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EFFICIENCY STUDY OF SPENT BLACK AND GREEN TEA LEAVES IN REMOVING LEAD AND COPPER IONS IN WATER

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Abstract

Today countries are paying great attention to protecting the environment from pollution and the accumulation of waste, which may affect the natural balance of the environment and thus affect the safety of natural resources (soil, water and air) and human uses. The study aimed at the possibility of using Spent black and green tea leaves as one of the alternative methods used in practical applications of solid-liquid. To get rid of chemical contaminants, including heavy metals, as cost-effective adsorbents. The results of the study showed similar kinetics of these substances, whether alone or in combination in their efficiency in removing the lead pb (II) and copper cu (II) combined under different conditions of pH, effect of adsorbent quantity, contact time, temperature and the effect of the Effect of synergistic action effect of the spent tea leaves. The best conditions were pH 6, contact time 60 min, agitation speed 150 rpm/min, temperature 25°C, amount of adsorbent 2g, initial metal concentration Pb(II) and Cu(II) 100 mgL^{-1} and was the best removal through the synergistic action of the spent as it reached 88.99%.

***Key words*:** Spent black and green tea leaves, lead (II) and copper (II), adsorption.

Introduction

Tea is one of the oldest and most popular drinks and the most consumed in the world after water as a cheap material (Mazzanti *et al*., 2009) is said to be known in the countries of Central Asia and depend on the types of tea, including green and black, which account for (20, 78%) as well as tea Chinese (Oolong) on processing method and fermentation. As a result of its complex chemical complexity it has been characterized by therapeutic and functional properties. The technical advances have led to the production of suitable products such as teas or powdered tea. The tea is extracted from the plant (*Camellia sinensis*), which make the dry leaves treated, while the extract is extracted from the leaves and the preparation of the drink from the leaves or extract of these varieties (Jung and Ellis, 2001, Wan *et al*., 2008).

Green tea is characterized by various health effects in the case of consumption, including increasing the ability to control diseases and anti-inflammatory and low cholesterol level and maintain blood fluidity and resistance to the occurrence of strokes and a causative to prevent the occurrence of cirrhosis and has an antifungal role and a broad impact against the occurrence of mutations and carcinogenesis, Preparation of pharmaceuticals, cosmetics and toothpaste due to a good proportion of fluorine known as tooth decay resistant (Li *et al*., 2004, Jin *et al*., 2006).

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It also has an anti-oxidant effect due to the presence of Epigallocatechin Gallate (EGCG), which is more than the proportion of black tea because of the different manufacturing processes each) Valcic *et al*., 1999, Lin *et al*., 2009). As well as poly phenol oxidase (ppo), which is the main component of it by 25 to 30% on the basis of dry weight (Yao *et al*., 2006).

It contains several different effective chemical groups, such as purine alkaloids, which include caffeine, triglycerides and flavons, Catechins, which is the main part. According to chemical analyses reported by Harler, 1963 (9).

The insoluble part of the spent tea leaves consists of mainly cellulose (37%), hemicellulose and lignin (14%), and polyphenols (25%), these components constitute almost 80% of the insoluble portion of spent tea leaves. The presence of hydroxyl and phenolic groups led us to think that these polar groups could work as active sorption sites for the uptake of transition metal ions like Cu(II). and thus its efficiency in the removal of mineral elements directly related to human health through its direct impact on the central nervous system, kidney system, as well as delay the maturity of red cells in the bone marrow and inhibition of hemoglobin pigment causing anemia, In addition to subtle effects on metabolism and intelligence (Fergusson, 1991, Bajpai and Arti, 2010, Vukovic GD *et al*., 2011).

Drinking water contaminated with Pb(II) and Cu(II) ions for long term, even if in a very low concentration, could lead to a wide spectrum of health problems. The maximum allowable Pb concentration in drinking water has been set at 0.015m L^{-1} by the US Environmental Protection Agency (2002). According to the World Health Organisation (WHO) and United State Environmental Protection Agency (USEPA), the maximum permissible limit of Cu in drinking water is 1.3 mg L^{-1} (Hach, 2003).

