Adsorption of Heavy Metal (Cu^{2+}, Ni^{2+} and Zn^{2+}) from Synthetic Waste Water by Tea Waste Adsorbent

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Abstract

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, Ni and Zn. 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 Nickel ion by tea waste is 94% and for Copper & Zinc ion are 89% & 90% 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/cm^3 and atomic number above 20[26]. Electroplating, battery manufactures, painting, paper, pigments, fuels, photographic materials, explosive manufacturing and metalworking industries discharge large amounts of heavy metals, including copper (Cu), zinc (Zn) and nickel (Ni) ions, in their effluent [22,8]. Heavy metals are major pollutants in the environment due to their toxicity and threat to creatures and human being at high concentrations [2], Copper is highly toxic because it is non biodegradable and carcinogenic [4], the effects of Ni exposure vary from skin irritation to damage of the lungs, nervous system, and mucous membranes [11] and zinc exposures causes depression, lethargy, neurological signs and increased thirst [15]. 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 [22].

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 [18]. 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 [17]. 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 [30]. 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 [31]. 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 [7] and in India yearly production of tea is approximately 857000 tonnes which is 27.4% of total world production [12], 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 [23]. 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 [29]. 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 (8). In this investigation experiment perform to evaluate the effectiveness of employing a tea waste for the adsorptive removal of Cu, Zn and Ni from synthetic wastewater, using batch experiment and isotherm studies to determine the adsorption capacities.

Table1: Various Norms for heavy metal composition

Heavy Metal	W.H.O. [For Drinking] (mg/l)	U.S.E.P.A. [For wastewater] (mg/l)	C.P.C.B. [For wastewater] (mg/l)
Cu	0.05	1.3	1.5
Ni	0.05	1	0.05
Zn	5	5	15.0

Source: [17, 25 and 30]

Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fibre production, pipe corrosion and metal plating industries [6]. 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 [24], 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 [27]. 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 [14]. Moreover, continued inhalation of copper-containing sprays is linked to an increase in lung cancer among exposed workers.

Nickel

Environmental contamination due to Nickel, electroplating is one important process involved in surface finishing and metal deposition for better life of articles and for decoration. Although several metals can be used for electroplating, nickel, copper, zinc and chromium are the most commonly used metals, the choice depending upon the specific requirement of the articles [21], during washing of the electroplating tanks, considerable amounts of the metal ions find their way into the effluent. Ni (II) is also present in the effluents of silver refineries, zinc base casting and storage battery industries etc (16). Its enter in the food chain progressively larger accumulation of nickel compounds takes place in humans and animals, higher concentration of nickel causes cancer of lungs, nose and bone [20], Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, acute poisoning of Ni (II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [21].

Zinc

Due to its remarkable resistant to atmospheric corrosion, zinc is commonly used to protect iron from rusting, in the process called galvanization. Zinc is widely used for the manufacturing of zinc white and several useful alloys such as brass, German silver, delta metal, for the preparation of gold and silver in the cyanide method, for the desilverization of lead in parks process and as an anode material in galvanic cells. Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, and accelerators for rubber vulcanisation, ceramics, textiles, fertilizers, pigments, steel production and batteries [16]. Zinc toxicity from excessive ingestion is uncommon but causes gastrointestinal distress and diarrhea [3].

Materials and methods:

Chemicals

Analytical grade reagents were used for heavy metal solution; ACS reagent grade concentrated sulfuric acid and NaOH were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

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 [18].

Adsorbate

$CuSO_4.5H_2O$, $NiSO_4.6H_2O$ and $ZnSO_4.7H_2O$ were obtained in analytical grade (Merck Co.) and used without further purification synthetic 1000ppm stock solution prepared for each metal.

i) Copper solution: 3.927 grams 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.

ii) Nickel solution: 4.477grams of $NiSo_4.6H_2O$ 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. Nickel concentration of this solution was 1000 mg/l.

iii) Zinc solution: 4.395 grams of $ZnSO_4.7H_2O$ 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. Zinc concentration of this solution was 1000 mg/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 2 List of Instruments used during the whole experiment

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)

Analysis of Adsorbate

Estimation of metals: The metals were estimated using standard methods as described by Al-Asheh(1) Copper as Cu (II) was determined spectrophotometrically at 312 nm. The residual concentration of nickel and zinc were determined spectrophotometrically at 392 nm (7) and 310nm (1) respectively.

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, Ni and Zn) solution of known concentration (10, 20, 50 and 100ppm) in 12 stoppered borosil glass flask at a fixed temperature (30 ^{0}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.

