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Research Article

Heavy Metal Adsorption with Eggshell of Phasianus Colchicus

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Abstract: Defining the adsorption behavior of common pheasant *Phasianus Colchicus* (PC) eggshells for some metal ions (Pb, Cu, Al, and Ag) is the subject of this study. In addition to that, these metals have also been chosen in many studies to prevent environmental pollution. In this study, the adsorption of some metal ions (Pb, Cu, Al and Ag) to *Phasianus Colchicus* (PC) eggshell was investigated by some spectroscopic methods. The adsorption process has taken place in an aqueous solution. Differences in inner, outer and membrane surface of *Phasianus Colchicus* (PC) eggshell were examined with AFM images, FTIR spectroscopy was used to determine the main structure of the eggshell, before and after adsorption. To detect the concentration of each metal on eggshell samples, the ICP-OES spectrometric technique is used. The results show that *Phasianus Colchicus* (PC) eggshell can be used as a biosorbent for adsorption of Pb, Cu, Al, and Ag from water.

Key words: AFM, Calcined Eggshell, Eggshell, FTIR, Heavy Metal, ICP-OES

Phasianus Colchicus'un Yumurta Kabuğu ile Ağır Metal Adsorpsiyonu

Öz: Sülün (PC) yumurta kabuğunun bazı metal iyonları (Pb, Cu, Al ve Ag) için adsorpsiyon davranışının belirlenmesi bu çalışmanın konusunu oluşturmaktadır. Buna ek olarak, çevre kirliliğini önlemek için birçok çalışmada da bu metaller seçilmiştir. Bu çalışmada bazı metal iyonlarının (Pb, Cu, Al ve Ag) PC yumurta kabuğuna adsorpsiyonu bazı spektroskopik yöntemlerle incelenmiştir. Adsorpsiyon işlemi sulu bir çözelti içinde gerçekleştirilmiştir. PC yumurta kabuğunun iç, dış ve zar yüzeyi farklılıkları AFM görüntüleri ile incelenmiş, adsorpsiyon öncesi ve sonrası yumurta kabuğunun ana yapısını belirlemek için FTIR spektroskopisi kullanılmıştır. Yumurta kabuğu numunelerindeki her metalin konsantrasyonunu saptamak için ICP-OES spektrometrik tekniği kullanılmıştır. Sonuçlar, PC yumurta kabuğunun sudan Pb, Cu, Al ve Ag adsorpsiyonu için bir biyosorbent olarak kullanılabileceğini göstermektedir.

Anahtar kelimeler: AFM, Ağır Metal, FTIR, ICP-OES, Kalsine yumurta kabuğu, Yumurta kabuğu

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1. Introduction

Pollution is one of the major problems not only for human beings but also for all living things. Water resources may be polluted in many ways, mainly the release of wastewater from industries. Industrial wastewater contains several heavy metals, which come from plastic, cosmetics, textile, leather, pulp, paint and paper industries [1].

Heavy metals pollution has been considerably concerned because of their nonbiodegradability, toxicity, and long-time adverse effects on ecosystems and public health [2]. Al, Cu, Ag, and Pb pollutions have long been considered a significant environmental issue. It is well-known that these heavy metals can cause many diseases, especially cardiovascular, nerve, bone, blood, and kidney diseases [3]. Therefore, they are promptly needed to remove these life-threatening pollutants from wastewater before their disposal in the environment [4]. To decrease or remove this pollution, several physicochemical methods, such as reverse osmosis and ultrafiltration, membrane process [5], solvent extraction [6], oxidation [7], adsorption [8-9], ion exchange, and sedimentation [10] have been employed.

From the environmental viewpoint, the adsorption technique is essential in treating wastewater due to its many advantages such as low cost, simplicity of design, easy handling, and versatility over other methods [11-12]. Naturally occurring resources because of free cost have drawn the attention of many researchers. Low-cost adsorbents for heavy metal removal (such as orange, tea waste, lemon peel, peanut hull, garlic, and eggshell) have been preferred as candidates for biosorbents [13, 14]. Eggshells are waste materials found everywhere, such as in poultries, homes, restaurants, and bakeries. On the other hand, eggshell membranes have been used in various applications such as wound healing products [15], energy storage prototypes [16] laser supports [17] adsorbents [18].

