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ORIGINAL ARTICLE

Application of activated carbon obtained from waste vine shoots for removal of toxic level Cu(II) and Pb(II) in simulated stomach medium

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Abstract

Copper and lead ions are the most important toxic metals that cause significant environmental and health problems. In this study, we focused on the development of a very cost-effective and environmentally friendly (renewable) remediation technique using vine sprout, an industrial beer waste and readily available agricultural biowaste. In this study, it was aimed to remove the copper and lead that enter the body for various reasons orally, from the simulated stomach medium (SSM) by adsorption in order to reduce their toxic effects on human health. Activated carbon (ACVS) obtained from vine shoots was used as adsorbent. By preparing an artificial stomach medium, the most suitable adsorption parameters (pH, time, mixing speed, amount of adsorbent, and the effect of other components) were examined in the batch system. Equilibrium adsorption data was interpreted using the Langmuir model. The initial Cu(II) and Pb(II) ion concentrations were 10 mg/L and the adsorbent amount was 0.3 g, and the maximum adsorption efficiency of Cu(II) and Pb(II) ions was 100% in the pH 3.5–6.5 range. The performance variables of the adsorbent used were compared with the performance variables of the commercial activated carbon (CAC) used in the emergency response. It was determined that the adsorbent used was more effective in removing copper and lead.

Keywords Activated carbon · Vine shoots · Cu(II) · Pb(II) · Simulated stomach · Adsorption

1 Introduction

Heavy metals spread to the environment as a result of both natural and anthropogenic activities and living things are exposed to them in various ways [1, 2]. Heavy metals, which pose a serious threat to human health and ecosystem integrity, affect living organisms for various reasons. Industrial activities, water and soil pollution, insecticide and fertilization activities, processes in the cultivation, preparation, and packaging and storage of foods are applications that cause heavy metal exposure [3]. Copper and its compounds have many uses in the pharmaceutical industry, electrical industry, agriculture, medicine, metallurgy, and construction industry [4–6]. Lead and its compounds are mainly used in the paint, ceramics, porcelain, vulcanized rubber industry, printing, lead pipe making, and as an insecticide (lead arsenate). At the same time, inhalation of airborne particulate matter is an important exposure route for lead [7, 8].

Poisoning occurs in the human body by ingesting high doses of soluble copper and lead species, accidentally consuming copper- and lead-contaminated water and food, or by

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deliberate ingestion of these species. There are many examples of acute copper poisoning in animals in the literature [9–15]. Lead is a heavy metal that can be toxic even in trace amounts. Lead is one of the most common environmental poisonings in the world [16]. It has been reported that exposure to high doses of lead and copper causes various tissue and organ damage, especially the liver, kidney, and brain, and even coma and death [17, 18]. In general, heavy metal poisoning is the accumulation of toxic amounts of heavy metals in the soft tissues and cells of the human body. Symptoms and physical findings related to heavy metal poisoning in the literature vary according to the metal deposited. In addition, many of the important heavy metals such as zinc, copper, chromium, iron, and manganese are required in very small amounts for bodily function. Unfortunately, if these metals accumulate in the human body in concentrations that cause poisoning, serious damage and hereditary diseases can occur. The heavy metals most commonly associated with human poisoning today are copper, lead, mercury, arsenic, and cadmium. In studies, heavy metal poisoning can occur as a result of industrial exposure, air or water pollution, foods, drugs, improperly coated food containers, or ingestion of lead-based paints.

Fast and efficient treatments are important in such poisoning cases. In order to reduce the harmful effects of copper and lead entering the body, it is a widely preferred method to remove copper and lead from metabolism by using activated carbon [19].

Activated carbons produced in the workshops are widely and effectively used to remove and dispose of hazardous and toxic components in various phases. Commercial activated carbons are mostly used to remove the toxic metal from the body in oral heavy metal poisonings in living beings. Commercially and industrially produced activated carbons can absorb toxic metals up to 5–10 times their actual volume due to their porous and porous structure. Since industrially produced activated carbon is a solid substance that is not absorbed in the intestines in the human body, it sorbs the toxic metal and makes it unabsorbable from the intestines. In addition, it should not be undesirable that people have a weak adsorption affinity of heavy metals and ions to the activated carbons used in the stomach environment at low pH. Many scientific studies highlight the use of chelate (dentate ligand structures) as an alternative in heavy metal poisoning. The fact that chelating agents are expensive and difficult to find, as well as having undesirable effects on the body, makes it important to actively use activated carbons in the human body, which are sorbet at low pH and are more inert (non-harmful) than chelating materials. Studies in the literature have shown that 70% of the metal toxin can be adsorbed when administered with commercial activated carbons within the first 30 min after ingestion of a toxic metal, and 35% when administered within 60 min [20–22].

Activated carbon is a unique adsorbent with high surface area and pore structure, with high performance adsorption from gas and solution phase. Today, one of the common research areas is the production of activated carbon from lignocellulosic agricultural waste products with high carbon content.

Heavy metals, which affect more than one million people a year, can accumulate in industrial production or polluted air, soil, drinking, or underground water resources. People who work in or live near fuel, ammunition, paint, rubber manufacturing, industrial smelting, mining, photo processing, agriculture, semiconductors, welding, and waste or radioactive waste areas are at increased risk for heavy metal toxicity. In addition, growing infants and children, those who are immunocompromised, and those with impaired liver function and low antioxidant levels are at higher risk of heavy metals. Heavy metals that can cause significant disorders such as memory loss; Alzheimer's; Parkinson's disease; lung, blood, or pancreatic cancers; osteoporosis; kidney or liver failure; and infertility should be determined and removed with the most effective elimination method such as adsorption.

In this study, it was aimed to remove Cu(II) and Pb(II) that can be taken orally into the human body by adsorption (in vitro) by preparing a simulated stomach environment (SSM) in order to reduce the possible toxic and undesirable effects on human health. Activated carbon (ACVS) obtained from industrial waste vine shoots was used as a precursor. The effects of the most suitable adsorption removal parameters (stirring speed, time, amount of adsorbent, pH, and the effect of other components) of copper and lead ions in the batch system in the laboratory environment were investigated by us. The obtained and used adsorbent was compared with the performance variables of commercial activated carbon (CAC) used in emergency response.

2 Materials and methods

An Analytic Jena ContrAA 300 model flame atomic absorption spectrometer (Jena, Germany) with a 50-mm burner head unit was used for all metal analysis. The experimental conditions used for instrumental parameters were followed based on recommendations of the company. Flame hood height and flame composition were investigated to obtain the highest analyte signal. The operating conditions for copper and lead by HR-CS FAAS are given in Table 1. HANNA brand HI 2211 digital pH meter (Europe/Romania) was used for pH measurements.

