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STUDIES ON ADSORPTIVE REMOVAL OF HEAVY METAL (CU, CD) FROM AQUEOUS SOLUTION BY TEA WASTE ADSORBENT

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ABSTRACT

Huge Industrial waste constitutes the major source of various kinds of metal pollution in natural water. There are at least 20 metals which cannot be degraded or destroyed. The important toxic metals are Cu, and Cd. There are numerous methods currently employed to remove and recover the metals from our environment and many physico-chemical methods have been proposed for their removal from wastewater. Adsorption is one of the alternatives for such cases and is an effective purification and separation technique used in industry especially in water and wastewater treatments. Cost is an important parameter for comparing the adsorbent materials. Therefore, there is increasing research interest in using alternative low-cost adsorbents. The use of tea waste as the low-cost adsorbents was investigated as a replacement for current costly methods of removing heavy metal ions from aqueous solutions. The experiment results showed that maximum removal of copper and cadmium ion by tea waste is 89% and 87% respectively at optimum condition.

INTRODUCTION

The term "heavy metal" is collectively applied to a group of metals (and metal-like elements) with density greater than 5 g/cm3 and atomic number above 20 (Raut *et al.* 2012). Electroplating, battery manufactures, painting, paper, pigments, fuels, photographic materials, explosive manufacturing and metalworking industries discharge large amounts of heavy metals, including copper (Cu), and cadmium (Cd) ions, in their effluent (Oteroa *et al.* 2009; Cay, S., Uyanik and Ozasik, 2004). Heavy metals are major pollutants in the environment due to their toxicity and threat to creatures and human being at high concentrations (Amarasinghe and Williams, 2007), Copper is highly toxic because it is non biodegradable and carcinogenic (Banum, 1982), the effect of copper, liver disease, renal dysfunction, fibromyalgia symptoms, muscle and joint pains, depression, chronic fatigue symptoms, irritability, tumor, anemia, learning disabilities and behavioral disorders, stuttering, insomnia, niacin deficiency, leukemia, high blood pressure. Zinc Nausea and vomiting. Cadmium Hypertension or high blood pressure, dulled sense of smell, anemia (Zhan *et al.* 2000). And cadmium exposure causes hypertension or high blood pressure,

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dulled sense of smell, anemia, joint soreness, hair loss, dry scaly skin, loss of appetite, decreased production of T cells and, therefore, a weakened immune system, kidney diseases and liver damage, emphysema, cancer and shortened lifespan (Liu, 2009). Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ion exchange, solvent extraction, adsorption, cementation onto iron, membrane processing and electrolytic methods (Oteroa *et al.* 2009). Adsorption is one of the alternatives for such causes the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid (Lopez *et al.* 2003). It has advantages over other methods are the simple design, sludge-free and can involve low investment in terms of both the initial costs and land (Liu *et al.* 2009). Adsorption onto activated carbon is a well-known method for removing toxic metal ions, but the high cost of activated carbon restricts its use in developing countries (Wasewar *et al.* 2008a). The adsorption abilities of a number of low-cost adsorbents (e.g., cheap zeolites, clay, coal fly ash, sewage sludge, agriculture waste and biomass) have been determined for the removal of heavy metals from water (Williams *et al.* 2007) Therefore, there is a need to look into alternatives to investigate a low-cost adsorbent which is effective and economic, for potential approach is the use of tea waste, Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world (Boonamnuayvitaya *et al.* 2004) and in India yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production (Jalali *et al.* 2002), the amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted (Pan *et al.* 2003). Amount of TW produced per year after processing is about 190400 tonnes in India alone, very few investigators have investigated TW as an adsorbent for the removal of heavy metals. In last few years, a vast number of publications have been dedicated to the removal of heavy metals from waste water by using adsorption techniques with different low cost materials, in recent years; tea waste (TW) is also gaining grounds due to its potential to overcome heavy metal pollutants. Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins (Wang, 2006). The adsorption ability of tea waste was investigated for the removal of Cu (II) and Cd (II) from single (non-competitive) and binary (competitive) aqueous systems (Cay *et al.* 2004). In this investigation experiment perform to evaluate the effectiveness of employing a tea waste for the adsorptive removal of Cu, and Cd from synthetic wastewater, using batch experiment and isotherm studies to determine the adsorption capacities.

Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fibre production, pipe corrosion and metal plating industries (Beliles, 1979). The other major industries discharging copper in their effluents are paper, pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes (Parker, 1980) , also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and drink. Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to deposition of copper in the lenticular nucleus of the brain and kidney failure (Sitting, 1976). In some instances, exposure to copper has resulted in jaundice and enlarged liver. It is suspected to be responsible for one form of metal fume fever (Kadirvelu,1998). Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers.

