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Adsorption of hazardous heavy metal copper(II) from aqueous effluents onto waste material fish (*Dicentrarchus labrax*) scales: optimization, equilibrium, kinetics, thermodynamic, and characterization studies

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ABSTRACT

This study presents the adsorption results of copper(II) ions onto waste material fish (*Dicentrarchus labrax*) scales (FS). For this purpose; the optimization, equilibrium, kinetics, and adsorbent characterization studies were carried out. Optimum initial pH, initial Cu(II) concentration, temperature, and adsorbent concentration were determined to be 3.0, 200 mg L⁻¹, 45°C, and 1.0 g L⁻¹, respectively. The monolayer coverage capacity of FS calculated from Langmuir isotherm model was found as 127.16 mg g⁻¹ with high regression coefficient ($R^2 = 0.9932$) and low error value (ARE = 4.9569) at optimum temperature. The studied adsorption kinetic was in the best agreement with the pseudo-second-order kinetic model; also, both intraparticle and film diffusion were effective in the removal. Furthermore, the adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), energy-dispersive X-ray (EDX) analyses for pre- and post-adsorption.

Keywords: Adsorption; Copper(II); Fish scales; Physicochemical removal; Water and wastewater treatment

1. Introduction

Large quantities of hazardous chemicals especially heavy metals have been released into waters worldwide due to rapid population growth and domestic activities, expanding industrial and agricultural production [1]. Copper(II) is known to be one of the heavy metals and is widely used in many industries including metal cleaning and plating baths, paints and

pigments, fertilizer, paper board, wood pulp, printed board circuit production, and so on [2]. US Environmental Protection Agency established 1.0 mg L⁻¹ of copper as the discharge limit of aqueous effluents. The aqueous effluents including more than 1.0 mg L⁻¹ of copper concentration cause serious environmental problems, and therefore, these aqueous effluents need to be purified. There are many available treatment processes for heavy metals from waters and wastewaters, such as chemical precipitation, coagulation/flocculation, ion exchange, cementation, electrochemical

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operation, membrane separation, reverse osmosis, solvent extraction, electroflotation, biological treatment, and adsorption. Among these processes, adsorption is generally regarded as an effective and economical method for water and wastewater treatment. The use of alternative materials as adsorbents, which, although less efficient, involve lower costs is attracting attention recently. The activated carbon has been till now the most used and effective adsorbent but is expensive to use on a large scale and the idea of using natural adsorbents from waste material rises in this perspective [3]. In this respect, fish scale, which contains numerous valuable organic and inorganic components, mainly collagen and hydroxyapatite, was chosen as adsorbent in this study. Basically, FS are composed of organic and inorganic compounds. Whether the amounts of these compounds vary by the types of FS, they contain approximately 41–84% organic-based protein, collagen, and the remainder is inorganic-based part, hydroxyapatite. Although FS are discarded as waste material from the fish industry, they become alternative low-cost adsorbents in the adsorption of heavy metal from aqueous solutions in the recent years.

2. Material and methods

The adsorption experiments were conducted in 250-mL Erlenmeyer flasks containing 100 mL of Cu(II) solution. The stock solution of Cu(II) was prepared in 1.0 g L^{-1} concentration using $\text{Cu}(\text{NO}_3)_2$ and then diluted to an appropriate amount. For preparing fish scales to adsorption experiments, firstly, mature FS were washed repeatedly with distilled water to remove various impurities from their surface. Then, FS were allowed to dry in shade for 48 h. FS were then kept in a drying oven at 110°C till the moisture evaporated. The prepared FS were used directly as an adsorbent without grinding. 0.1 g of adsorbent, except for the adsorbent concentration experiments, was contacted with 100 mL of heavy metal solution at desired initial Cu(II) ion concentration and pH in an Erlenmeyer flask, and then, the flasks were agitated on a constant temperature and shaking rate for 48 h. Samples (3.0 mL) were taken at predetermined time intervals. Samples were centrifuged at $3,500 \text{ rev min}^{-1}$ for 5.0 min, and the supernatant liquid was analyzed with Chebios UV-vis spectrophotometer. For analyzing unadsorbed Cu(II) ion concentration in the supernatant, 0.2 mL of 1% (w/v) sodium diethyl dithiocarbamate solution and 20 mL of 1.5 N NH_3 solution were added to 1 mL of the supernatant and diluted to 25 mL with distilled water. The absorbance of the yellow-brown colored solution was read at 460 nm.

The experiments were repeated in order to determine the effect of different parameters to the adsorption.

3. Results and discussion

In this study, the effects of initial pH, initial Cu(II) concentration, temperature, and adsorbent concentration on adsorption of Cu(II) ions onto fish scales were investigated in a batch mode and the results were given in Fig. 1.