2.1 Reagents and chemicals

Throughout the experiment, all the chemicals and reagents used were of high purity analytical grade. All the chemicals

Table 1 The operating conditions for HR-CS AAS for Pb and Cu determination

Variables	Cu	Pb
Wavelength, nm	324.75	217.00
Flow rate of C_2H_2-air, L/h	55	65
Burner height, mm	6	8
Evaluation pixels, pm	3	3
Background correction	Simultaneous	Simultaneous

used were purchased from the Merck Company (Darmstadt, Germany). All aqueous solutions were prepared with ultrapure water that had been obtained by Milli-Qwater purification system (Millipore, Corporation, MA, USA). Standard stock solutions (1000 mg/L) were purchased from Merck Co. (Darmstadt, Germany). The working solutions were daily prepared by suitable dilutions of the stock solutions. A buffer solution (1 mol/L, pH = 5.0) was prepared using acetic acid with sodium acetate solutions. Commercial active carbon in the adsorption studies CAC (Aqua-Carbo® 50 g/240 ml, Avicenna Farma, Istanbul, Turkey) is provided.

2.2 Preparation of adsorbent

Activated carbon from grapevine shoots (ACVS) used in the experiments presented in this paper was synthesized and characterized as reported by Erdem et al. [23]. Industrial waste vine shoots were impregnated by conditioning with zinc chloride at six different impregnation ratios in the range of 40/0 to 40/30 (weight ratio of waste vine shoots/zinc chloride). Conditioning was performed using an orbital shaker at 150 rpm at room conditions at 25 °C for a 24-h contact time. The conditioned industrial waste vine shoots were dried at 105 °C until the constant humidity was gone and then thermally activated in a programmable chamber oven [23].

The BET device provides precise determination of the surface area and pore size distribution of solid materials. In the analysis performed with the static volumetric method, the amount of gas required to cover the sample surface with a single molecular layer is determined and the surface area is calculated as m^2/g or cm^2/g. In this study, surface areas of activated carbon samples obtained as a result of experimental studies were determined by Micromeritics brand ASAP2020 model BET device in the Research Center.

In the scanning electron microscope (SEM), which consists of three basic parts, the optical column, the sample cell, and the imaging system, the image is obtained by focusing electrons accelerated by high voltage on the sample. It is obtained by scanning this electron beam on the sample surface and collecting the effects between electron and sample atoms in suitable detectors and transferring them to the screen of a cathode ray tube. In this study, SEM images of activated carbon samples were obtained. SEM (scanning electron microscope) images were taken with Zeiss brand Evo 50 model microscope in order to examine the surface structure of activated carbons in imaging.

Infrared spectroscopy, which is used in structural analysis, is a field based on the absorption of infrared rays by matter. The device sends the beam produced in the infrared region of the electromagnetic spectrum to the sample being examined. The vibration and rotation of the bonds of the molecules in the sample take place with the absorption of the beam. The vibration frequencies observed as a result of these interactions provide quantitative and qualitative analyses of the inorganic/organic molecules in the sample and provide information about the functional groups in the molecule. The IR beam energies are in the vibrational energy levels of the molecules and in many vibration centers in the molecule. IR active substances that give IR spectrum are dipole molecules and they absorb IR rays and give bands. Bands seen in the range of 4000–400 cm^{-1}, in the IR spectrum, are recorded against % transmittance or absorbance. In the spectrum, the functional group region is between 4000 and 1500 cm^{-1}, and the fingerprint region is between 1500 and 600 cm^{-1}. In this study, FTIR analysis was performed on raw material and activated carbon samples obtained as a result of experimental studies, and Thermo-Scientific brand Nicolet model FTIR device was used. A certain amount of sample was placed in the device unit and analyzed in the band range of 525–4000 cm^{-1}.

2.3 Preparation of SSM (simulated stomach medium)

The chemical composition given in Table 2 was prepared for the artificial stomach environment recommended by the National Institute of Occupational Health and Safety (NIOSH), determined from the literature. In this study, SSM (simulated stomach medium) was used as stated by the institute.

By following the steps in Fig. 1, the affinity of activated carbons (ACVS and CAC) to Cu(II) and Pb(II) was investigated.

At the end of the batch adsorption processes, the concentrations of Cu(II) and Pb(II) ions in the solution medium were determined by using Analytical Jena ContrAA 300 (GLE, Germany) (HR-CS FAAS) in Kırşehir Ahi Evran University Laboratories. The removal efficiencies (*R* %) and sorption capacities of metal ion pollutants were determined by Eqs. 1 and 2, in the order given below.

$$\text{Adsorption\%} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{1}$$

Table 2 Chemical composition of simulated gastric media recommended by the National Institute of Occupational Health and Safety and used extensively in the literature [24]

Component	Amount (g/L)
Electrolytes and ionic components	
Calcium chloride dihydrate ($CaCl_2.2H_2O$)	0.2646
Magnesium chloride hexahydrate ($MgCl_2.6H_2O$)	0.1525
Potassium chloride (KCl)	0.8647
Sodium chloride (NaCl)	2.8559
0.04 M hydro chloric acid (HCl)	1.4263
Sodium bromide (NaBr)	0.0008
Copper(II) chloride dihydrate ($CuCl_2.2H_2O$)	0.0003
Sodium fluoride (NaF)	0.0009
Phosphorus pentachloride (PCl_5)	0.4707
Organic acids and carbohydrates	
D (+)-Fructose ($C_6H_{12}O_6$)	0.1380
D (+)-Glucose ($C_6H_{12}O_6$)	0.3500
D (+)-Sodium salt of glucuronic acid, monohydrate($C_6H_9NaO_7$ H_2O)	0.0241
Sialic acid ($C_{11}H_{19}NO_9$)	0.0731
Amino acid tablet	0.2672
Nitrogenous compounds	
1 M ammonium hydroxide (NH_4OH)	0.1996
Urea (CH_4N_2O)	0.0840
Uric acid ($C_5H_4N_4O_3$)	0.0080
Vitamin tablet	0.9502
Pepsin	3.2000

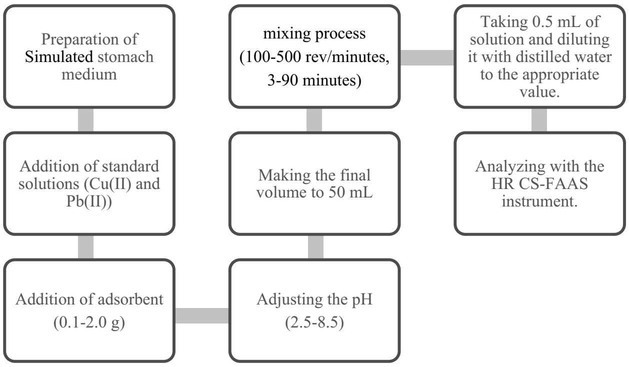


Fig. 1 Flow chart followed in the adsorption process with ACVS and CAC

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{m} \tag{2}$$

In these equations, m is the mass of activated carbon produced by activating (g), V (L) is the volume of toxic metal solutions, and C_0 and C_e are the initial concentration of toxic metal solutions and toxic metal concentrations at equilibrium (mg/L). Adsorption experiments of toxic metals were performed on 3 parallel/identical samples. When the metal removal results differ/deviate from each other by no more than 2%, it was confirmed by calculating the normal average of 3 parallel experiments. In cases where there was a slight but greater deviation, the fourth and fifth experiments were performed and the calculations were repeated by averaging the close experiments.