Metal ion removal (%) = $[(C_o - C_e) / C_o] \times 100$ ……………………………… (1)

Where C_o: initial metal ion concentration of test solution, mg/l; C_e: final equilibrium concentration of test solution, mg/l [3].

Results and discussion

Effect of contact time

Fig. 1, 2, and 3 shows the variation in the percentage removal of heavy metals with contact time using 0.5 g/100ml of tea waste adsorbent at 5pH for varying initial metal ions concentration ranging from 10ppm to 100ppm. It is observed that for Ni (II) ions, the percentage removal is nearly 91% 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, maximum removal obtained at 120 minutes. In case of Cu (II) and Zn (II) ions is also increase with time, then after 180 minutes. Slowly decrease, the maximum percent removal of copper and zinc ion are 87% and 90% respectively at 120 minutes.

It is evident from the results that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with tea waste adsorbent is 120 minutes.

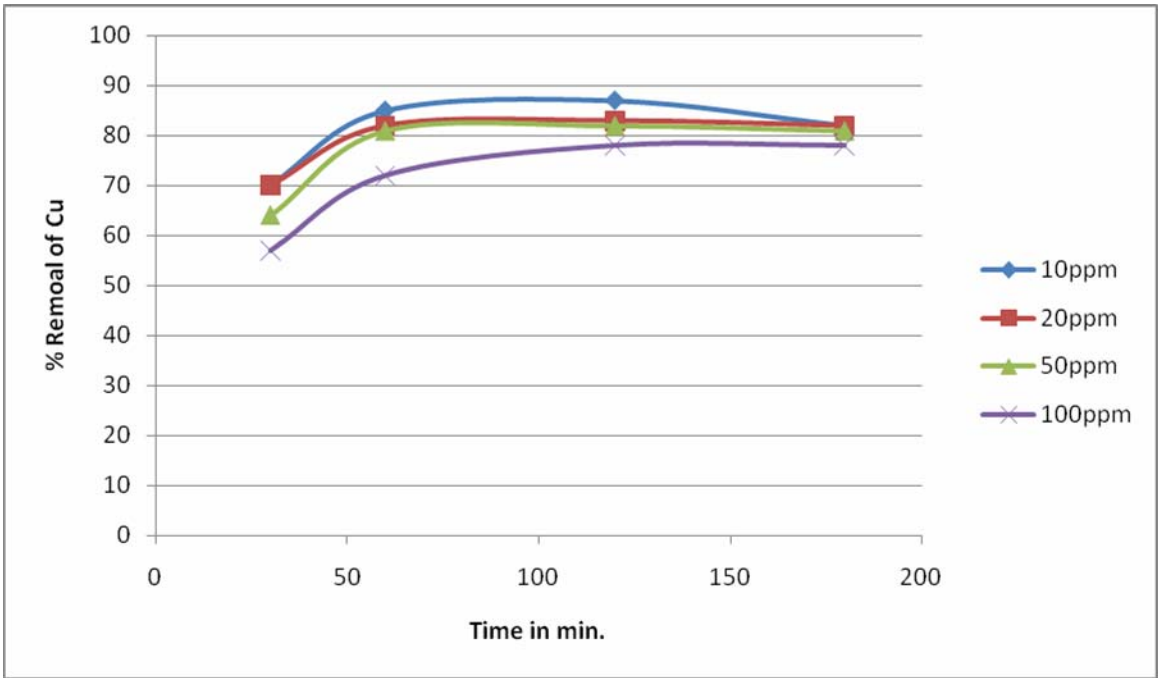

Figure1: Effect of contact time on %removal of copper ion by tea waste adsorbent.