While the Iraqi Quality Standard, 2001 for drinking water No. 417 allowed concentrations of lead and copper element 0.01 and 1.0 mg L^{-1} Respectively. The study aimed at the possibility of using the large quantities of residues of spent tea, which are thrown as waste in Iraq or developing countries as one of the alternative ways to remove metal elements, including lead and copper as a solid material cheap and efficient.

Material and Methods

Experimental Arrangement and Procedure

Study samples:

Spent black and green tea leaves were used for the experiments were obtained from coffee shops selling tea in the city of Baghdad. Soluble and coloured components were removed from the leaves by repeated washing with boiling water until the filtrate was virtually colourless. Then the solid was washed with distilled water and oven dried at 60°C for 48 h. The plant was classified by the college of Science/Department of Science in Biology University of Baghdad, confirming that the plant its scientific name (*Camellia sinensis* L.), than stored in plastic stopper bottles containers for further use. No other physical or chemical treatment was performed on the spent tea leaves thus obtained.

Adsorbate (Stock Solutions):

A stock solution of lead Pb(II) and copper Cu(II) ions with a concentration of (1000 mg/l) were prepared by using Pb $(NO_3)_2$, Cu $(NO_3)_2$ minimum purity 99.99%. The desired concentrations obtained after diluting limited volume of concentrated solution with Deionized (DI) Water (APHA, 1998).

All glassware used in the preparation of aqueous solutions for mineral elements has been sterilized according to Quintelas *et al*., (2008), using a solution of distilled water and nitric acid (HNO_3) at a concentration of 55% and 1:1, then washed with sterile distilled water. To get rid of the acid residues, dry using the oven at 100°C for 1 to 2 hrs. to be ready for use. The process was repeated after the completion of each experiment to get rid of the remnants of metallic elements suspended on the walls of Erlenmeyer flask.

Experimental

Procedure: The method described (Cheraghi *et al*., 2015) has been used to determine the efficenicy of the study samples in the removal of lead Pb(II) and copper Cu(II) from aqueous solution at a concentration of 100 mg/l by added 2g of Spent black and green tea leaves were carried out in 250 ml Erlenmeyer flasks and the total volume of the reaction mixture was kept at 100 ml and the pH of solution was maintained at 6 by adding 0.1 M NaOH or HNO_3, Subsequently the mixture was agitated using a shaker incubator with a stirring speed of 150 rpm/ min for contact time 60 min and temperature 25°C. The flasks were withdrawn and the reaction mixtures were filtered through Whatman filter paper (No. 42 µm) than exact concentration were determined by Atomic Absorption Spectrophotometer (AA700 Shimadzu/ japan). The percent lead and copper removal efficiency was expressed as:

$$\text{Removal \%} = \frac{C_0 - C_f}{C_0} \times 100$$

where, C_0 and C_f are the initial and final concentrations of lead and copper (mg L^{-1}) in the aqueous solution.

Study of factors affecting the removal of lead and copper ions by study samples:

In order to obtain maximum removal of Pb(II) and Cu(II) ions optimum conditions have to be used. Such studies are described as follows (Cheraghi *et al*., 2015).

Effect of pH: The effect of the solution pH on the adsorption of Pb(II) and Cu(II) concentration 100 mg l^{-1} onto Spent black and green tea leaves was assessed at different values (4, 5, 6, 7, 8) stirring speed of 150 rpm/ min, contact time 60 min., adsorbent 2g and temperature 25°C.

Effect of mass of adsorbent: Effect of adsorbent quantity on the removal of Pb(II) and Cu(II) from aqueous solution by Spent black and green was varied from (1, 1.5, 2, 2.5, 3)g taking all other parameters constant such as pH 6, initial study ions concentration 100 mgl^{-1}, contact time 60 min., temperature 25°C and agitation speed of 150 rpm /min.