3 Results and discussion

3.1 Characterization of activated carbon

Activated carbon material obtained as a result of chemical activation of waste vine shoots dried in an oven and powdered in a herb grinder with $ZnCl_2$ solution was used. Adsorbents were prepared by pyrolysis of carbonized materials with zinc chloride at weight ratios of 40 g/30 g (w/w) (industrial waste vine shoots/zinc chloride) in the atmosphere controlled pyrolysis unit of the samples activated at 700 °C in a chamber furnace [23]. It was determined that the Brunauer–Emmett–Teller (BET) surface area of activated carbons was 1689 m^2 g^{-1}, the total pore volume was 0.842 cm^3 g^{-1}, and it also contained 89.65% carbon, had a pHzpc value of 4.8, and could be used to actively remove toxic metal ions. In order to determine the adsorption properties on the surface of the produced activated carbon, the iodine number was found to be 1276 mg g^{-1} [23]. Phenolic, lactans, and carboxylic groups are acidic surface oxides in activated carbon. Boehm, the pioneering determinant of activated carbon studies, characterized these acidic groups by neutralizing them with different base solutions. Activated acidic groups of activated carbon obtained from waste materials were determined as 0.0484, 0.1082, 0.095, and 0.02367 meq g^{-1} active, respectively, by the Boehm titration (basic method) method [24]. In this study, it has been determined that there are significant organic acidic surface functional groups by the titration method (Boehm) on the activated carbon pores we produced. As in other studies, the presence of carboxylic groups in this study is consistent with the data obtained by basic titration. On the other hand, functional groups were determined by FT-IR (ATR) (Fourier transform infrared spectroscopy) in order to recognize functional groups more scientifically in industrial waste vine shoot samples. For this purpose, FT-IR (ATR) spectrum of activated carbon samples produced after 700 °C pyrolysis heat treatment very efficiently is in Fig. 1, elemental analysis results (C;H;N;O) are in Table 3, and SEM (scanning electron microscope) image is given in Fig. 3.

In order to determine the functional groups, in the FT-IR spectrum of the activated carbon given in Fig. 2, (a) pyrolysis product obtained at 700 °C, (b) raw vine

Table 3 Elemental analysis (C;H;O;N) results of the carbonized substance used in toxic metal removal experiments [23]

C: 89.65	N: 1.58	H: 0.71	S: 0.062	O: 8.00

shoot wastes, and (c) zinc chloride activated material. Peaks at 3400 cm^{-1} in all three samples indicate the presence of alcohol, phenol, and carboxylic groups. FTIR peaks between 2850 and 2920 cm^{-1} show C-H structure; FTIR peaks at 1740 cm^{-1} show C = O structure, 1614 cm^{-1} C = C, and 1510 cm^{-1} C–C structure. A total of 600–870 cm^{-1} indicates that the structure most likely has an aromatic ring structure in two bands. According to the (C;H;N;O) elemental analysis results given in Table 2, when compared to the elemental analysis values of the activated carbons in the literature, it can be considered high quality because it has high carbon content and contains less ash [25].

SEM (scanning electron microscope) image of the carbonized material produced in this study shows cavities, pores, channels, cavities, and common outer surface cracks from the SEM (scanning electron microscope) image in Fig. 3. In addition, since it has sufficient pore volume and size, large surface areas, and a highly porous structure, it has shown high adsorption properties of toxic metals and ions [26].

3.2 Parameters affecting the adsorption of Cu(II) and Pb(II) ions

Optimization studies of metals in the artificial stomach environment were carried out by changing one process variable

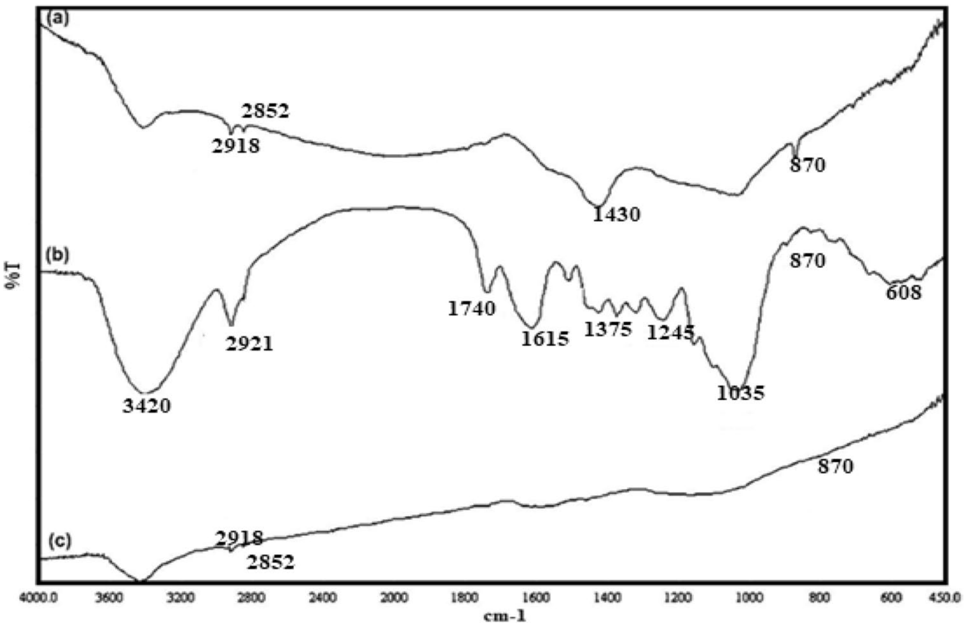


Fig. 2 FT-IR (Fourier transform infrared spectroscopy) spectra of activated carbon used in toxic metal removal experiments ((**a**) pyrolysis product at 700 °C, (**b**) ındustrial waste vine shoots, (**c**) carbonized products activated with zinc chloride) [23]