Isoelectric point of FS was determined experimentally as 7.25 by solid addition method. Surface of FS become negative under the isoelectric point which is resulting to a very high adsorption of Cu(II) ions due to electrostatic interaction (Fig. 1(a)) [4]. The experiments could not be carried out at the initial pH values above 6.0 because insoluble copper hydroxide started precipitating from the solution, making true sorption studies impossible. Consequently, the optimum pH was found to be 3.0 with a maximum removal amount of 77.4 mg g^{-1} .

As seen from Fig. 1(b), for the study of the effect of temperature on Cu(II) ions adsorption onto fish scales, experiments were carried out at 25, 35, 45, 60, and 70°C . It was noticed that Cu(II) ions adsorption increased with temperature up to 45°C and decreased thereafter, so, the decrease in the adsorption at higher temperature suggested decrease in surface activity [5].

According to Fig. 1(c), the adsorption of Cu(II) ions increased with increasing the initial Cu(II) concentration up to 150 mg L^{-1} and then did not change with further increase initial Cu(II) concentration; the adsorption percentage decreased with increase in initial Cu(II) concentration. The increase in Cu(II) adsorption might be attributed to an increase in the driving force of concentration gradient with the increase in the initial concentration. However, the decrease in the adsorption percentage is probably due to the saturation of the active binding sites on the fish scales [6].

As seen from Fig. 1(d), Cu(II) adsorption decreased with increasing the adsorbent concentration. The decrease in the adsorption capacity with increasing adsorbent concentration may be due to the particle interaction, such as aggregation that would lead to a decrease in total surface area of the adsorbent and an increase in the diffusional path length [7].

Consequently; optimum initial pH, initial metal ion concentration, temperature and adsorbent concentration for Cu(II) adsorption on FS were determined to be 3.0, 200 mg L^{-1} , 45°C and 1.0 g L^{-1} , respectively.

The Langmuir ($(1/q_e) = (1/Q^0 b C_e) + (1/Q^0)$) and Freundlich ($\ln(q_e) = \ln(K_F) \cdot (1/n) \ln(C_e)$) isotherm models were applied to the experimental equilibrium

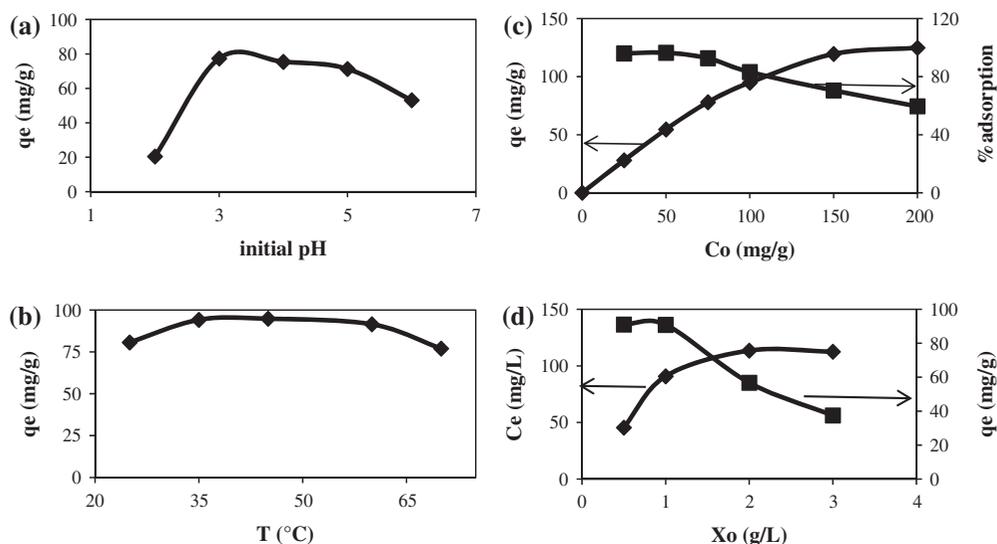


Fig. 1. Effects of environmental conditions on Cu(II) ions adsorption onto fish scales.

data and the isotherm constants with regression coefficients and error values ($ARE = (100/P) \sum [(q_{e,cal} - q_{e,exp})/q_{e,exp}]$) were presented in Table 1. As can be seen from Table 1, the equilibrium data best fitted to Langmuir isotherm model with higher regression coefficients and lower error values than Freundlich isotherm model.

Many researchers reported the maximum copper adsorption capacities for various adsorbents, and the comparison of FS with the literature is given in Table 2. According to the comparisons of maximum copper adsorption capacities, fish (*Dicentrarchus labrax*) scales used in the present study showed significant potential for the removal of copper ions from aqueous solution. This could be due to differences on the surface properties of each adsorbent such as functional groups, surface area, pore size, etc.

