Detachment of Cu (II) and Co (II) ions from synthetic wastewater via adsorption on *Lates niloticus* fish bones using LIBS and XRF

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**Abstract**

Natural fish bones, that are known to have unique adsorption capacity, have been used in the present work for removal of heavy metals, copper, and cobalt, from wastewater. It has been found that sorption process depends on the initial metal concentration and on the contact time. Laser-induced breakdown spectroscopy (LIBS) as a spectrochemical analytical technique was used for qualitative and quantitative analysis of the water samples. X-ray Fluorescence (XRF), as another spectrochemical analytical method, was exploited to characterize the remediation of wastewater. The optimum contact time values for the removal of Cu (II) and Co (II) were 270 and 300 min, respectively. Furthermore, the percentages of adsorbed Cu (II) and Co (II) were high for low initial concentrations and decreased with increasing the heavy metal initial concentrations. The Langmuir and Freundlich isotherm models were used to analyze the equilibrium adsorption data and Freundlich isotherm was found to represent the experimental results well with a correlation factor close to one. However, the pseudo-second-order kinetic model provided the best fit to the experimental data for the adsorption of heavy metals using fish bones compared to the pseudo-first-order model. The obtained results demonstrate the potential of using both LIBS and XRF in the analysis of contaminant wastewater effectively.

Introduction

Contamination of water by heavy metals poses serious ecological problems because of their pernicious effects on human, animals, and plants [1,2]. Heavy metals such as copper and cobalt find their way to aquatic environment as a result of the rapid...
The concentration of the adsorbed copper and cobalt on fish bone. Because of the simplicity of XRF analysis, it has been widely used simple and suitable for in situ. More recently, biogenic hydroxyapatite (HAP) of different origins, such as fish and animal bones, bone chars, and food waste, has been used as sorbent materials for remediation of wastewater [8–11]. Fish bones as a distinctive material of low cost and natural abundance have proven to be one of the most effective heavy metal sorbents used in industrial applications [12]. The adsorption efficiency of fish bones is due to the presence of hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) structure, that dependence on the exchange reaction with calcium ions with heavy metals [12–16].

Spectrochemical analytical techniques, such as Laser-Induced Breakdown Spectroscopy (LIBS) and X-ray Fluorescence (XRF) could be used effectively to follow up the adsorption procedure. LIBS uses laser-generated plasma as a source of material vaporization, atomization, and excitation. This technique has been successfully applied to analyze solid, liquid, and gaseous samples. LIBS also offers attractive features for real-time multi-elemental analysis at atmospheric pressure, including remote applications with no or minimal sample preparation in addition of being noninvasive and quasi-nondestructive. This laser spectroscopic technique has the capability for qualitative and semi-quantitative elemental analysis, with detection of most existing species such as major components and/or trace elements with low and high Z-number. It is also possible to use LIBS in situ with portable systems because of its simplicity and compactness of the required equipment contrary to other techniques such as Atomic Absorption Spectroscopy or Inductively Coupled Plasma Optical Emission Spectroscopy. LIBS has significant potential in the environmental applications, for tracing pollutants and for the detection of heavy metals contamination [17–19]. On the other hand, XRF as a well-established spectrochemical analytical technique offers some unique advantages as being fully non-destructive, requiring minimal sample preparation, simple and suitable for in situ use with portable equipment. Because of the simplicity of XRF analysis, it has been widely used for numerous environmental applications [20]. The limit of detection of both LIBS and XRF for metals is typically in the ppm range [19–21]. The main goal of this research work is to confirm the adsorption efficiency of fish bones for heavy metals. The variation of initial metals concentrations and contact times as adsorption parameters were examined. The LIBS results were validated by the XRF technique measurements. Adsorption isotherms and kinetics studies were reported to account for fish bones as an effective adsorbent of copper and cobalt from wastewater. Our results indicate that the fish bones filtrates were then collected and dried, and the treated wastewater has been collected and stored in glass bottles.