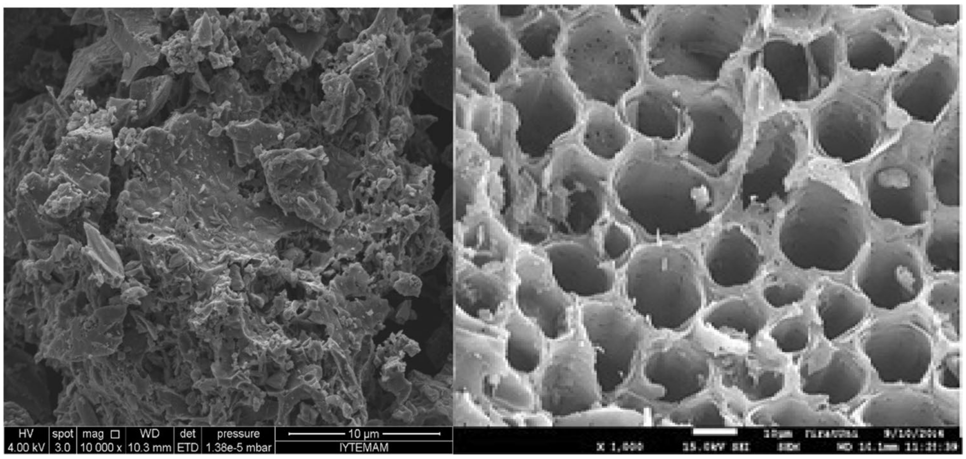


Fig. 3 SEM (scanning electron microscope) image of carbonized material and untreated material obtained from pyrolysis at 700 °C used in toxic metal removal experiments [23]

at a time and keeping other process variables constant, and applications were made. In addition, the adsorption parameters of the produced activated carbon (ACVS) and commercially purchased CAC were compared.

3.2.1 Effect of pH on adsorption

In order to examine the effect of pH in the first step of the optimization, studies were carried out with a solution containing Cu(II) and Pb(II) ions at a concentration of 10 mg/L and pH values of 2.5–8.5 with the amount of 0.3 g adsorbent. The adsorption capacity (q_e) at the specified pH was calculated and the q_e values were plotted against pH (Fig. 4).

When we examined the effect of pH on the adsorption of Cu(II) and Pb(II) ions, it was understood that the ambient pH is one of the important parameters for the adsorption of these ions by activated carbon. It has been observed that the adsorption capacity is high between pH 3.5 and 6.5, and the adsorption capacity decreases as the pH falls below 3.5 or rises above 6.5. Subsequent studies were continued at pH 5.0 [27–29].

Tahtat et al. [30] studies have been conducted on the potential use of their newly developed alginate gel beads for the elimination of Pb(II) poisoning. In this in vitro study, adsorption kinetics were effectively studied at 37℃, pH 2.5, and 50–200 mg/L lead (Pb(II)) concentrations in SSM. It was determined that the swelling rate of the obtained bead-shaped adsorbents increased significantly over time. It was determined that the adsorption of lead with bead-shaped adsorbents in SSM increased with increasing time and initial lead concentration. Adsorption kinetics of lead ions by bead-shaped adsorbents (hydrated alginate particles) indicated that for all lead concentrations, it was rapidly adsorbed during the first 15 min and could be actively used for this purpose.

3.2.2 Effect of contact time on adsorption

In order to determine the ideal contact time in the study with ACVS and CAC, studies were carried out in 50 mL sample with an initial concentration of 10 mg/L, at a mixing speed of 250 rpm, for 3–90 min. The % adsorption efficiencies we obtained for Cu(II) and Pb(II) separately in our studies were plotted against time (Figs. 5 and 6).

It was observed that the highest adsorption efficiency was between 5 and 90 min for ACVS and between 10 and 90 min for CAC, and our further studies were continued with a contact time of 15 min for ACVS and 30 min for CAC. It was revealed that ACVS has faster adsorption ability compared to CAC [29].

Neijzen et al. [31] investigated the use of AC in common gamma hydroxybutyrate (GHB) poisonings in the study. In 100 mL of artificial intestinal fluid at 37 °C, GHB, 2.5; 5.0; at doses of 7.5 and 10.0 g, standard AC was mixed with a dose of 800 g and the AC was separated from the liquid by centrifugation and the remaining amount of GHB was measured by gas chromatography. It has been observed that the binding of GHB to AC is dose-dependent, with adsorption being higher in gastric pH than in the intestine. They showed that very high doses of GHB may be appropriate to treat with AC in children.

3.2.3 Adsorption effect of adsorbent amount

In order to determine the ideal adsorbent amount, studies were carried out in 50 mL sample, at a mixing speed of 250 rpm, at a contact time of 5 min for ACVS, and at an initial ion concentration of 20, 40, and 80 mg/L. The variation of the adsorption efficiency (%) we obtained in our studies with different adsorbent amounts is given in Fig. 7 and Fig. 8.

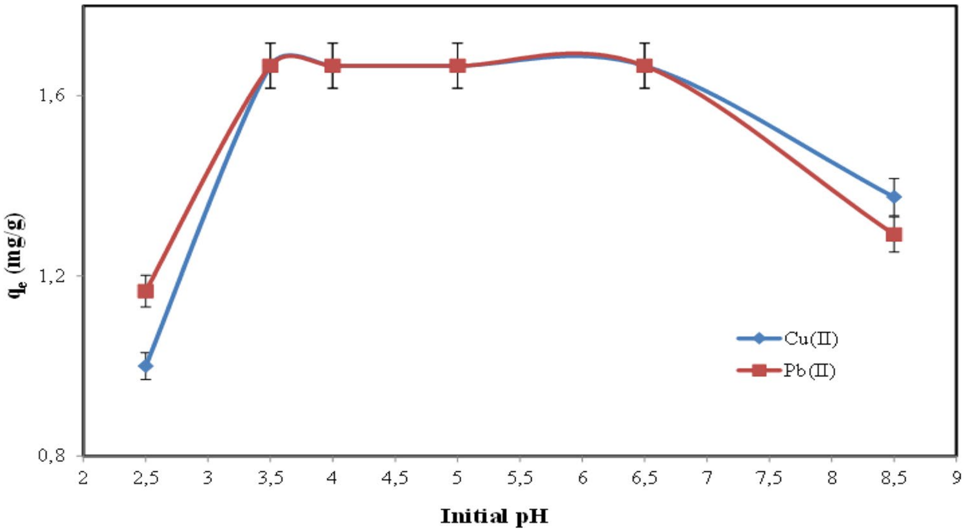


Fig. 4 Effect of pH on the adsorption of Cu(II) and Pb(II) ions (sample volume: 50 mL; C_o: 10 mg/L; stirring speed: 250 rpm; contact time: 90 min; adsorbent: 0.3 g ACVS)

