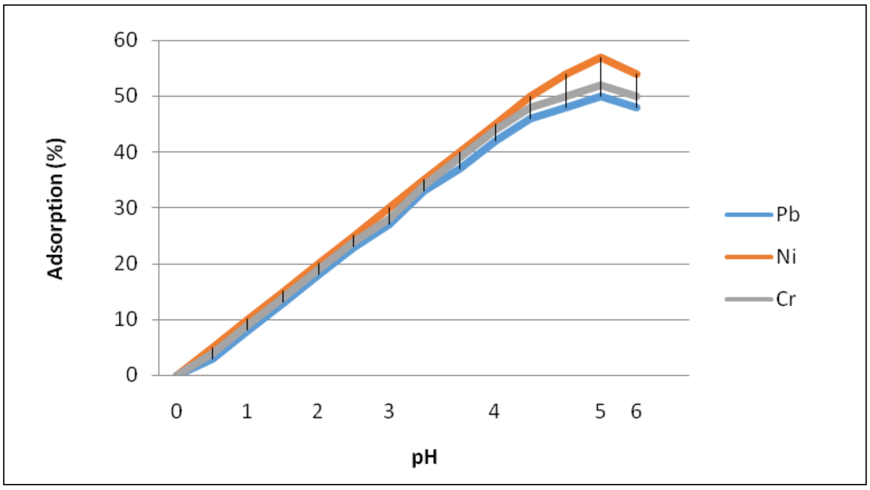

Fig. 1: Adsorption rate of studied heavy metals in different pH values; concentration=200mg/L, volume=200mL, contact time=90 min.

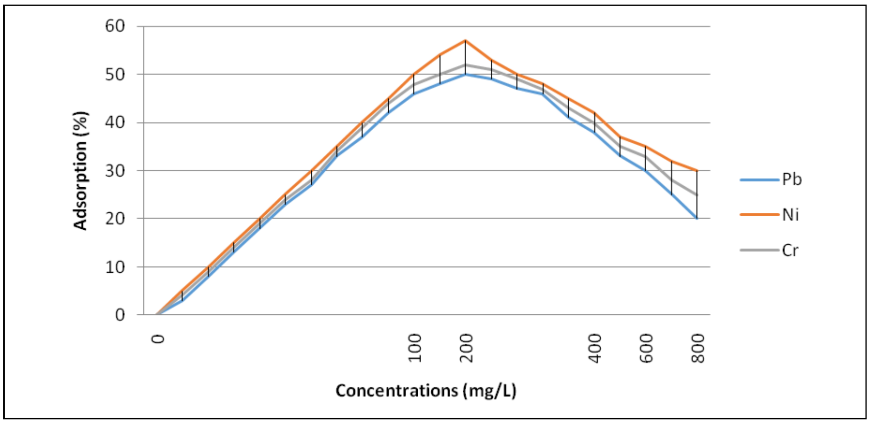

Fig. 2: Adsorption rate of studied heavy metals in different concentrations.

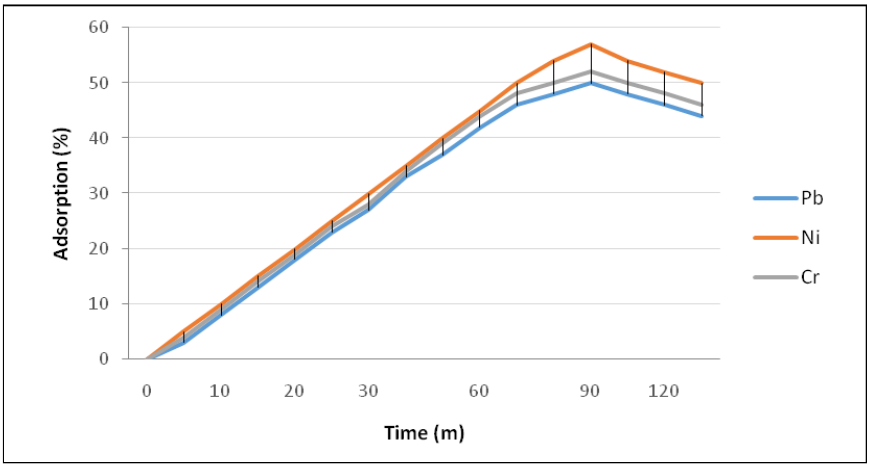

Fig. 3: Adsorption rate of heavy metals in different contact times; concentration = 200mg/L, volume=200mL, pH=5).