Effect of contact time: Same procedure maintained previously used Effect of pH, mass of adsorbent, but with variable contact time (30, 60, 90 and 120) min. pH 6, weight of adsorbent 2g, temperature 25°C and agitation speed of 150 rpm/min.

Effect of Temperature: Different solutions were prepared containing fixed amounts of Pb(II) and Cu(II) 100 mgl^{-1}. The volume 100 mL, pH 6, adsorbent 2g, contact time 60 min. and stirring speed of 150 rpm/min were fixed with variable Temperature value (25, 35, 45, 55)°C.

Effect of synergistic action: Finally the purpose of this experiment was to effect the synergistic action of spent black and green tea leaves weighting 1g and 1g for both of them on the removal efficiency Pb(II) and Cu(II) 100 mgl^{-1}, by used volume 100mL, pH 6, contact time 60 mins and agitation speed of 150 rpm/min temperature 25 °C.

Results and Discussion

The chemical composition of the insoluble portion, obtained after hot water extraction of Spent black and green tea leaves, is cellulose (37%), lignin and structure proteins (14.9%) hot water insoluble proteins (13%) and polyphenols (25%) as major constituents.

Being polar in nature, these may have specific binding sites available for adsorption of other molecular or ionic species. For example, polyphenols may bind with Pb(II) and Cu(II) ions. In addition, electron-rich oxygen atom of hydroxyl groups of cellulose can also act as binding sites for uptake of Cu(II) ions. Hence, there are good prospects for of adsorption of various types of inorganic/ organic compounds onto waste tea residues. These results coincided with what he mentioned (Bajpai and Arti, 2010).

As for other physical and chemical properties of adsorbent which are presented Coincided with a study (Cay and Özasik, 2004) in Table 1.

Table 1: Physical and chemical characteristics of spent tea leaves sorbent.

Value	Parameters
5.95	pH
3.0	Ash content (%)
11.75	Moisture content (%)
1.03	Density (g cm-3)
84	Dissolved material (%)
112	Solution particles total (mg l^{-1})
87	Organic matters (%)

Effect of pH

Several studies have shown the importance of pH as one of the critical factors influencing the adsorption of metal element ions from aqueous solutions due to their effect on the metallic ion solubility and the ionization of the adsorbent material during the reaction as well as the effect of ion exchange on the adsorbents surfaces that affect the removal process (Das and Karthika, 2008). fig. 1 shows the similar kinetic in the ratios of removal of Pb(II) and Cu(II) by the two study samples with a pH increase of 4-8 as they reached 54.08-98.88%. The studies differ in determining the effect of pH, where he found (Sheela and Nayaka, 2012).

That the pH value of adsorption of heavy metal element ions is between 4.5 and 6, while the pH drop or the height above these values leads to a lack of concentration of the adsorbed metallic elements. It is also observed that the amount of adsorbent material increases if the surface of the cell acquires a charge that is contrary to the synthesized charge, while lower if surface and similar charge elements are acquired, While researchers (Dursun *et al*., 2006) and (Cheraghi *et al*., 2015) shows that mineral elements begin to precipitate in base water

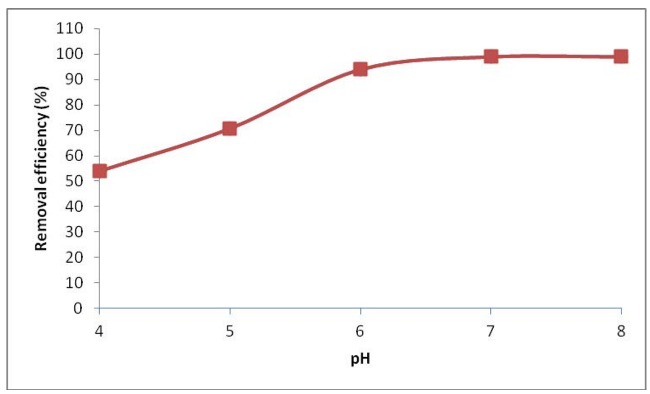

Fig. 1: Effect of pH solution on the removal efficiency of pb(II) and Cu(II) from aqueous solution by spent black and green tea leaves.