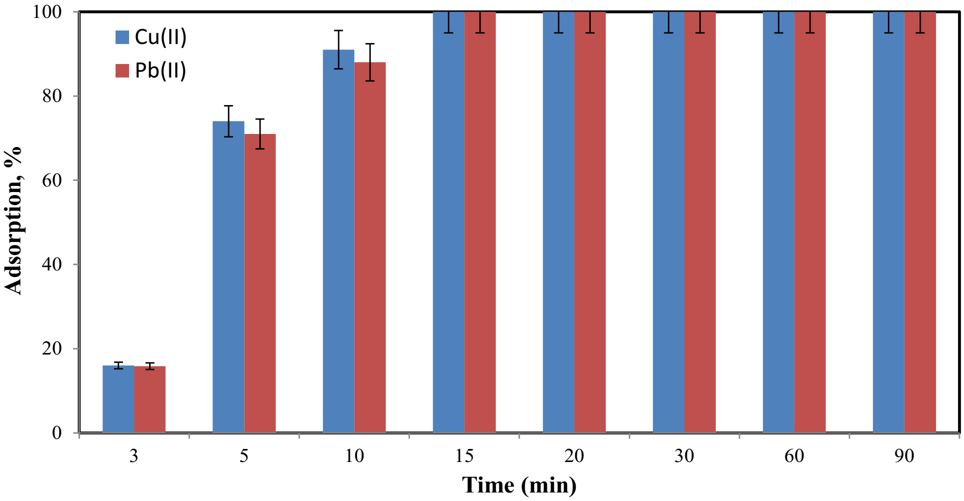


Fig. 5 The effect of contact time on the adsorption efficiency of Cu(II) and Pb(II) ions (sample volume: 50 mL; pH: 5.0; C_o: 10 mg/L; stirring speed: 250 cycle/min; adsorbent: 0.3 g ACVS)

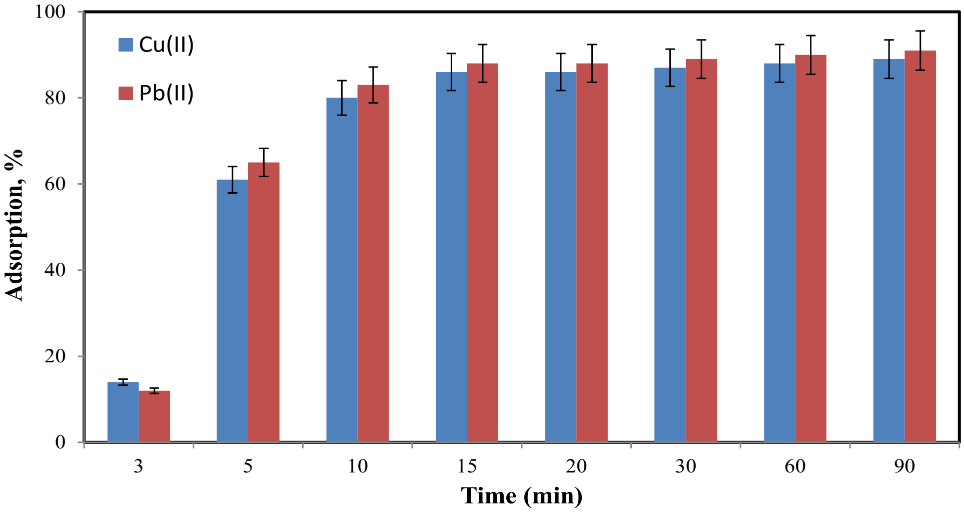


Fig. 6 Effect of contact time on adsorption efficiency of Cu(II) and Pb(II) ions (sample volume: 50 mL; pH: 5.0; C_o: 10 mg/L; mixing speed: 250 rpm; adsorbent: 0.3 g commercial AC)

When we examined the effect of the amount of adsorbent on the adsorption efficiency of Cu(II) and Pb(II) ions, it was found that in 50 mL sample volume, 20, 40, and 80 mg/L initial Cu(II) and Pb(II) ion concentrations and between 0.1 and 2.0 g adsorbent quantities have been studied. The best adsorption efficiency was achieved with 0.3 g adsorbent. Subsequent studies continued by using 0.3 g of activated carbon.

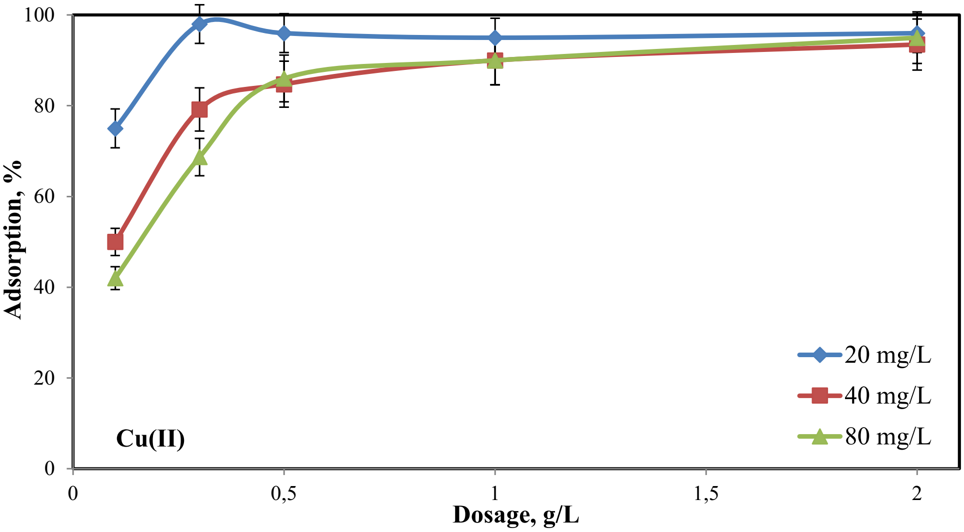
Hoegberg et al. [32] investigated the use of AC in the high-dose drug intake seen in multiple drug poisonings in their study in an artificial stomach and intestinal environment. In the study, ready-to-use Carmix and Norit ready-to-use preparations for which mixed drug adsorption bottles were prepared by mixing combined paracentemol and activated amitriptyline were used and the results were analyzed by HPLC, and it was observed that the two preparations had different adsorption values under the same conditions. This study showed that AC use may be important in preventing nausea, vomiting, and subsequent aspiration.

3.2.4 Effect of stirring speed on adsorption

In our study, in which we investigated the effect of mixing speed on the adsorption of Cu(II) and Pb(II) ions, adsorption studies were performed on 50 mL sample, 5-min contact time, 10 mg/L initial ion concentration, and 100–500 rpm mixing speeds. The adsorption capacities (q_e) of the ions obtained in our studies at different mixing speeds are plotted in Fig. 9. When we examined the effect of mixing speed on the adsorption of Cu(II) and Pb(II) ions, in our study at 100–500 rpm, the highest adsorption capacity was reached at 250 rpm and it was seen that high adsorption capacity reached up to 500 rpm (Fig. 9). Subsequent studies were continued at 250 rpm [27–29].