or glass containers was negligible. In this study we examine the adsorption rate of studied three heavy metals in different (a) pH values, (b) concentrations, and (c) contact times.

pH values: The results of the effect of increasing initial pH of synthetic wastewaters on adsorption rate of heavy metal ions by sawdust particles at fixed contact time (90 min) and fixed concentration and volume are shown in Fig. 1.

As the adsorption rate of each metal from pH=0 to pH=2 is shown, their value is almost equal and 11 to 13%. Ascending trend of increasing adsorption rate of each metal was different with the increase of pH value such that adsorption curve slope for Ni was higher than Cr, and for Cr it was higher than Pb. In the end, for all three metals, the adsorption rate reached its highest value in pH=5 which was between 50 to 65%.

Concentrations: Since the adsorption rate of metal ions in pH 5 was in its maximum value, so the effect of increasing initial concentration of wastewaters on the adsorption rate of metal ions with the volume of 200mL, contact time of 90 min and concentrations of 100, 200, 400 and 800 mg/L was tested. The results are illustrated in Fig. 2.

As can be seen in Fig. 2, the adsorption rate of heavy metals by sawdust particles in concentrations between 100 and 200mg/L was in high level, but in higher concentrations than 400mg/L, adsorption rate was declined for all metals because of the saturation of sawdust particles. Adsorption rate of heavy metals by sawdust particles for Pb, Ni and Cr was respectively equal to 50, 57 and 52 %.

Contact time: Results of assessing the effect of contact time on adsorption rate of metal ions are presented in Fig. 3. As can be seen, the increase in the contact time can result in the increase of adsorption rate of metal ions. Adsorption rate of these ions is high in initial times of 30, 60, and 90 min, and some percent of them are adsorbed by sawdust particles.

The considered concentration for this step is 200 mg/L with pH 5, because according to figures 1 and 2, in this value of pH and concentration, the adsorption was in its highest rate.

According to Fig. 3, speed of the reaction is so high and in average, 50% of total adsorption is conducted in the initial minutes, such that after 20 min, 30-40% and after 30min, 45-55% of metal ions were absorbed. It is in agreement with the findings of other studies (Taty-Costodes et al. 2003, Yu et al. 2001). According to the result, in 90 min contact time, adsorption of Ni by sawdust particles was higher than other two metal ions.

CONCLUSION

In this research we investigated the removal of heavy metals Pb (II), Ni (II) and Cr (III) from wastewaters by *Populus* sawdust. Obtained results showed that the adsorption rate of heavy metal ions by organic structure of sawdust particles were in high level. A small percentage of ions were absorbed by the glass containers and filter paper. With the increase in the pH of synthetic wastewater for each metal separately, adsorption rate of metal ions showed uniform upward process and in pH 05 it reached its maximum value; however, adsorption rate was dependent on the type of metal, such that Ni ions had higher adsorption ability compared to other two metal ions. In pH values higher than 5, metal ions were changed into sediment and were precipitated, so in high pH ratios, metal ions are less absorbed by sawdust particles. At the end, it was found that in final steps, adsorption rate by sawdust particles was decreased, because at low pH, hydrogen (H^+) ions are isolated from carboxyl group of sawdust particles, and metal ions are attached to the carboxyl group.

We also found that adsorption rate of Ni was higher than Cr and Pb in different concentrations. The highest rate of adsorption was observed in 200 mg/L concentration. Our findings also indicated that in higher contact times, the adsorption rate decrease. The best contact time for their adsorption was 90 min has where the reaction was reached ultimate balance after 2hrs.

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