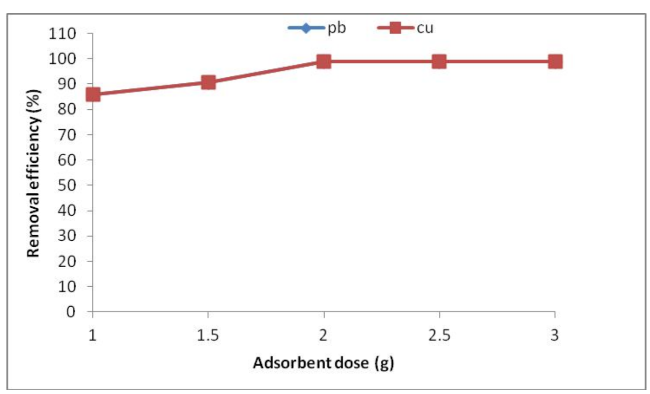

Fig. 2: Effect of adsorbent quantity on the removal efficiency of pb(II) and Cu(II) from aqueous solution by spent black and green tea leaves.

solutions due to the abundance of hydroxyl groups ions without being applied to the surfaces of the material and are consistent with (Gupta and Saleh, 2011, Cheraghi *et al*., 2015).

Effect adsorbent quantity

The purpose of this experiment was to obtain the ideal weight of the adsorbent material to achieve the best removal of the adsorption material, represented by lead and copper. It was observed that the removal efficiency of the study elements ranged from 85.98 to 98.95% illustrated in fig. 2. Thus, these two substances have followed similar behavior in the removal process that occurred in the effect of pH. Where the studies indicated that the adsorption process of the nature of the absorbent material was significantly affected in terms of its chemical properties, depending on the presence of the active groups on the surface of the material that is absorbed or not.

Adsorption is increasing by increasing the surface area due to the increase in the number of active sites and their polarity. So the surfaces containing polarity groups tend to have the most polarity in the solution.

The abundance of pores on the surface of the adsorbate material increases the amount and selectivity of the adsorbed material and the volume of the ion plays a large role in the adsorption process and its capacity, the lead ion adsorption is twice as much as the amount of cadmium ion because it is larger than expected (Adamson and Gast, 2001) and (Wang *et al*., 2013) indicates that the increased concentration of the mass of the adsorbent material reduces the removal of mineral elements due to the bonding of these substances with each other and the reduction of their surface area, as in the removal of Zn(II) by graphene oxide from aqueous solutions. The results of this study coincided with (Andini *et al*., 2006) conducted on organophilic bentonite.

Effect of Contact time

The study of the time required to reach the equilibrium state of concentration in the ionization of study, study of Pb(II) and Cu(II) combined on the powder surface of the spent black and green tea leaves alone. The objective of this process is important in terms of economic cost in shortening the time required for the removal process, this can be seen in fig. 3.

The efficiency of removing the lead element using the two study samples ranged from 88.52% within 30 min and increased to 94.76% within 60 min and then stabilized, while the efficiency of removal of the Cu(II) component with the same materials of the adsorbent 76.80% during the first 30 min and then rose to 89.60% and stability of the ratio after that, the duration of the

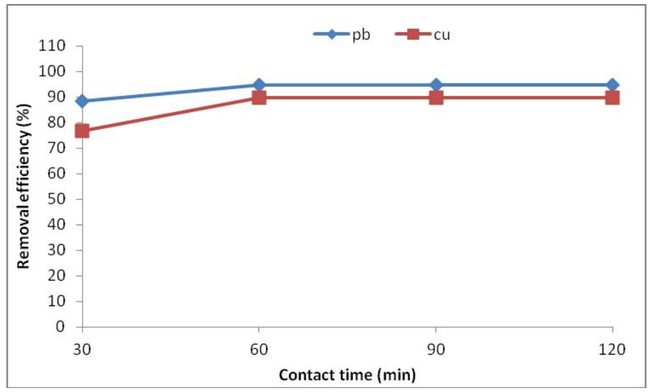

Fig. 3: Effect of contact time on the removal efficiency of pb(II) and Cu(II) from aqueous solution by spent black and green tea leaves.

application, the treatment of heavy metal elements with the adsorbent material for the purpose of removal, is an important factor determining the efficiency of the adsorption process, the highest adsorption capacity of the metal elements occurs in the initial stages of the seam and can reach the equilibrium state within 50 min.