Altınışık [32] synthesized two different hydrogel films, polyethylene glycol (PEG) and polyvinyl alcohol (PVA), cross-linked to tartaric acid, in environments using amoxicillin as a model drug, KCl/HCl buffer as SSM, and phosphate-buffered saline (PBS) buffer as intestinal medium.

Fig. 7 The effect of adsorbent amount on the adsorption efficiency of Cu(II) ions (sample volume: 50 mL; C_o: 10 mg/L; pH: 5.0; stirring speed: 250 rpm; contact time: 5 min)



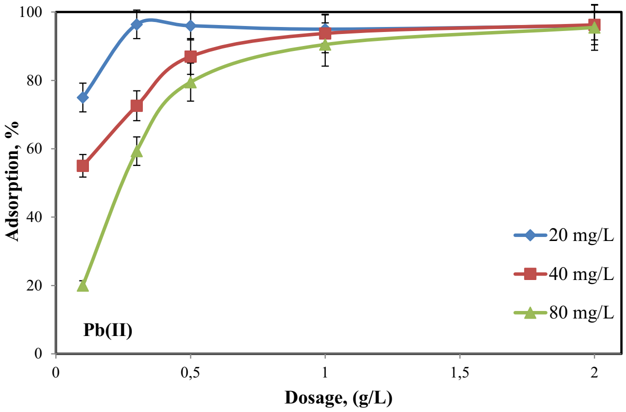


Fig. 8 The effect of adsorbent amount on the adsorption efficiency of Pb(II) ions (sample volume: 50 mL; C_o: 10 mg/L; pH: 5.0; stirring speed: 250 rpm; contact time: 5 min)

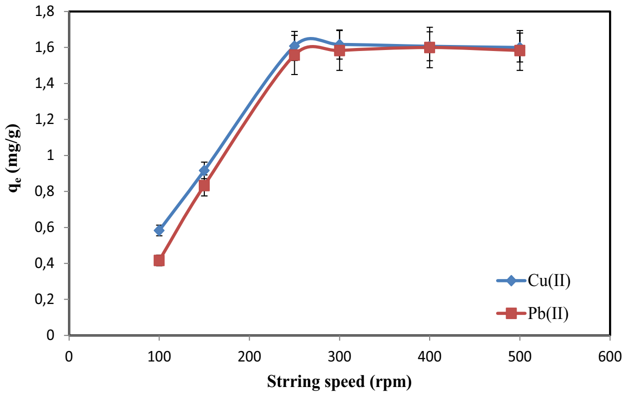


Fig. 9 Effect of mixing speed on the adsorption of Cu(II) and Pb(II) ions (sample volume: 50 mL; C_o: 10 mg/L; pH: 5.0; contact time: 5 min; adsorbent: 0.3 g ACVS)

Drug release was studied. All samples were found to be partially released in the artificial intestinal fluid while SSM was oscillating.

3.2.5 Effect of ınitial toxic metal concentration on adsorption

In our study, in which we investigated the effect of initial ion concentration (C_0) on the adsorption of Cu(II) and Pb(II) ions, studies were carried out in 50 mL sample, 5-min contact time, 250 rpm mixing speed, and 10–100 mg/L initial ion concentrations. In our studies, the adsorption capacities of the ions obtained at different initial ion concentrations were plotted (Fig. 10). Adsorption values for ACVS and CAC are given in Table 4 and Table 5.

It was observed that as the initial Cu(II) and Pb(II) ion concentrations increased, the adsorption capacity increased and remained constant after 80 mg/L (Fig. 10). Depending on the concentration increase, saturation was reached in a shorter time. It was observed that as the concentration of the starting Cu(II) and Pb(II) ions increased, the equilibrium values increased and the yield values decreased [29].

In another study conducted by us, Caliskan et al. [33] studied the removal of Ni(II) from the human body by adsorption technique to reduce its toxic effects on the human body. The most suitable adsorption parameters (mixing speed, time, pH, amount of adsorbent, and the effect of other components) for nickel ions in the batch system using AC obtained from industrial waste vine shoots were also investigated in simulated stomach medium (SSM). Heavy metal analyses were performed with HR CS-FAAS. In the studies where the initial Ni(II) ion concentration was 10 mg/L and the adsorbent amount

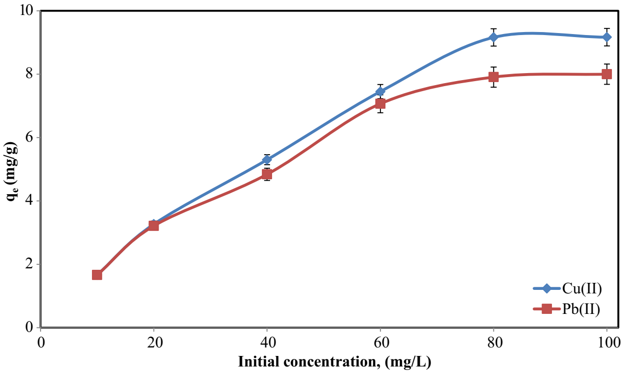


Fig. 10 Effect of initial concentration on adsorption capacity for Cu(II) and Pb(II) ions (sample volume: 50 mL; pH: 5.0; stirring speed: 250 rpm; contact time: 5 min; adsorbent: ACVS)

Table 4 Adsorption efficiencies (for ACVS) at different Cu(II) and Pb(II) ion concentrations

Initial concentration C_0 (mg/L)	Cu(II) Ads, %	Pb(II) Ads, %
10	100.00	100.00
20	98.00	96.40
40	79.50	72.60
60	74.50	70.67
80	68.70	59.30
100	55.00	48.00

Table 5 Adsorption efficiencies (for CAC) at different Cu(II) and Pb(II) ion concentrations

Initial concentration C_0 (mg/L)	Cu(II) Ads, %	Pb(II) Ads, %
10	90.00	85.00
20	71.50	77.50
40	65.25	62.00
60	56.20	53.30
80	51.20	43.75
100	40.00	35.00

was 0.5 g, it was found that the maximum adsorption efficiency of Ni(II) ions in the pH 3.5–5.5 range was 92%.