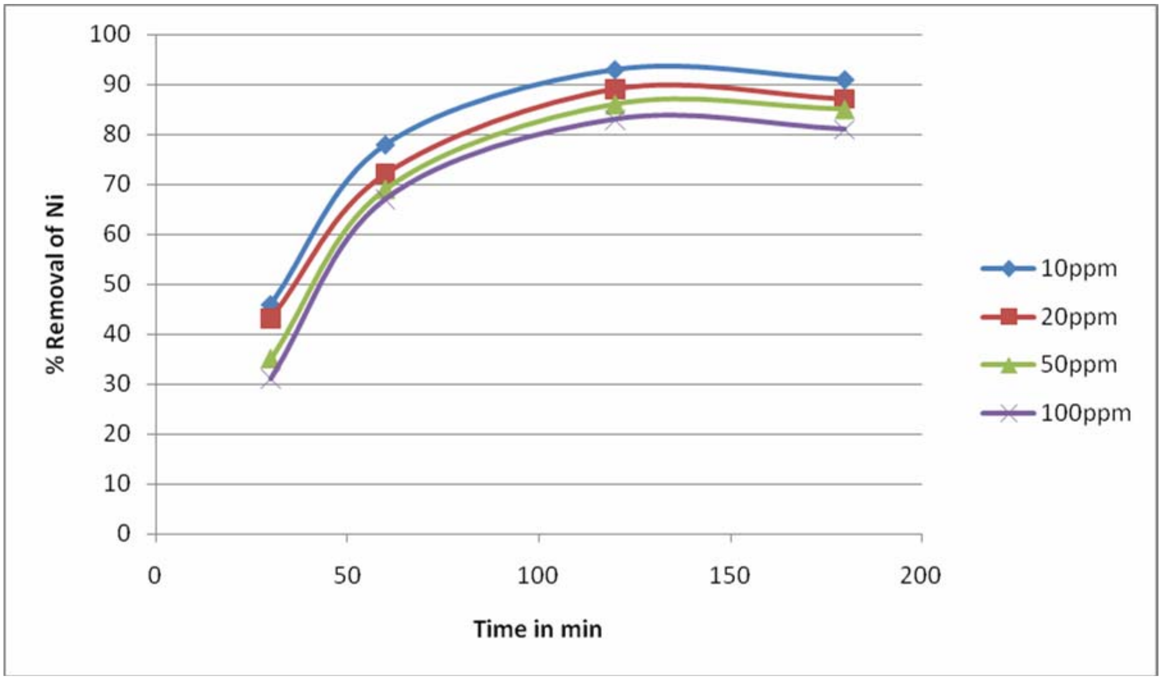

Figure2: Effect of contact time on %removal of nickel ion by tea waste adsorbent.

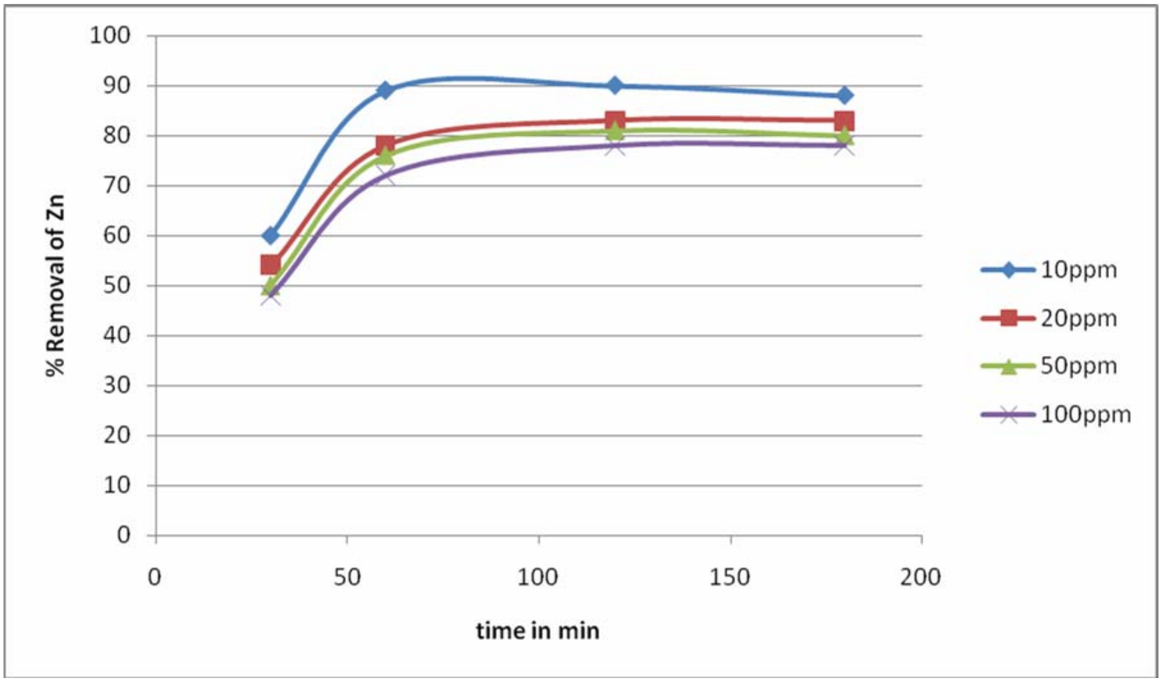

Figure: Effect of contact time on %removal of zinc ion by tea waste adsorbent.