The reason for the stability of the adsorption at a given limit is due to the lack of additional binding sites on the surface of the adsrobent material no matter how long the contact is.

It is likely that lead is the most adsorbent element because it differs from other ions in terms of atomic weight, electrons in external orbitals and its location in the periodic table (Agarry *et al*., 2013) and is similar to the (Guo *et al*., 2014) study.

Effect of Temperature

Fig. 4 shows that the efficiency of the adsorbent materials under study in the removal of metallic elements, is affected by temperature.

Different mineral elements, where the temperature increases.

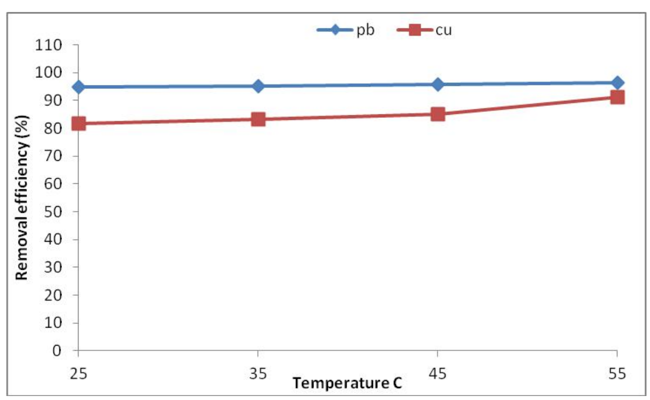

Fig. 4: Effect of temperature on the removal efficiency of pb(II) and Cu (II) from aqueous solution by spent black and green tea leaves.

Table 2: Effect of synergistic action on the removal efficiency of pb (II) and Cu (II) from aqueous solution by spent black and green tea leaves.

Cu	Pb	Removal efficiency (%) / synergistic action
98.99	98.99	spent black and green tea leaves

The adsorption of the ions increases by increasing the temperature, which proves that the process of chemisorption process with the possibility of the process of adsorption as the diffusion of ions within the pores and the crystalline retina of the powder of spent tea varieties and increase the speed of spread with the increase of temperature, that is a process of sorption, which means sorption and absorption together (Awlaa and AL Jamal, 2011).

The efficiency of removal of Pb(II) and Cu(II) was (96.28, 91.20)% respectively at 55°C and was consistent with (Jeyaseelan and Gupta, 2016).

Effect of synergistic action

This experiment was conducted in order to determine the compatibility of the adsorbate materials in the removal of the adsorbents. The results illustrated in (Table 2) their efficiency in the removal of 98.99%, this is due to the abundance of active groups of hydroxyl and carboxylic responsible for the structural and functional structure of cellulose based plant fiber, which is one of the components of spent black and green tea leaves (Zhou and Guo, 2005, Demirbas, 2008). The phenolic compounds found in the adsorption compounds are very relevant to the efficiency of removal of the two elements of the study through their ability to bind these two elements in water solutions. (Yu *et al*., 2001). The results of this study were identical with (Cheraghi *et al*., 2015) and (Zuorro and Lavecchia, 2010).

Conclusions

This study proved that the efficiency of black and green tea leaves, whether alone or in combination, in the removal of lead Pb(II) and copper Cu(II), which pose a direct threat to the human systems of humans through some of the optimum conditions used in removing them from water solutions. In practical applications, the solid-liquid phase is a solid, efficient and inexpensive adsorbents material.

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