While planning this study, a search of the WOS database was conducted with the keywords eggshell, adsorption, and heavy metal. It has been seen that the number of literature made using eggshells in the last ten years is more than 5000, and it includes 25 different scientific fields. Numerical data of chemical adsorption and heavy metal adsorption studies using eggshells are presented in Figure 1. When the numerical data are evaluated, it is concluded that the use of eggshells in adsorption and heavy metal adsorption studies is on an increasing trend. This orientation encouraged us to do this study. The fact that the PC eggshell, which we prefer as a biomaterial, has never been used in adsorption studies before, made our study unique.

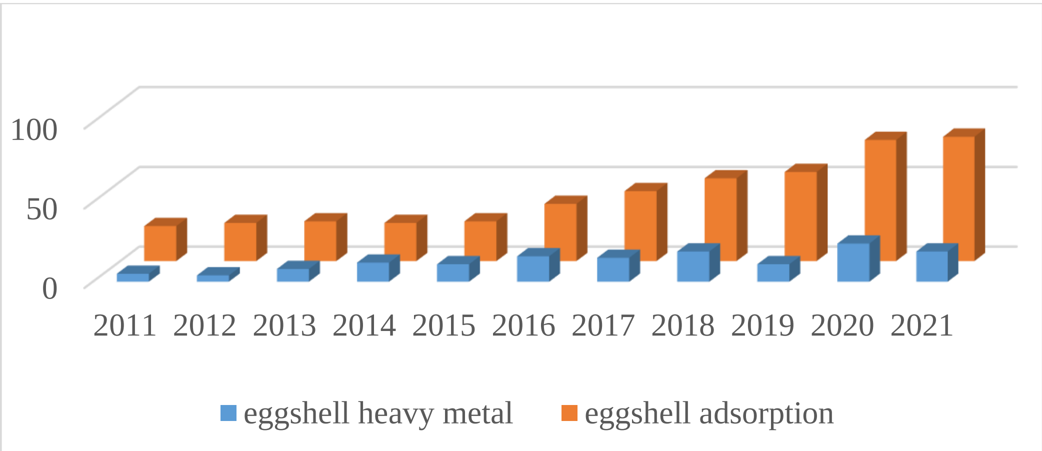

Figure 1. Numerical data of chemical adsorption and heavy metal adsorption studies using eggshells

In this study, PC eggshell and calcined PC (CPC) eggshell residues were used as a biosorbent material. The primary of this study is to investigate the adsorption of heavy metal on PC eggshell (PC-Pb, PC-Al, PC-Ag, and PC-Cu) and CPC eggshell samples (CPC-Pb, CPC-Al, CPC-Ag, CPC-Cu) by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES), Atomic Force Microscopy (AFM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. Figure 1 shows PC, male PC, and egg of PC photographs.

Figure 2. Photographs of PC, male PC, and egg of PC

2. Material and Method

Eggshell samples were taken from incubation wastes of hatched chicks produced and researched by Isparta University of Applied Sciences, Education Research and Application Farm.

Firstly, an elaborate washing procedure was performed to remove impurities from the eggshell. Pheasant eggshell was boiled at 200 °C for 2 hours. After that, the inner membrane was peeled off, boiled in distilled water for 1 hour. After 4 hours, in an ultrasonic bath to remove the residues, it was dried on filter paper at room temperature.

Before the adsorption process characterized by the dried eggshell, samples were chosen from approximately 0.5 cm^2 area. AFM images were recorded in the XE Series Parking Systems device at 250x250 pixel resolution in non-contact mode.

Subsequently, 0.05 M, 100 mL $Pb(NO_3)_2$, $CuCl_2$, $AgNO_3$, and $AlCl_3.6H_2O$ solutions were prepared with ultra-distilled (18.2 Ω) water. Each of the prepared solutions was treated with 1g eggshell and adsorption was applied for 48 hours by mixing in an ultrasonic bath from time to time. FTIR Spectroscopy analyzed filter and dried eggshell samples, ICP-OES, and all analyzes were also performed for metal ions adsorbed on PC and CPC to investigate differences. FTIR spectroscopic analyses were carried out by Thermo Scientific Nicolet iN10 model.

3. Results

The eggshell contains more than % 96 Calcium Carbonate ($CaCO_3$) [19]. Although the amount of metal ions in the eggshell samples are included in the table, it was observed whether there was a change in the Ca ratio of the eggshell. These results are shown in Table 1.

3.1. ICP-OES analyses

ICP-OES results were evaluated to determine whether metal adsorption occurred in the calcined (CPC) and uncalcined amount samples (PC) states. Table 1 shows the amount of metal ions adsorbed in the PC and CPC samples.