Effect of pH

pH variation is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Fig. 4, 5 and 6 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 50 and 100ppm in 100ml solution, and constant adsorbent dose 0.5 g/100ml solution and agitation period are 120 minutes for all heavy metal ions at varying the pH in each solution.

The percentage adsorption increases with pH to attain a maximum at 5 pH and thereafter it decreases with further increase in pH. The maximum removals of Cu (II), Zn (II) and Ni (II) at 5 pH were found to be nearly 89%, 89% and 94%, respectively. The maximum adsorption at 6 pH may be attributed to the partial hydrolysis of M^+, resulting in the formation of MOH^+ and M $(OH)^2$.M $(OH)^2$ would be adsorbed to a greater extend on the non-polar adsorbent surface compare to MOH^+. With increase of pH from 2 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[1]. In Fig. 4, 5 and 6 higher pH, that is, above optimum pH of 5, increase in OH− ions cause a decrease in adsorption of metal ions at adsorbent–adsorbate interface.

Lower solubilities of hydrolysed metal ions species may be another reason for the maximum adsorption at 6 pH. Since, in lower pH range, metal is present predominantly as metal ions in the adsorptive solution, there is a competition between H+ andM+ ions for adsorption at the ion-exchangeable sites, leading to a low removal of metal. The extensive repulsion of metal ions due to protonation of the adsorbent surface at lower pH may be another reason for decrease in adsorption of metal in lower pH range [1].

The mechanism of metal ion adsorption may also be explained based on ion exchange model. In carbon aerogel, carbon–oxygen complexes are present. The surface oxygen complexes hydrolysed water molecules are shown below:

$2COH + M^{+} \rightarrow (CO)_2 M^{+} + 2H^{+}$ ……………….(2)

$COH_2^{2} + M^{+} \rightarrow COM^{2+} + 2H^{+}$ ………………. (3) [9]

The above mechanism has been confirmed by an increasing initial metal ion concentration in aqueous solution as the final pH of solution decrease. This clearly indicates that uptake of more metal ions causes release of more H+ ions. The increase in metal removal as the pH increases can be explained on the basis of a decrease in competition between proton and metal cations for the same functional groups and by the decrease in positive surface charge, which results in a lower electrostatic repulsion between the surface and the metal ions. Decrease in adsorption at higher pH (above 6pH) is due to the formation of soluble hydroxy complexes [9].