Cadmium

When people breathe in Cadmium it can severely damage the lungs. This may even cause death. Animals eating or drinking Cadmium sometimes get high blood-pressures, liver disease and nerve or brain damage. A maximum acceptable concentration of 0.005 mg/L (5μg/L) for cadmium in drinking water has been established on the basis of health considerations (Liu *et al.* 2009).

MATERIALS AND METHODS

Chemicals

All chemicals used in present work were either of analytical reagent (AR) or laboratory reagent (LR) grade. $CuSO_4.5H_2O$ (99%), Cd $(NO_3)_2$ (99%), H_2SO_4 (98% w/w, 36N), HCl (98% w/w, 36N) supplied by s.d.fine-chem limited, Mumbai. Distilled water was used in all preparations. Copper sulphate ($CuSO_4$) and Cadmium nitrate Cd $(NO_3)_2$ and deionized water were used to prepare synthetic heavy metals containing wastewater.

Adsorbent

Tea waste collected from tea stalls and restaurants were washed and boiled with hot distilled water (85°C) up to colour removal. After colour removal it is dried in hot oven at 105°C for 12 hours. The dried material converted into powder form by mixer grinder and screened to size 120 µm. Again this powder dried at 105°C for 6 hours and then stored in plastic bags at room temperature. Now it was ready to use as an adsorbent (Lopez *et al.* 2003).

Adsorbate

$CuSO_4.5H_2O$, and $Cd(NO_3)_2$ were obtained in analytical grade (Merck Co.) and used without further purification synthetic 1000ppm stock solution prepared for each metal.

Copper solution: 3.927 g of $CuSO_4.5H_2O$ was added in the 100mL of distilled water in 1000mL volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Copper concentration of this solution was 1000 mg/L.

Cadmium solution: 2.2.1 g of $Cd(NO_3)_2$ was added in 100 mL of distilled watwe in 1000 mL volumetric flask. It was dissolved by shaking and the volume was made up to the mark. Lead solution concentration of this solution was 1000 mL/L.

Glassware and apparatus used

All glass wares (Conical flasks, Pipette, Measuring cylinders, Beakers, Petri plates and Test tubes etc.) used are of Borosil/Rankem. The instruments and apparatus used throughout the experiment are listed in Table below-

Table 1. List of Instruments used during experimentation

S.No.	Instrument	Make
1.	uv-visible spectrophotometer	systronics spectrophotometer 118
2.	Digital Weight Balance	Atco Company
3.	What man filter paper no.1	-
4.	Orbital shaker	Remy
5.	pH meter	Adair dutt (AOP-Series)

Batch mode adsorption studies

The adsorption of heavy metals on tea waste was studied by batch technique. The general method used for this study is described as below:

A known weight of tea waste adsorbent (e.g. 0.5 g adsorbent) was equilibrated with 100 mL of the each heavy metals (namely Cu and Cd) solution of known concentration (10, 20, 50 and 100ppm) in 8 stoppered borosil glass flask at a fixed temperature (30 °C) in a orbital shaker for a known period (30-180 Min.) of time. After equilibration, collect sample (10mL) from each flask in time interval of 30, 60, 120 and 180 minuts, the suspension of the adsorbent was separated from solution by filtration using Whatman No. 1 filter paper.

The concentration of heavy metal ions remaining in solution was measured by uv visible spectrophotometer (systronic 118). The effect of several parameters, such as pH, concentrations, contact time and adsorbent dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using sulfuric acid, sodium hydroxide and buffer solutions when required adsorption of metal ions on the walls of glass flasks determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The percent heavy metal removal was calculated using Eq.

$$\text{Metal ion removal (\%)} = [(C_o - C_e)/C_o]\times 100 \qquad (1)$$

Where C_o: initial metal ion concentration of test solution, mg/L Ce: final equilibrium concentration of test solution, mg/L (Babel and Kurniawan, 2003).

RESULTS AND DISCUSSION

Effect of contact time

Fig. 1 and 2 show the variation in the percentage removal of heavy metals with contact time using 0.5 g/100mL of tea waste adsorbent at 5 pH for varying initial metal ions concentration ranging from 10ppm to 100ppm. It is observed that maximum removal for Cu (II) and Cd (II) ions are nearly 87% and 82% respectively even throughout the 120 min. contact times. It is observed that in all cases the percentage removal is comparatively lower for 30 min. contact time, with increasing removal efficiencies at higher contact time up to 120 min and then gradually decrease at 180 minutes.