**LIBS setup**

All experiments were carried out using a typical single pulse LIBS setup that employs a Q-switched, Nd: YAG laser (BRIO, Quantel, France) operating at a wavelength of 1064 nm. The laser pulse energy was 96 mJ, at 5 ns pulse duration and 10 Hz repetition rate. The measurements were performed in air at ambient atmospheric pressure. The laser was focused by a 10 cm focal length plano-convex quartz lens onto the target surface. A 2 m length optical fiber of 600 μm diameter has been mounted at a 45-degree angle with respect to the target surface to collect the emission from the plasma plume then fed it to the entrance slit of an echelle spectrometer (Mechelle 7500, multichannel, Sweden), covering the spectral wavelength range of 200–1000 nm (displayable in a single spectrum). An intensified CCD camera (DiCAM-PRO, PCO-computer optics, Germany) detects the spectra of the plasma emission. LIBS software has been used for the analysis and identification of the obtained LIBS spectral lines. Each LIBS spectrum represents the average of 25 spectra taken as 5 spectra at 5 different positions on each fish bone sample target [16]. Detailed study of the experimental parameters of the present setup can be found in our previous work [19]. The optimum experimental conditions for LIBS analysis such as delay time ($t_d$) which is the time interval between firing the laser and triggering the detector (ICCD camera), and gate width ($At$) which is the time during which the detector is sensitive, were 1500 ns, and 2500 ns, respectively. These conditions provided very good spectral signal-to-noise ratio. For quantitative analysis using LIBS, the laser-induced plasma should satisfy the conditions of local thermodynamic equilibrium (LTE) [22]. Under the present experimental conditions, the plasma temperature $T_e$ ranges from 6267 to 10676 K and the values of electron density $N_e$ (cm$^{-3}$) is greater than $10^{16}$ which fulfills McWhirter criterion ($T_e > 5000$ K, $N_e > 10^{16}$).

**XRF setup**

As mentioned above, the samples have been also analyzed via the XRF technique. An XRF spectrometer (Portable XRF, Thermo Scientific, NITON/XLT 8138, 592 GKV, USA) having a 40 kV X-ray
tube with a gold anode excitation source. The detection range of this spectrometer expands from sulfur to uranium with a low limit of detection for high-Z elements. The advanced NITON software has been used for the analysis of the obtained XRF spectra [23].

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM, FEI Quanta FEG 250 series, Japan) [24] investigations were performed at magnifications of 10× to 10,000×. It has been used for the morphological characterization of the samples to elucidate the porous properties of the biosorbents. For cross-sectional inspection, the fragmented samples were embedded in carbon tab.

Results and discussion

Scanning electron microscope (SEM) analysis

To show clearly the adsorption effect on the bones surface morphology, the physical morphology of fish bones surface is shown in Fig. 1. The SEM micrographs depict the surface morphology before and after adsorption processes at the highest concentration of 300 mg L\(^{-1}\) for 270 min at initial pH (6.6 ± 0.1).

For comparison studies, all images have had the same 2000× magnification. Analysis of SEM image presented in Fig. 1(a) revealed that the dried pure fish bones have numerous small pores on the surface which are responsible for increasing the surface area.

Fig. 1. SEM images of fish bones (a) before adsorption (b) after adsorption of Cu (II) (c) after adsorption of Co (II) [in 300 mg L\(^{-1}\) concentration after 270 min with initial pH (6.6 ± 0.1)].
and consequently the increase of adsorption capacity and efficiency [25]. Fig. 1(b) and (c) displays a comparison between the adsorption processes of both Cu (II) and Co (II) on fish bones surface. Fig. 1(b) indicates that all pores appearing on the adsorbent surface are almost completely covered by Co (II) ions. On the other hand, Fig. 1(c) apparently shows that fish bones surface is partially covered by Co (II) ions.

Influence of contact time and metal ions initial concentration on removal process

Fig. 2(a), (c) depicts the effect of contact time on adsorption uptake of Cu (II) and Co (II) onto fish bones from synthetic wastewater at different concentrations using LIBS analysis, respectively. The results indicate that both LIBS intensity and adsorption uptake increase with increasing contact time until reaching the equilibrium point of 270 min for Cu (II) and 300 min for Co (II). The effect of contact time on adsorption uptake of Cu (II) and Co (II) onto fish bones is accentuated by making use of XRF analysis at the same experimental conditions as shown in Fig. 2(b), (d). The trend of the XRF curves indicates a significant consistency; that lends confidence to the LIBS results.

Fig. 3(a), (b) shows the effect of contact time on removing Cu (II) and Co (II) respectively from the synthetic wastewater by means of XRF analysis with same initial concentrations. In Fig. 3(a) it is clear that the reduction in the intensities arises as a consequence of increasing the contact time. By repeating the experiment for Co (II), Fig. 3(b) demonstrates similar trend of decreasing intensities; which shows the increase in the removed amount of Co (II) from synthetic wastewater with longer contact time for the same initial concentrations measured for Cu (II).

It should be noted that the metal cations adsorption on the fish bones is higher in the beginning due to the availability of a large surface area with specific sites of the adsorbent. Reaching saturation means that all active sites in the adsorbent are occupied [26,27].

Adsorption isotherm

The adsorption percentage efficiency of metal ion removal E has been calculated by the following equation:

$$E = \frac{C_i - C_e}{C_i} \times 100$$  \hspace{1cm} (1)
where $c_i$ is the initial metal ion concentration (mg L$^{-1}$), and $c_e$ is the equilibrium metal ion concentration (mg L$^{-1}$). The calculations are performed at a fixed contact time of 30 min with initial pH (6.6 ± 0.1) and temperature (25 ± 2°C).