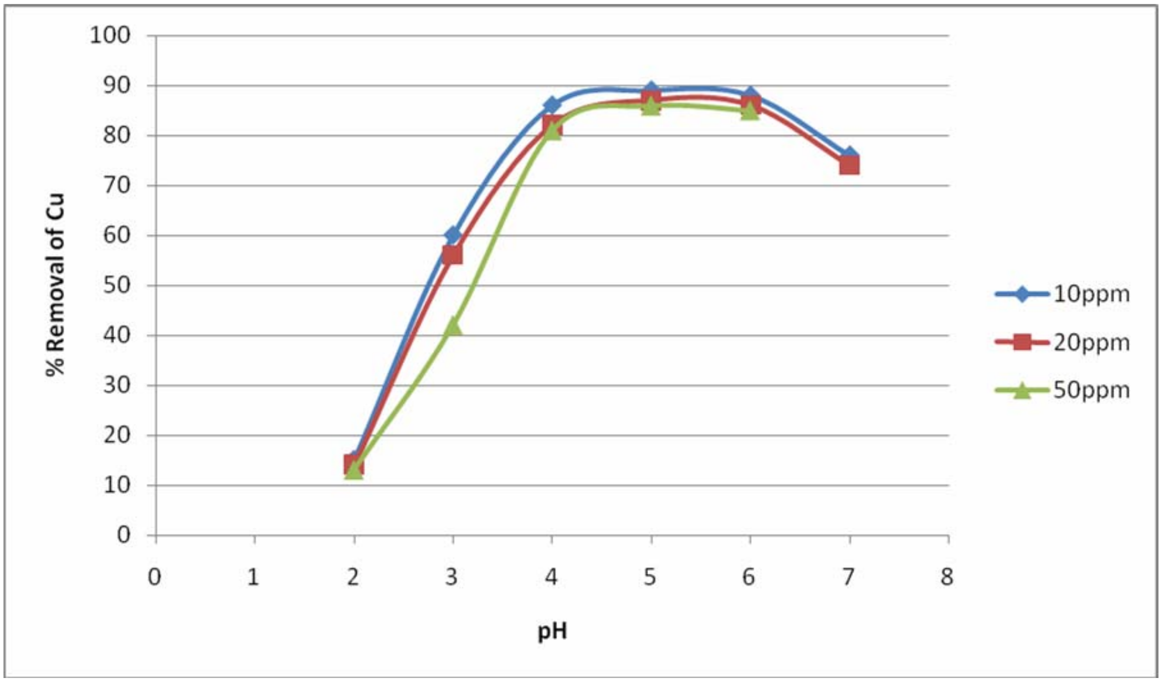

Figure 4. Effect of pH on % removal of copper ion by tea waste adsorbent.

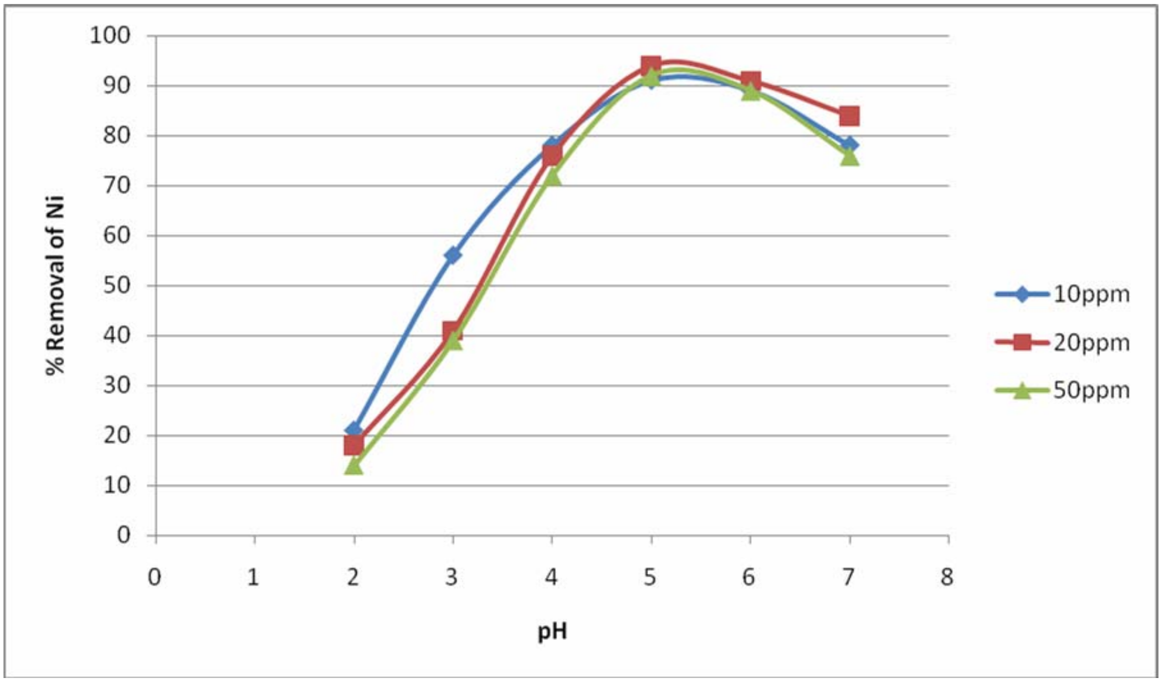

Figure 5: Effect of pH on % removal of nickel ion by tea waste adsorbent.