Effect of pH

pH variation is one of the most important parameters

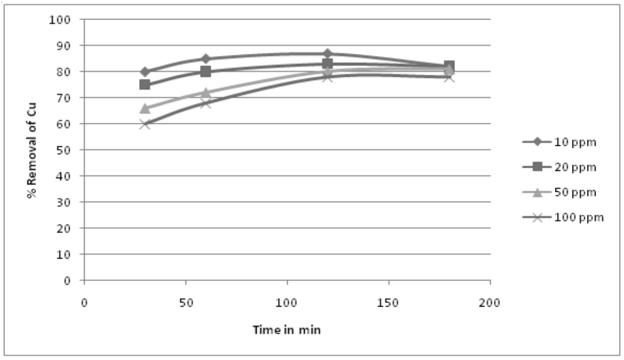

Fig. 1 Effect of contact time on % removal of copper ion by tea waste adsorbent at adsorbent dose 0.5 g and pH 5

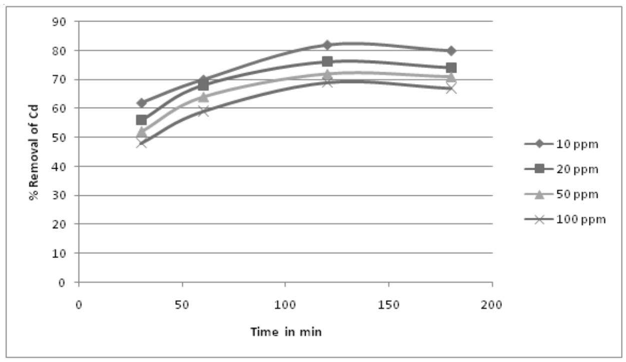

Fig. 2 Effect of contact time on % removal of cadmium ion by tea waste adsorbent at adsorbent dose 0.5 g and pH 5

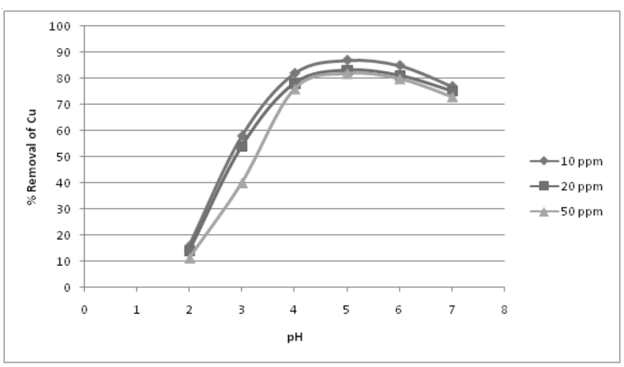

Fig. 3 Effect of pH on % removal of copper ion by tea waste adsorbent at adsorbent dose 0.5 g and contact time 120 min

controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 3 and 4 shows the effect of pH on heavy metals removal efficiencies of tea waste adsorbent. These studies were conducted at an initial metal ions concentration of 10, 20 and 50ppm in 100mL solution, and constant adsorbent dose 0.5g /100mL solution and agitation period are 120 min. for all heavy metal ions at varying the pH in each solution.

The percentage adsorption increases with pH to attain a maximum a 6 pH for Cd^{2+} and there after it decreases with further increase in pH. The percentage adsorption increase with 5 pH for Cu^{2+} thereafter, it decreases with further increase in pH. The maximum removals of Cu^{2+} at 6 pH and Cd^{2+} at 6 pH were found to be nearly 87% and 82%, respectively. The maximum adsorption at 6 pH may be attributed to the partial hydrolysis of M^{+}, resulting in the formation of MOH^{+} and M $(OH)^2$ would be adsorbed to a greater extend on the non-polar adsorbent surface compare to MOH^{+}. With increase of pH from 5 to 6, the metal exists as $M(OH)^2$ in the medium and surface protonation of adsorbent is minimum, leading to the enhancement of metal adsorption.

Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Fig. 5 and 6 over the range 0.2 to 1g/100mL, at pH 5 and 120 minutes contact time. The percentage removal of heavy metals is seen to increase with adsorbent dose. It is observed that there is a sharp increase in percentage removal with adsorbent dose for Cu (II) and Cd (II) ions. The maximum removal of Cu and Cd are 85% and 83% respectively at 0.6 g dose amount of tea waste adsorbent.

It is apparent that the percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents due to the greater availability of the exchangeable sites or surface area. Moreover, the percentage of metal ion adsorption on adsorbent is determined by the adsorption capacity of the adsorbent for various metal ions.