Fig. 4 shows the percentage removal efficiency calculated by Eq. (1) versus different initial metal concentrations, under the previously specified conditions. These results assure that the removal efficiency for copper is higher than that of cobalt at all concentrations. The difference in ion exchange capacity on the adsorbent surface for the two elements could justify this difference in removal efficiency [28]. However, the dependence on charge density of each element, extent of hydrolysis, and solubility of hydrolyzed metal ions in the solution can also be taken into consideration in this issue [29].

**Langmuir isotherm**

At a fixed temperature, the adsorbate quantity adsorbed to that remaining in the solution is called adsorption isotherm and it describes the equilibrium relation between the concentrations in both adsorbent and solution phases [29]. Langmuir and Freundlich isotherm models are the most widely adsorption isotherm models that are used to quantify the sorption capacity of adsorbate.

### Langmuir isotherm

This model assumes that adsorbent has sites with uniform energy for adsorption of adsorbate providing a monolayer homogeneous adsorption [30,31]. The linear form of Langmuir isotherm is presented as follows [32]:

$$
\frac{1}{q_e} = \frac{1}{bq_{\text{max}}} + \frac{1}{q_{\text{max}}} \left(\frac{c_e}{q_{\text{max}}}\right)
$$

where $q_e$ (mg g$^{-1}$) is the amount of metal ion adsorbed at specified equilibrium, $q_{\text{max}}$ (mg g$^{-1}$) is the maximum amount of the metal ion per unit weight of sorbent and $b$ (L mg$^{-1}$) is Langmuir adsorption equilibrium constant related to the energy of adsorption.

Fig. 5(a), (b) shows the Langmuir adsorption isotherm plot of $1/c_e$ versus $1/q_e$ for Cu (II) and Co (II), respectively. The values of Langmuir constants, $q_{\text{max}}$ and $b$, are calculated from the intercept is equal to $1/q_{\text{max}}$ and the slope is equal to $1/bq_{\text{max}}$ through linear regression. Usually, high correlation coefficient, 0.8888 and 0.8623 respectively, indicates that the application of the Langmuir equation supports monolayer formation on the surface of the adsorbent.

The Langmuir isotherm constants for the adsorption of copper and cobalt ions are given on the corresponding figures. The obtained values of $b$ and $q_{\text{max}}$ are 0.25 and 35.12 for Cu (II) and 0.06 and 23.46 for Co (II), which prove that the adsorption process depends on both the concentration and contact time.

Langmuir isotherm can be described by a dimensionless constant known as the separation factor or the equilibrium factor $R_L$, given by [28,33,34]:

$$
R_L = \frac{c_o}{q_{\text{max}}} \left(\frac{1}{bq_{\text{max}}} + \frac{1}{q_{\text{max}}} \left(\frac{c_o}{q_{\text{max}}}\right)\right)
$$

$R_L$ is used to predict the shape of the isotherms, which gives information about the favorability of the adsorption of metal ions on the adsorbent. According to equation (3), the values of the separation factor ($R_L$) for all selected concentrations (50–300 mg L$^{-1}$) of metal ions are found to be less than 1, which indicates the favorable biosorption conditions. Fig. 6 provides the relation between $c_o$ (mg L$^{-1}$) and $R_L$ values which shows that by increasing the concentration the $R_L$ values decrease exponentially in the range 50–300 mg L$^{-1}$. The error bars represent the standard deviation of the experimental data.
of 0 < \( R_L < 1 \). This consequently assures that the adsorption of Cu (II) and Co (II) is still favorable even at higher concentrations.

**Freundlich isotherm**

Freundlich model [35] is an empirical expression used to describe both the heterogeneous surfaces and multilayer sorption. The mathematical form of Freundlich adsorption isotherm is represented by the following equation:

\[
\ln q_e = \ln k_f + \frac{1}{n} \ln c_e
\]

where \( k_f \) and \( n \) are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and adsorbent, respectively. The coefficient \( k_f \) (mg\(^{-1}\cdot\)L\(^{-1}/\)g\(^1/n\)) is a measure of the adsorption capacity; the greater is the surface accessible for adsorbate particles, the greater is the value of \( k_f \) [5]. Plotting \( \ln c_e \) versus \( \ln q_e \) will yield an intercept of \( \ln k_f \) and a slope of \( 1/n \).

Fig. 7(a), (b) shows the fitting plot of Freundlich isotherm for Cu (II) and Co (II), respectively. The constant values obtained from Freundlich adsorption isotherm and its correlation coefficient \( R^2 \) are summarized in the figures. Regression values of 0.992 for Cu (II) and 0.981 for Co (II) are acceptable to describe the adsorption of both heavy metals on fish bones. The constants obtained from \((1/n)\) are 0.689 for Cu (II) and 0.561 for Co (II).
Co (II) indicate favorable and high-affinity adsorption of fish bones for metallic ions.