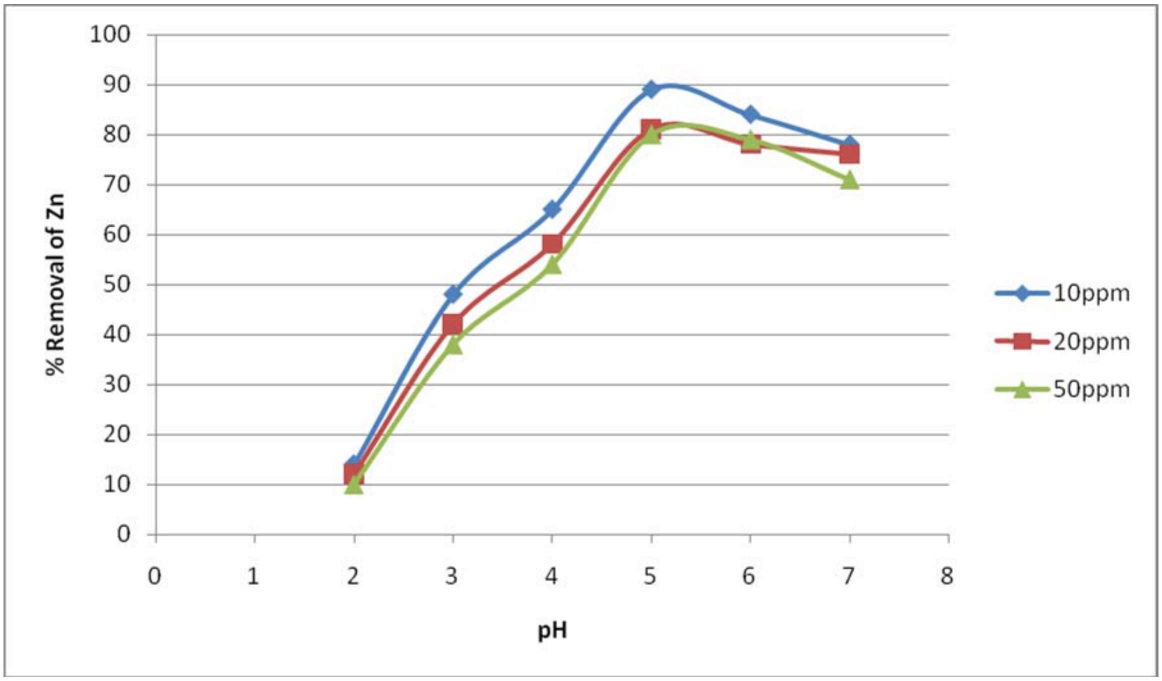

Figure 6: Effect of pH on % removal of zinc ion by tea waste adsorbent.

Effect of adsorbent dose

The results for adsorptive removal of heavy metals with respect to adsorbent dose are shown in Fig. 7, 8 and 9 over the range 0.2 to 1gram/100ml, at pH 5 and 120 minutes contact time. The percentage removal of heavy metals is seen to increase with adsorbent dose. From Fig. 7, 8 and 9, it is observed that there is a sharp increase in percentage removal with adsorbent dose for Ni (II), Cu (II) and Zn (II) ions. The maximum removal of Cu and Zn are 84% and 91%respectivaly at 0.6 gram dose amount of tea waste adsorbent and from fig.8 maximum removal Ni is 91% at 0.4gram adsorbent dose.

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.

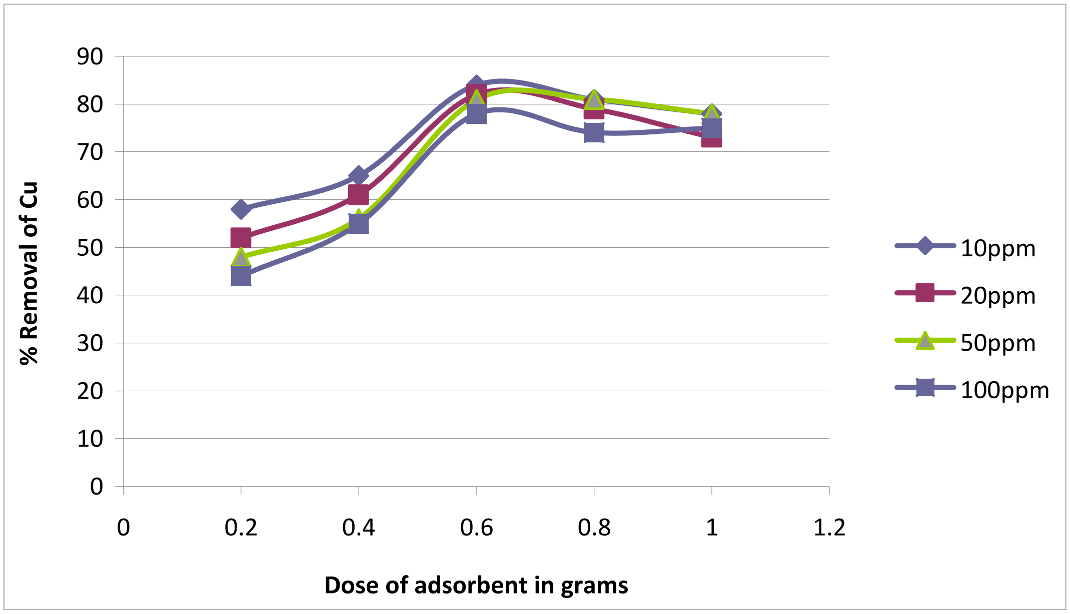

Figure 7: Effect of adsorbent (amount) dose on % removal of copper ion by tea waste adsorbent.