Table 1. Amounts of metals and Ca in samples (mg\kg)

	PC-Pb		**PC-Cu**		**PC-Al**		**PC-Ag**
Pb	251511.917	**Cu**	17803.163	**Al**	1721.218	**Ag**	1809.727
Ca	56403.415	**Ca**	53514.938	**Ca**	203330.162	**Ca**	45691.126
	CPC-Pb		**CPC-Cu**		**CPC-Al**		**CPC-Ag**
Pb	259795.571	**Cu**	223820.483	**Al**	3046.407	**Ag**	2337.408
Ca	56235.094	**Ca**	302454.929	**Ca**	227719.561	**Ca**	44914.425

Al ions show the least adsorption capacity on eggshell samples for PC form. Ag ions show the lowest quantity for the CPC form of samples. When the metal adsorption of CPC and PC forms are compared, in Table 1, CPC forms provide superiority for all metal samples. For PC samples, the amount of metal ions adsorption ordered Pb> Cu>Ag>Al, the ranking varies for CPC forms. The adsorption amount ordered Pb>Cu>Al>Ag for CPC samples. Table 1 shows that the highest amount of Ca is PC-Al in the PC samples, and the highest amount of Ca is in the sample of CPC-Cu among the samples with CPC.

3.2. AFM analyses

The porosity of the eggshell makes it a remarkable material that can be used as an adsorbent. The eggshell characteristically has a three-layered structure. The outer layer is namely cuticles and is a ceramic material, the middle layer is spongy (calcareous) and the innermost third layer is defined as mammalian [20, 21]. The eggshell is represented by spongy and mammalian layers of protein fibers attached to calcite (calcium carbonate). The presence of many circular pores in these layers makes them a very efficient adsorbent. The pores allow an increase in the number and surface area of binding sites for the biosorption process [21, 22].

The characteristics of the three (3D) dimensional surface topography of the eggshells' inner, outer, and membrane parts of the eggshells were analyzed by AFM and shown in Figure 2 comparatively. In Figure 2, the dark blue and brown regions show pit and peak, respectively. When Figure 2 is examined, it is seen that the outer form of the pure dried PC eggshell has many pores and pits scattered over the entire surface, the inner part is flatter, and the hills and troughs of the membrane part are very prominent. In addition, it is seen that the depth difference between the peak and pits points of the samples is highest in the membrane and the lowest in the outer part of the region histogram. The rough and porous surface of the pheasant eggshell suggests that metal salts are mostly retained in this region.