3.2.6 Investigation of other components affecting adsorption in simulated stomach medium solution

Table 6 Effect of components in SSM on adsorption efficiency of Cu(II) and Pb(II) ions (sample volume: 50 mL; pH: 5.0; stirring speed: 250 rpm; contact time: 5 min; adsorbent: 0.3 g ACVS)

Components	Cu(II) (Ads, %)	Pb(II) (Ads, %)
KCl (0.5 g)	97 ± 2	97 ± 2
PCl_5 (0.5 g)	98 ± 2	98 ± 2
NaCI (1.5 g)	96 ± 1	98 ± 1
$MgCl_2$ $6H_2O$ (0.3 g)	98 ± 2	96 ± 2
$CH_4(N_2O)$ (0.2 g)	99 ± 2	98 ± 2
$C_6H_{12}O_6$ (0.5 g)	100 ± 3	97 ± 3

In our study, in which we examined the effect of other components in SSM on the adsorption of Cu(II) and Pb(II) ions, at the initial Cu(II) and Pb(II) ion concentrations of 10 mg/L in 50 mL sample volume, the excess of the components in SSM was given to our samples, such as KCl (0.5 g); $PC1_5$ (0.5 g); NaCl (1.5 g); and $MgCl_2.6H_2O$ (0.3 g). The adsorption efficiency of Cu(II) and Pb(II) ions was determined by adding $CH_4(N_2O)$ (0.2 g) and $C_6H_{12}O_6$ (0.5 g) separately to the medium, and the excess of the components did not have a significant effect on the adsorption efficiency of Cu(II) and Pb(II) ions observed (Table 6).

3.3 Adsorption ısotherm

The relationship between the equilibrium concentrations of Cu(II) and Pb(II) ions adsorbed per unit mass of ACVS and CAC samples was evaluated using Langmuir adsorption isotherm model. The isotherm equation data were obtained by contacting solutions containing Cu(II) and Pb(II) ions with an initial concentration of 10 to 100 mg/L for 90 min. According to the linearized Langmuir equation, C_e/q_e vs. C_e values were plotted considering the metal concentration in the solution (C_e) in the solution at the end of the experiment and the amount of metal adsorbed on the unit active adsorbent (q_e) at the end of the experiment. Values for ACVS are given in Fig. 11 and values for CAC are given in Fig. 12. The obtained data were applied to the Langmuir isotherm, whose mathematical expression is given in Eq. 3, respectively [27–29].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \tag{3}$$

In studies performed according to the linearized Langmuir equation, the correlation coefficients for ACVS (R^2), Cu(II), and Pb(II) were determined as 0.9792 and 0.9817, respectively. The compatibility of the adsorption behavior of toxic metals from the R^2 value of the obtained line with the Langmuir model was evaluated depending on the literature. The data obtained as a result of the experiments reveal that toxic metal adsorption takes place in a single layer on the adsorbent surface (Langmuir sorption theory). In addition, the maximum toxic metal adsorption capacity

Fig. 11 Linearized Langmuir adsorption isotherm for Cu(II) and Pb(II) (sample volume: 50 mL; pH: 5.0; stirring speed: 250 rpm; contact time: 5 min; adsorbent: ACVS)

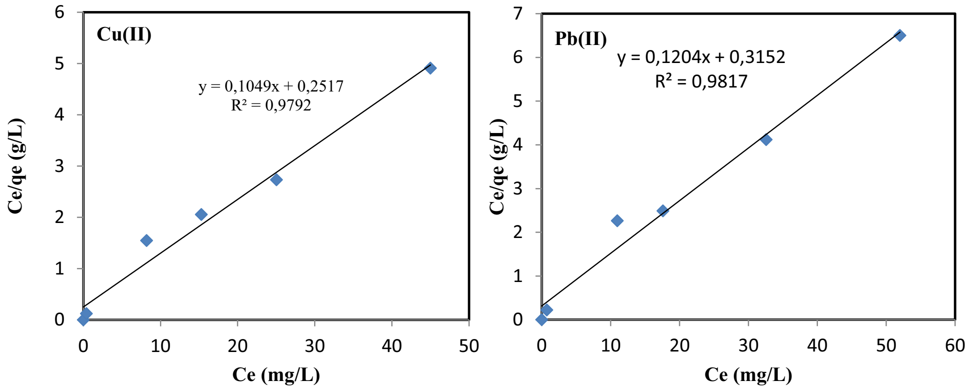


Fig. 12 Linearized Langmuir adsorption isotherm for Cu(II) and Pb(II) (solution volume: 50 mL; solution pH: 5.0; solution stirring speed: 250 rpm; adsorption contact time: 5 min; commercial activated carbon: CAC)

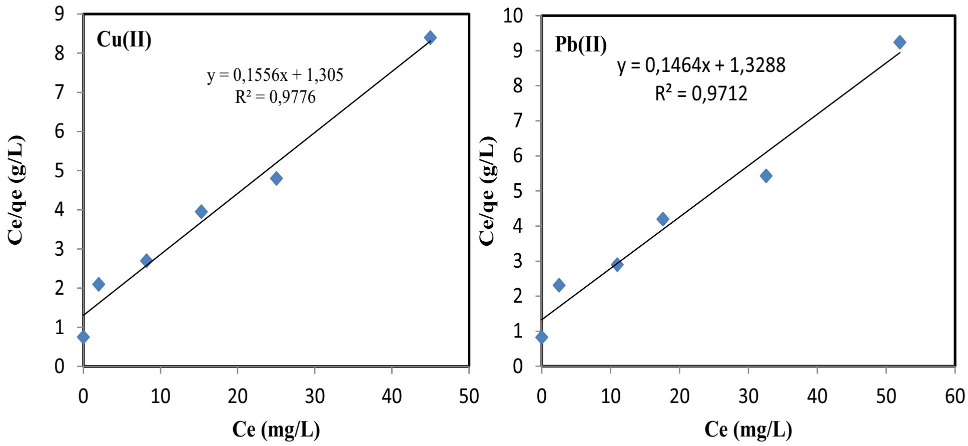


Table 7 Langmuir isotherm parameters for Pb and Cu sorption by ACVS and CAC samples

Isotherm model	ACVS		CAC	
	Cu(II)	Pb(II)	Cu(II)	Pb(II)
q_{max} (mg/g)	9.533	8.305	7.76	6.99
K_L (L/mg)	0.4168	0.3820	0.9036	0.084
R^2	0.9792	0.9817	0.9777	0.9712

(q_{max}) and adsorption energy constant (K_L) were calculated from the slope (L/q_{max}) and cutoff point ($1/K_L.q_{max}$) of this line obtained as a result of the experiments. The q_{max} and K_L values were calculated as 9.533 mg/g and 0.4168 L/mg for Cu(II), and 8.305 mg/g and 0.3820 L/mg for Pb(II), respectively (Table 6). In our study for CAC, the q_{max} and K_L values of commercial activated carbon were calculated as 7.76 mg/g and 0.9036 L/mg for Cu(II), and 6.99 mg/g and 0.084 L/mg for Pb(II), respectively (Table 7).