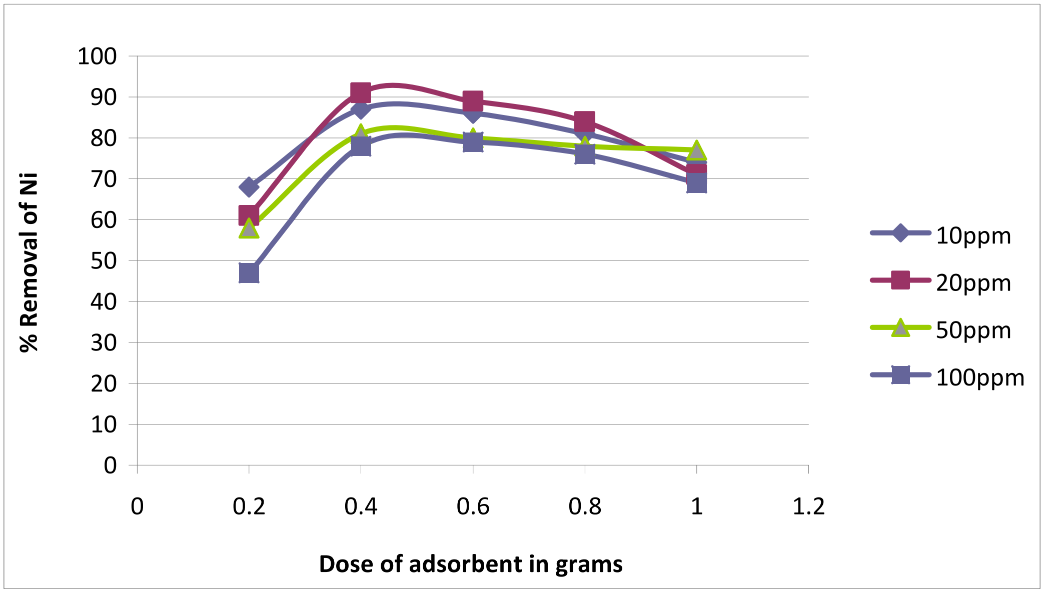

Figure 8: Effect of adsorbent (amount) dose on % removal of nickel ion by tea waste adsorbent.