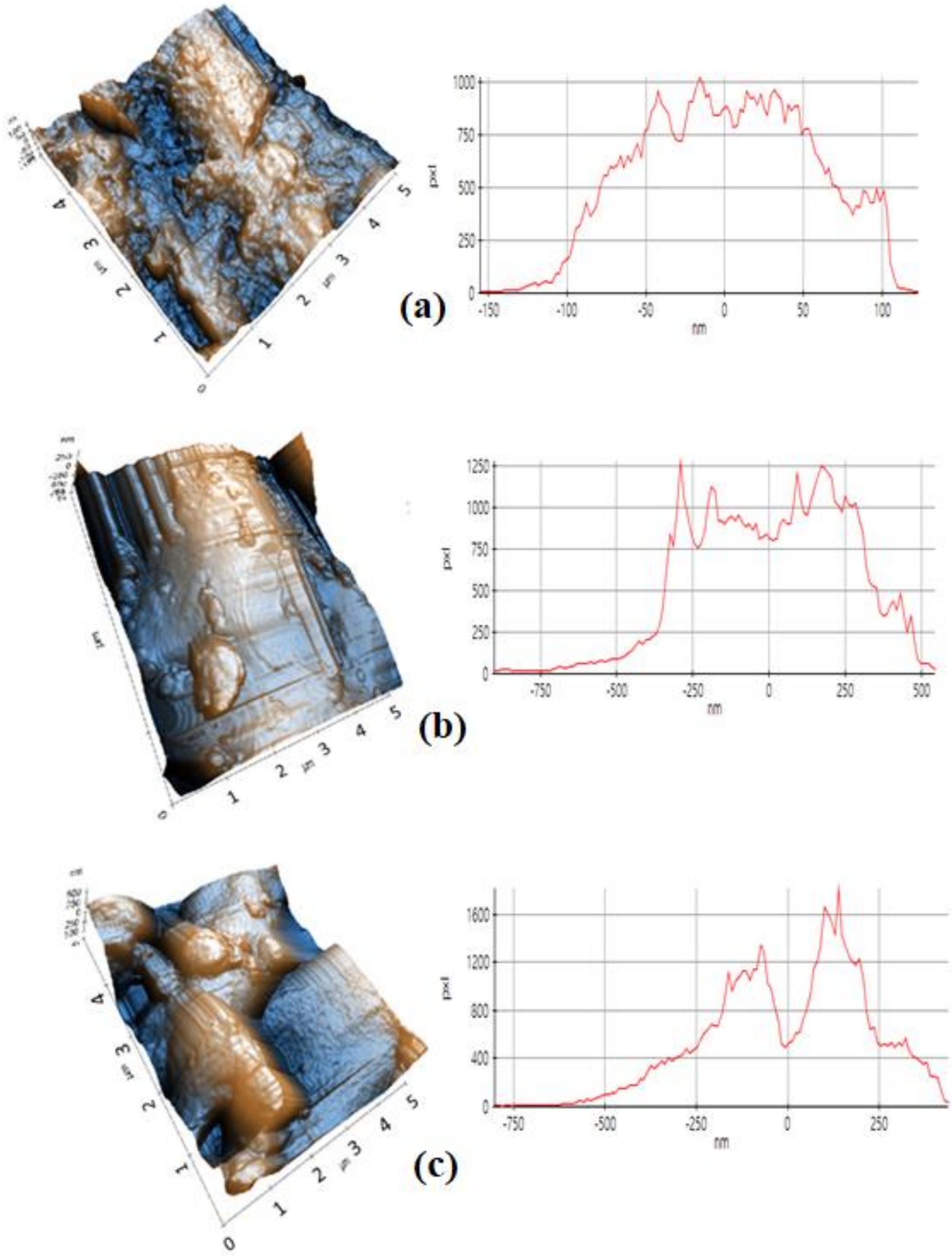

Figure 3. AFM Images and region histogram of Eggshell Sample (a) outer (b) inner (c) membrane

3.3. FTIR spectra analyses

FTIR spectra analyzes were performed to examine the structural differences between PC and CPC after some metal adsorption. Figures 4 and 5 show the FTIR spectra of PC, PC-Pb, PC-Cu, PC-Ag and PC-Al and FTIR spectra of PC, PC-Pb, PC-Cu, PC-Ag, respectively. Table 2 shows FTIR spectra assignments of PC, PC-Cu, PC-Pb, PC-Ag, PC-Al, CPC, CPC-Cu, CPC-Pb, CPC-Ag and CPC-Al.