Adsorption capacity of activated carbon was obtained from vine shoot wastes in removing Cu(II) and Pb(II) ions. Compared with commercially sold activated carbon, ACVS showed higher adsorption capacity compared to CAC.

Many studies have been carried out in the literature to remove Cu(II) and Pb(II) ions from aqueous solutions using adsorbents. In particular, there have been many studies on the removal of Cu(II) and Pb(II) ions from wastes. These studies were carried out to obtain the experimental parameters related to both kinetic/thermodynamic and equilibrium. In general, these studies aimed to find adsorption capacities. The adsorption capacities of some adsorbents used in the adsorption of Cu(II) and Pb(II) ions in the literature are given in Table 8 and Table 9, respectively. In the literature, there is no study in which the removal of Cu(II) and Pb(II) ions from the artificial stomach environment with the solid phase extraction technique and its effectiveness compared to commercial activated carbon in the artificial stomach environment is not available.

3.4 Adsorption mechanism

The adsorption process is usually controlled by three diffusion steps: transport of the solute from the solution to the film layer around the adsorbent; transport from the film layer to the adsorbent surface; its transport from the surface to active sites in the interior. The slow step determines the rate

Table 8 Studies in the literature on the adsorption of Cu(II) ion

Sorbent	Solution medium	pH	Sorption capacity (mg/g)	References
GAC	Solution	5.0	5.37	[34]
Hazelnut husk	Solution	5.7	6.64	[35]
Palm shell	Solution	5	30.8	[36]
Chestnut shell	Solution	5.0	12.56	[37]
Sewage sludge	Solution	5.0	7.73	[38]
Grape bagasse	Solution	5.0	43.47	[39]
ACVS	Simulated stomach medium	5.0	9.533	This work
Commercial activated carbon	Simulated stomach medium	5.0	7.76	This work

Table 9 Studies in the literature on the adsorption of Pb(II) ion

Sorbent	Solution medium	pH	Sorption capacity (mg/g)	References
Dindé stones	Solution	5.0	50	[40]
Activated carbon	Solution	-	6.7	[41]
Hazelnut husk	Solution	5.7	13.05	[35]
Potato peels	Solution	6.0	171.2	[42]
ACVS	Simulated stomach medium	5.0	8.305	This work
Commercial activated carbon	Simulated stomach medium	5.0	6.99	This work

of the adsorption process and is generally considered to be the surface adsorption step and the intraparticle adsorption step.

For example, it is stated that the adsorption of a dissolved compound by activated carbon takes place in three steps: transport of the adsorbed substance to the outer surface of the adsorbent; diffusion of the substance adsorbed into the pores of the carbon, except for a small amount of adsorption occurring on the outer surface; adsorption of the solution on the inner surfaces of the adsorbent. In film diffusion, the solute molecules to be adsorbed enter the carbon particles and form a surface film. Diffusion of metals/ions takes place in this film formed on the surface of the adsorbent. In pore diffusion, it involves the migration of solute molecules from the carbon pores to the adsorption center. In the adhesion of soluble molecules to adsorbent surfaces (adhesion), adhesion occurs when the solute molecule attaches to the carbon pore surface. The diameter, concentration, etc. of the adsorbent molecules. It is the diffusion that proceeds into the pores on the adsorbent surface depending on other conditions [43] (Fig. 13).

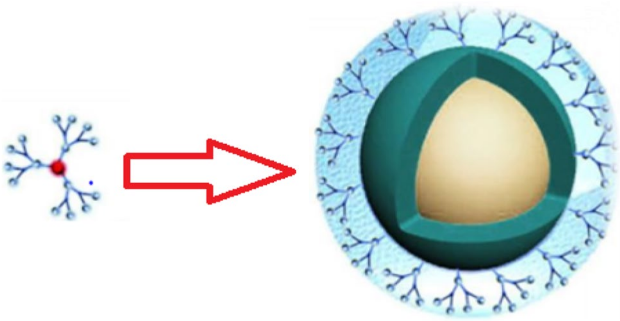


Fig. 13 Adsorption mechanism demonstration of metals by activated carbon

3.5 Cost analysis of activated carbon used for adsorption

The industrial aspect of competitive and regenerative reuse of low cost effective adsorbents remains the main goal of many scientists when dealing with the removal of heavy metals, dyes, and pests. Cost analysis study in activated carbon production and removal studies is a very important parameter to evaluate and estimate the price of activated carbon material and to allow comparison of this study with another method. In addition, cost, technological superiority, geographical advantage, proximity to raw materials, etc. According to previous studies, besides estimating the cost of adsorbent, it can be said that this study has never been applied in the field of adsorption. Activated carbon, which is indispensable for many areas of the industry, has strategic importance especially in adsorption processes, water filters, gas masks, and defense industry. However, the cost of raw materials and the high energy consumption of the production processes increase the cost of activated carbon production considerably. The estimated price for producing 1 kg of adsorbent is estimated to be around \$1.1. From these estimated cost results, it can be said that the produced activated carbon is a low-cost adsorbent.

4 Conclusion

The treated activated carbon has been prepared and characterized by a sequential and methodical approach to understand the surface morphology, porosity, and selectivity of the material for good and rapid retention of the Cu(II) and Pb(II). In this study, it was aimed to remove the copper and lead that enter the body orally from the artificial stomach environment by solid phase extraction technique in order to reduce their toxic effects on human health. Activated carbon obtained from vine shoots was used as adsorbent. By preparing an artificial stomach medium, the most suitable adsorption parameters (pH, time, mixing speed, amount of adsorbent, and the effect of other components) were examined in the batch system. A sensitive, accurate, and precise analytical method has been developed for the removal of copper and lead, which have toxic effects on human health, from the artificial stomach environment with activated carbon obtained from the vine shoot waste. The cost analysis shows that activated carbon is inexpensive and is estimated to cost around \$1.1 per 1 kg. Overall, these results clarified that our activated carbon adsorbent is potential and exhibits a good specific surface area leading to a very high adsorption capacity compared to other adsorbents found in the scientific literature. The performance variables of the adsorbent used were compared with the performance variables of the commercial activated carbon used in the emergency response. It has been determined by the study that ACVS is applicable for copper and lead adsorption in emergency applications.

Author contribution Harun Çiftçi: conception and design of study, acquisition of data, drafting the manuscript, review and editing. Çiğdem Er Çalışkan: conception and design of study, analysis of data, drafting the manuscript, approval of the version of the manuscript to be published. Yusuf İçtüzer: conception and design of study, analysis of data. Hasan Arslanoğlu: writing, analysis of data, revising the manuscript critically for important intellectual content, approval of the version of the manuscript to be published.

Data availability The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Code availability Not applicable.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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