Finally, from all parameters of both isotherms, it has been found that the equilibrium data are well-fitted to Freundlich isotherm. This assumes that it is applicable for non-ideal adsorption on heterogeneous adsorbent surfaces.

**Adsorption kinetic model**

To evaluate the kinetics of the adsorption of the Cu (II) and Co (II) from wastewater, the pseudo-first-order, and pseudo-second-order kinetic models were tested to interpret the experimental data.

**Pseudo-first order kinetic model**

The pseudo-first-order equation of Lagergren is generally expressed as [36]:

\[
\frac{dq}{dt} = q_e (1 - e^{-k_1t})
\]  

(5)

where \(dq\) is the adsorption capacity at time \(t\), \(q_e\) (mg g\(^{-1}\)) is the equilibrium adsorption capacity, and \(k_1\) (min\(^{-1}\)) is the rate constant of

![Figure 8](image1.png)

**Fig. 8.** The linear pseudo first-order kinetic sorption data for (a) Cu (II) and (b) Co (II) at different concentrations.

![Figure 9](image2.png)

**Fig. 9.** The linear pseudo second-order kinetic sorption data for (a) Cu (II) and (b) Co (II) at different concentrations.

**Table 1**

Pseudo-first order kinetic model parameters for different initial concentrations of Cu (II) and Co (II).

| Initial metal concentration (mg L\(^{-1}\)) | \(K_1\) (min\(^{-1}\)) \times 10^{-3} | \(R^2\) | \(q_e\) (cal.) | \(q_e\) (exp.) |
|------------------------------------------|---------------------------------|--------|----------------|----------------|
| Cu (II) | Co (II) | Cu (II) | Co (II) | Cu (II) | Co (II) | Cu (II) | Co (II) | Cu (II) | Co (II) |
| 50      |        |        |        |        |        |        |        |        |        |        |
| 10      |        |        |        |        |        |        |        |        |        |        |
| 150     |        |        |        |        |        |        |        |        |        |        |
| 200     |        |        |        |        |        |        |        |        |        |        |
| 250     |        |        |        |        |        |        |        |        |        |        |
| 300     |        |        |        |        |        |        |        |        |        |        |
The pseudo-second-order kinetic model

The pseudo-second-order equation is also based on the sorption capacity of the solid phase and is expressed as [37]:

\[
\frac{dq}{dt} = k_2(q_e - q)^2
\]

where \( q \) is the adsorption capacity at time \( t \) and \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) represents the pseudo-second-order rate constant.

After integration and application of the boundary conditions \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \), the integrated form becomes:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

Fig. 8(a), (b) shows the plot of \( \ln(q_e - q_t) \) versus \( t \) for different metal concentrations to obtain the rate constant \( k_1 \) from the slope and \( q_e \) from the intercept.

Table 1 shows the parameters from the pseudo-first-order model for both Cu (II) and Co (II). By comparing the presented results, it is clear that the rate of cobalt adsorption on fish bones is less than that of copper for all concentrations. Therefore, the adsorption of Cu (II) onto fish bones is much higher than that of Co (II). On the other hand, there is an observable difference between calculated adsorption capacities and the experimental values for both metallic ions.

### Conclusions

In the present work, *Lates niloticus* fish bones (Egyptian Nile Perch) that dried and ground to 300 \( \mu m \) size have been used as a sorbent for the removal of the toxic heavy metals (Cu (II) and Co (II)) from wastewater. LIBS and XRF as well-established spectrochemical analytical techniques were applied for the qualitative and quantitative monitoring of the heavy metals removal. The efficiency of fish bones in adsorption of heavy metals is mainly due to its content of the natural hydroxyapatite (HAP) that depend on the ion exchange reaction with calcium ions on the bone surface. The obtained optimum contact time values for the heavy metal ion removal of Cu (II) and Co (II) were 270 and 300 min, respectively. Furthermore, the highest percentage values of adsorbed ions were found at the low initial ion concentrations. Based on correlation coefficients, the best fit model is the Freundlich isotherm that was found to provide the best correlation of Cu (II) and Co (II) adsorption onto fish bones. The kinetic studies revealed that the adsorption process of both ions followed well the pseudo-second-order kinetic model. These experimental studies accentuate the potential of using LIBS and XRF as powerful spectrochemical analytical techniques for environmental analysis, which develop an appropriate technology regarding the removal of heavy metals from contaminated industrial effluents. However, the results obtained are preliminary and further studies are planned in future work on real wastewater samples and highly optimized experimental conditions.

### Conflict of interest

The authors have declared no conflict of interest.

### Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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