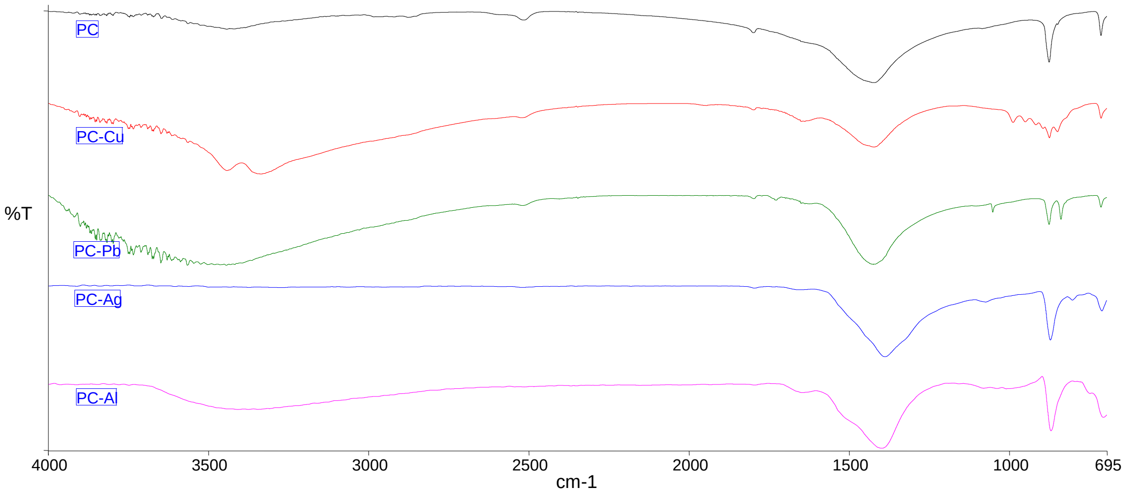

Figure 4. FTIR spectra of PC, PC-Pb, PC-Cu, PC-Ag and PC-Al

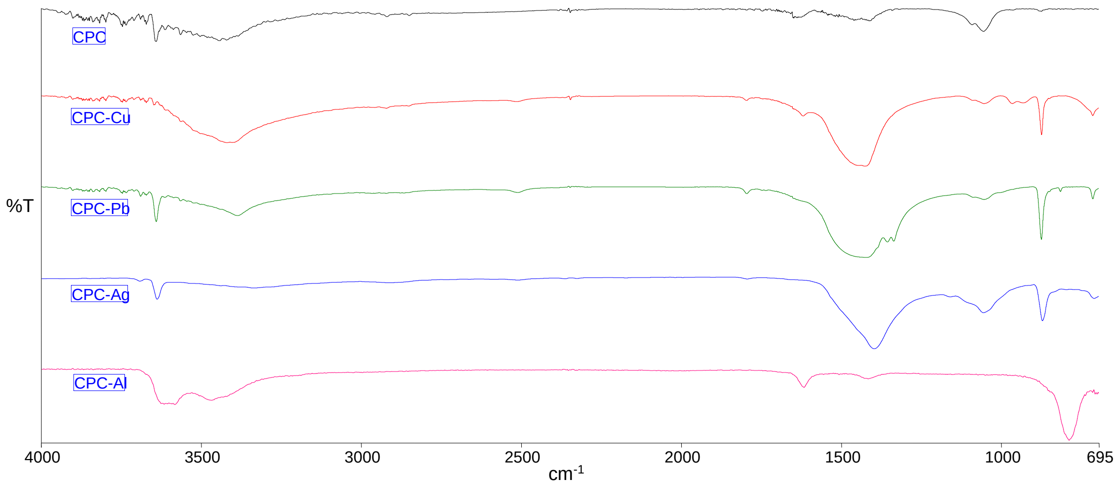

Figure 5. FTIR spectra of CPC, CPC-Pb, CPC-Cu, CPC-Ag and CPC-Al

The band characteristics of the OH groups are usually observed around the range of 3600-3200 cm^{-1} as a broad band [23]. When Figure 4 was examined, this band wasn't sharp and deep in the uncalcined pure PC sample. This band was seen except for PC-Ag after being treated with aqueous solution of metal compounds. 2516, 1798, 1640, 1424, 1084, 875 and 713 cm^{-1} are characteristic peaks of eggshells belonging to the vibration of CO_3^{2-} generally [8, 24–26]. All these peaks were observed in all samples except 2516 cm^{-1} in PC-Al. The weak bands around 1798 cm^{-1} [27] and 1084 cm^{-1} [28] were attributed to C=O bonds of CO_3^{2-} and the symmetric stretching of carbonate, respectively. The band around 1640 cm^{-1} as seen shoulder and weak band in PC and other samples, was attributed to carbonyl group vibration [29]. As seen in all samples, the strongest band around 1424 cm^{-1} could belong to C-O stretching of symmetrical vibration of carbonate [8]. The peaks, the C-O stretching belonging to the out-of-plane and in-plane deformation vibration bands of $CaCO_3$, were observed mainly as medium bands at around 875 and 713 cm^{-1}, respectively [30, 31].

When Figure 4 and 5 was examined, OH vibration bands were observed in the range of 3642- 3332 cm^{-1} in eggshell samples. The vibration band, which was attributed to belonging to OH stretching at 3420 cm^{-1} in the literature was observed at 3444, 3445, and 3409 cm^{-1} in PC-Cu, PC-Pb, and PC-Al, respectively. On the other hand, this band was seen at 3422, 3387, 3332 and 3469 cm^{-1} in CPC-Cu, CPC-Pb, CPC-Ag and CPC-Al samples, respectively[32], [33]. Most of the characteristic peaks of eggshells were seen in calcined eggshells samples. The peaks at 2516 and 1798 cm^{-1} were seen in most of samples as weak bands, but these bands disappeared in CPC and CPC-Al. This is thought to be because of the interaction between the calcined eggshells and metal ions.

The weak band thought to belong to NO_2 was observed at 1728 and 1736 cm^{-1} in PC-Pb and CPC-Pb, respectively. In the studies of Zang et al. and Shen et al., the N-O vibration band seen in about 1070 cm^{-1} [34, 35], was seen as in 1051,1073,1053 and 1057 cm^{-1} with shifts in PC-Pb, PC-Ag, CPC-Pb and CPC-Ag, respectively. In addition, the vibration band, which was attributed to belonging to NO_{3-} stretching at 803 cm^{-1} in the literature [35], [36] was observed at 838, 802, 814 and 716 cm^{-1} in PC-Pb, PC-Ag, CPC-Pb and CPC-Ag, respectively. This shift was thought to be due to the interaction of an aqueous solution of metallic salts and eggshells.