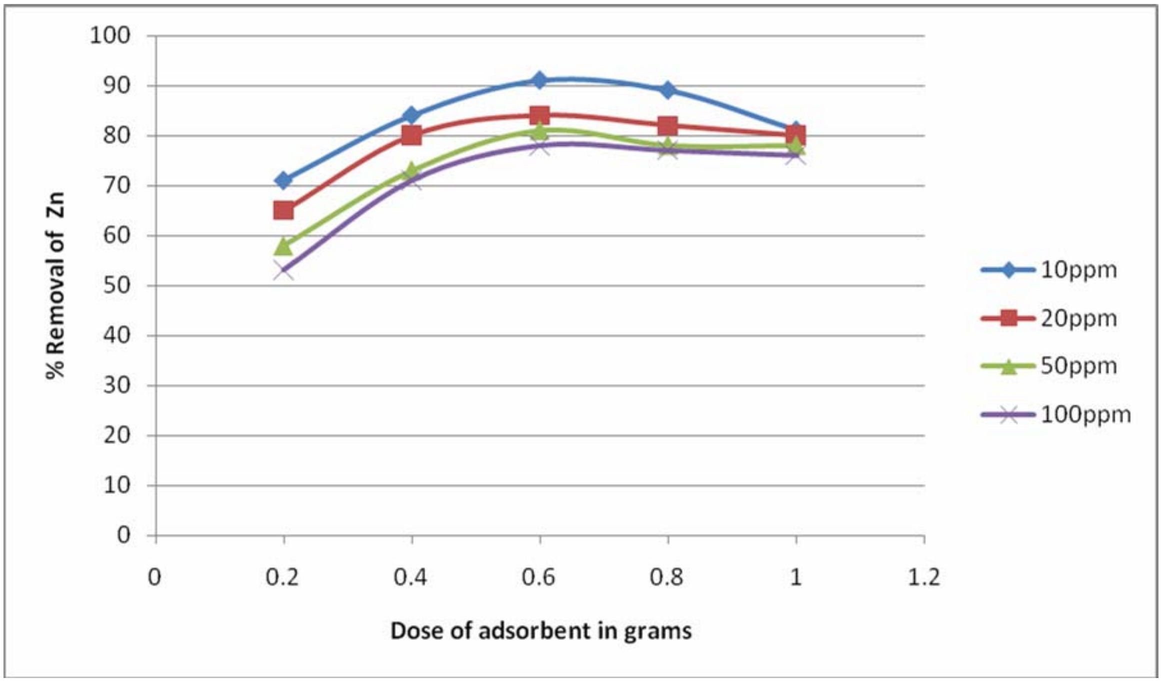

Figure 9: Effect of adsorbent (amount) dose on % removal of zinc ion by tea waste adsorbent.

Effect of initial concentration of heavy metal

The effect of concentration at 0.5g/100ml adsorbent dose, 5pH, 110 rpm and 120 contact time. The effect of initial concentration on the percentage removal of heavy metals by tea waste is shown in Fig. 10. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration for Ni (II), Zn (II) and Cu (II), the percentage removal is highly effective on the 10ppm initial concentration after which percentage removal decreases gradually to below 70%. At higher initial concentrations (20ppm), Ni (II) shows greater percentage removal than Zn (II) and Cu (II). At lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption of the heavy metals ions. Therefore, the fractional adsorption is independent 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 zinc ions are 89% and 91% respectively at 10ppm concentration but nickel ion maximum removal 94% at 20ppm concentration.

Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent (11).

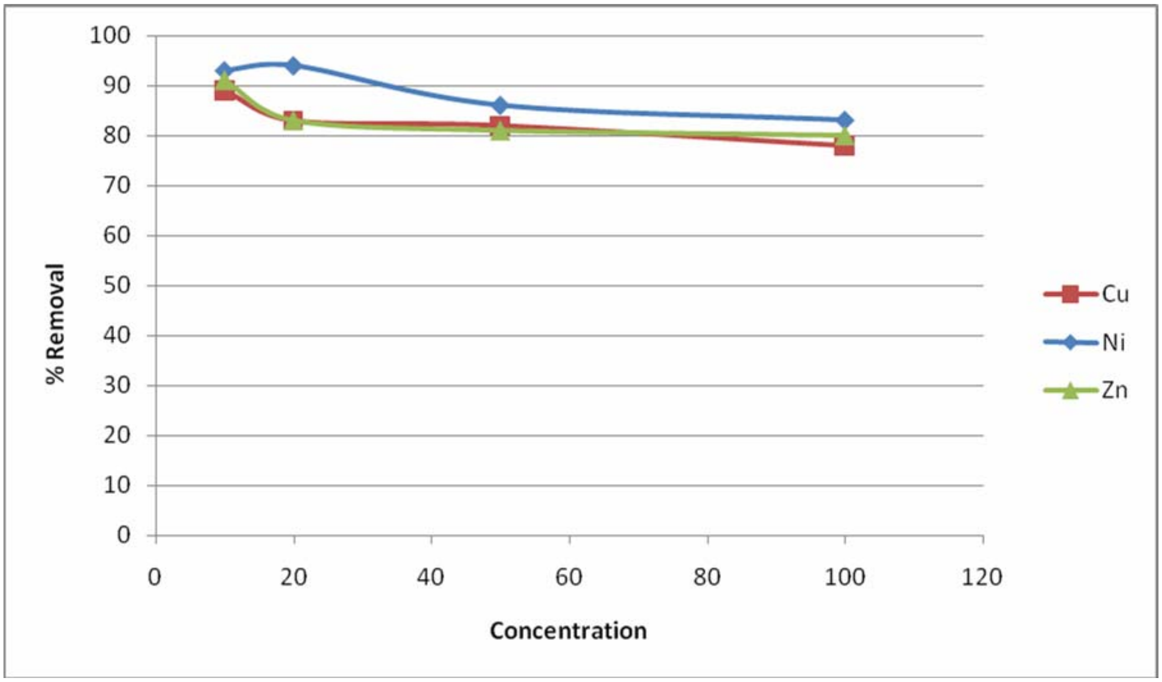

Figure 10: Effect of concentration on % removal of metal ions by tea waste adsorbent.

Conclusions

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 Nickel ion by tea waste at optimum condition (5 pH, 120 min. contact time, 0.5g/100ml adsorbent dose and 20ppm concentration) is 94% and for Copper & Zinc ion are 89% & 91% respectively at optimum condition (5 pH, 120 min. contact time and 0.5g/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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