Effect of initial concentration

The effect of concentration at 0.5g/100mL adsorbent dose, 5pH and 120 contact time were observed. The effect of initial concentration on the percentage removal of heavy metals by tea waste is shown in Fig. 7. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration for (II), Cu (II) and Cd (II), the percentage removal is highly effective on the 10ppm initial concentration after which percentage removal decreases gradually to below 69%. At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is indepen-

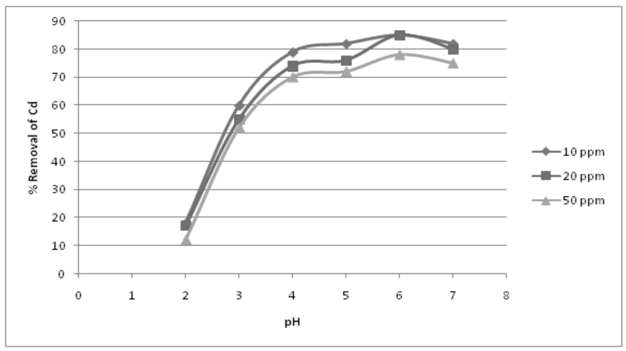

Fig. 4 Effect of pH on % removal of cadmium ion by tea waste adsorbent at adsorbent dose 0.5 g and contact time 120 min

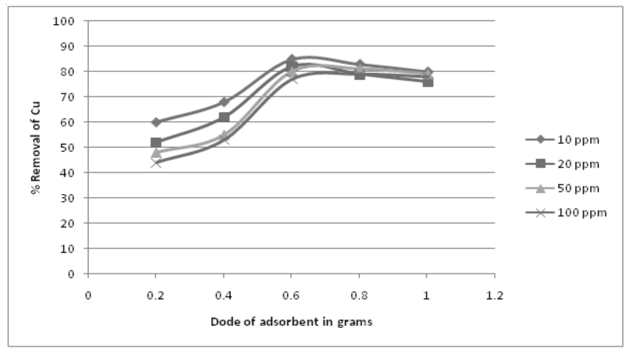

Fig. 5 Effect of adsorbent (amount) dose on % removal of copper by tea waste adsorbent at pH 5 and contact time 120 min

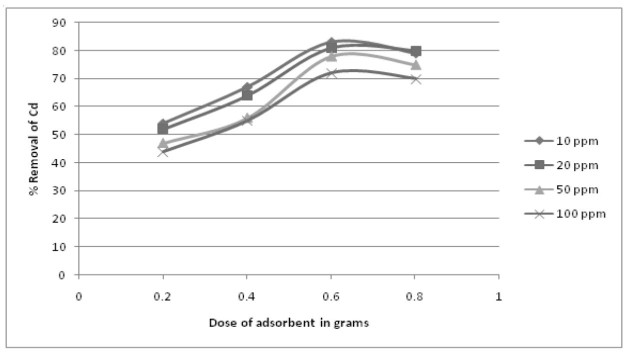

Fig. 7 Effect of concentration on % removal of metal ions by tea waste adsorbent at adsorbent dose 0.5 g pH 5 and contact time 120 min

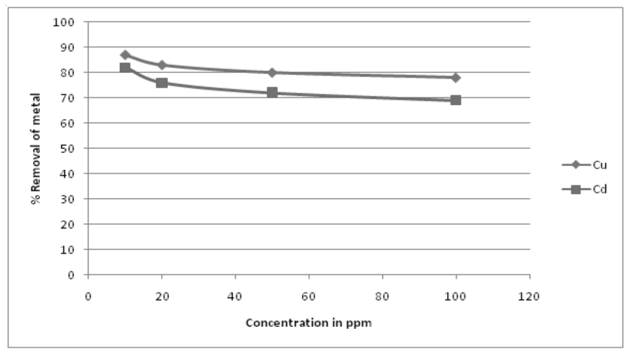

Fig. 6 Effect of adsorbent (amount) dose on % removal of cadmium by tea waste adsorbent at pH 5 and contact time 120 min

dent of initial metal ion concentration. However, at higher concentrations the numbers of heavy metal ions are relatively higher compared to availability of adsorption sites. The maximum removal of copper and cadmium ions are 87% and 82% respectively at 10ppm concentration. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration.

CONCLUSION

Tea waste is a cheap and effective adsorbent for the removal of Cu, Zn and Ni ions from wastewater without requiring any pretreatment. Experiment results showed that maximum removal of copper ion by tea waste at optimum condition (5 pH, 120 min. contact time, 0.5g/100mL adsorbent dose and 10 ppm concentration) is 89% and for Cadmium ion are 87% at optimum condition (6 pH, 120 min. contact time and 0.6g/100mL adsorbent dose, 10ppm concentration). These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

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