Riesgraf and May had observed vibrational bands around 1000 cm^{-1} originating from Al-O-H_2 [37]. In our study, this weak band for PC-Al and CPC-Al was observed at 995 and 989 cm^{-1}, respectively. Also, the band for PC-Al and CPC-Al at 743 and 736 cm^{-1}, respectively, could be relevant to interaction $AlCl_3$ with eggshell.

In addition, the peaks observed at 1054, 987, 949 cm^{-1} (in PC-Cu) and 1053, 965, 932 cm^{-1} (in CPC-Cu) were thought to be due to the interaction between the copper aqueous solution and the eggshell.

Table 2. FTIR vibrational bands assignments of PC, PC-Cu, PC-Pb, PC-Ag, PC-Al, CPC, CPC-Cu, CPC-Pb, CPC-Ag and CPC-Al

Assignments	PC	PC-Cu	PC-Pb	PC-Ag	PC-Al	CPC	CPC-Cu	CPC-Pb	CPC-Ag	CPC-Al
OH groups						3641vs		3642s	3641s	3617br
OH groups	3442-3423br	3444s-3337s	3445br		3409br		3422br	3387br	3332br	3469br
CO_3^{2-} stretching	2516w	2524w	2518w	2522vw	2517vw	-	2514w	2511w	2507vw	-
CO_3^{2-} stretching	1798w	1798vw	1798w	1797w	1797vw	-	1797w	1794w	1797vw	-
NO_2 stretching			1727w					1736vw		
R_2CO_3 group stretching	1638sh	1648w	1648w	1651w	1643w	1635vw	1618w	1631sh	-	1616s
CO_3^{2-} stretching	1424vs	1424s	1424vs	1388vs	1396vs	1411m	1424vs	1424s	1396vs	1415m
CO_3^{2-} stretching	1084vw	1066sh	1093sh	1072w	1080vw	1057m	1088sh	1086sh	1096sh	-
N-O stretching			1051m	1072w				1053w	1057s	
		1054sh, 987w, 949w					1053m, 965w, 932w			
Al-O-H_2 bend					995w					989vw
CO_3^{2-} in plane deformation	875s	874m	875s	871s	871s	863w	873s	874s	871s	787vs
NO_3^-			838s	802w				814w	796vw	
					748w					736w
CO_3^{2-} out of plane deformation	713s	712m	713m	709m	709m	694w	713s	713m	709m	706w

PC: Phasianus Colchicus, CPC: Calcined Phasianus Colchicus, Cu: Copper, Pb: Lead, Ag: Silver, Al: Aluminum, Sh: Shoulder, Br: Broad, w: weak, s: strong, m: medium, vw: very weak

4. Conclusion and Comment

This study used PC eggshell and CPC eggshell residues as biosorbent material.

According to the ICP-OES results, it was seen that Pb was the most adsorbed and Ag was the least adsorbed among the heavy metals. It was seen that calcined forms are adsorbed by more metals.

The AFM results show that the outer side of the pure dried PC eggshell has pores and pits scattered over the entire surface, the inner side is flatter, and the membrane part has distinctive pits and peaks structure. The rough and porous surface of the pheasant eggshell indicates that metal ions are more attached to this area.

It has been observed that some characteristic bands in the FTIR spectra undergo significant changes due to the adsorption process. It is observed that some bands decrease and some increase. This shows that the adsorption process was successful, just as in the ICP-OES and AFM results.

The prepared PC and CPC were used to remove some toxic heavy metal ions from the aquatic environment. Studies showed that the new biosorbent has a high sorption capacity for relevant metal ions. In summary, PC-Pb, PC-Al, PC-Ag, PC-Cu and CPC-Pb, CPC-Al, CPC-Ag, CPC-Cu samples showed beneficial properties for their use in the treatment of polluted water.

Author Statement

Deniz Türköz Altuğ: Investigation, Resource/Material/Instrument Supply, Original Draft Writing
Neslihan Kaya Kınaytürk: Investigation, Original Draft Writing, Visualization
Taner Kalaycı: Investigation, Original Draft Writing, Review and Editing
Belgin Tunalı: Investigation, Supervision, Observation, Advice, Original Draft Writing

Acknowledgment

As the authors of this study, we declare that we do not have any support and thank you statement.

Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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