The pseudo-first-order (PFOKM) ($\log(q_e - q_t) = \log(q_e) - k_1 t/2.303$) and pseudo-second-order (PSOKM) ($(t/q_t) = (1/q_e^2 k_2) + (t/q_e)$) kinetic models were used to describe the kinetic data and also, Weber–Morris intraparticle diffusion model was applied to Cu(II)

adsorption on FS. The model constants with regression coefficients were presented in Table 3. As seen from Table 3, adsorption kinetic was in the best agreement with the pseudo-second-order kinetic model with higher regression coefficients ($R^2 > 0.99$); moreover, it was observed by Weber–Morris model that both intraparticle and film diffusion were effective in the removal.

The adsorbent was characterized by using FTIR (Fourier transform infrared spectroscopy), EDX (energy-dispersive X-ray), and SEM (scanning electron microscope) analyses pre- and post-adsorption. According to Fig. 2, the absorption peaks of FS at 1,646, 1,541, and 1,242 cm^{-1} correspond to the organic components, namely amide I, II, and III bands of collagen, respectively. The amide I peak is associated with the C = O stretching vibrations, the amide II peak represents the N–H bending vibration and the C–N stretching vibrations, the amide III peak is related to C–N stretching. The inorganic content of FS mainly comes from the hydroxyapatite, and the hydroxyapatite peaks correspond to phosphate and carbonate

Table 1
Isotherm model constants with regression coefficients and error values

T (°C)	Langmuir isotherm model				Freundlich isotherm model			
	Q^o (mg g ⁻¹)	b (L mg ⁻¹)	ARE	R^2	K_F (mg/g (L/mg) ^{1/n})	1/n	ARE	R^2
25	79.8594	3.2609	4.8404	0.9911	46.1602	0.1528	12.8361	0.8692
35	111.5325	2.0298	7.3292	0.9931	50.3538	0.2197	10.7375	0.9344
45	127.1617	0.2466	4.9569	0.9932	35.0244	0.3074	14.9509	0.8909
60	109.3135	0.1130	11.9585	0.9905	17.1122	0.4630	6.7659	0.9828
70	99.6015	0.1067	17.1424	0.9915	16.7429	0.4049	23.6599	0.9670

Table 2

The comparison of FS with adsorbents in the literature for Cu(II) adsorption

Adsorbent	Q^o (mg g ⁻¹)	Refs.
<i>S. platensis</i>	67.9	[8]
Palm shell-activated carbon	30.8	[9]
Chitosan beads	52.6	[10]
Potassium hydroxide-activated charcoal	21.2	[11]

Table 3

Kinetic and mass transfer model constants with regression coefficients

$C_{o,exp}$ (mg L ⁻¹)	PFOKM		PSOKM		Weber–Morris		
	k_1 (min ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	R^2	K_i (mg g ⁻¹ min ^{-1/2})	Intercept	R^2
29.1666	0.002646	0.6127	0.0013140	0.9997	0.0353	17.0123	0.9961
56.5000	0.002931	0.8444	0.0004940	0.9997	0.1572	18.0845	0.9912
84.1666	0.003030	0.9775	0.0002245	0.9985	0.0915	32.9865	0.9944
114.0000	0.002256	0.9293	0.0001586	0.9979	0.2767	17.8223	0.9986
169.5000	0.002478	0.9721	0.0001450	0.9973	0.1842	29.9445	0.9967
207.3333	0.002620	0.9771	0.00005617	0.9933	0.3031	4.1061	0.9929

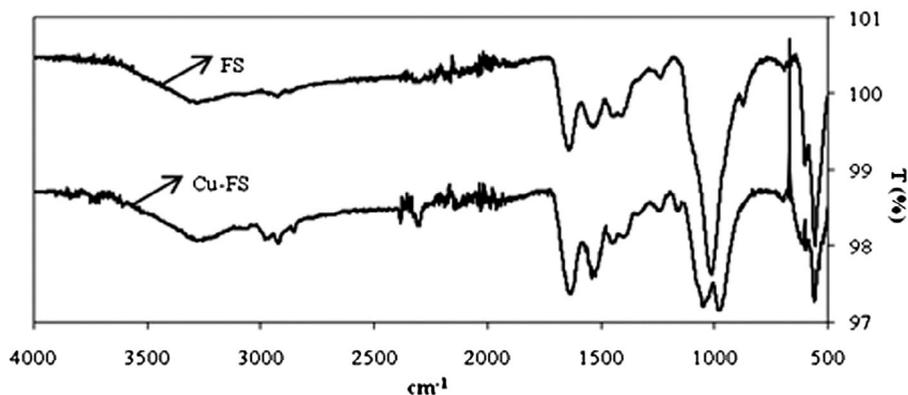


Fig. 2. FTIR spectra of fish scales before (FS) and after (Cu-FS) adsorption.

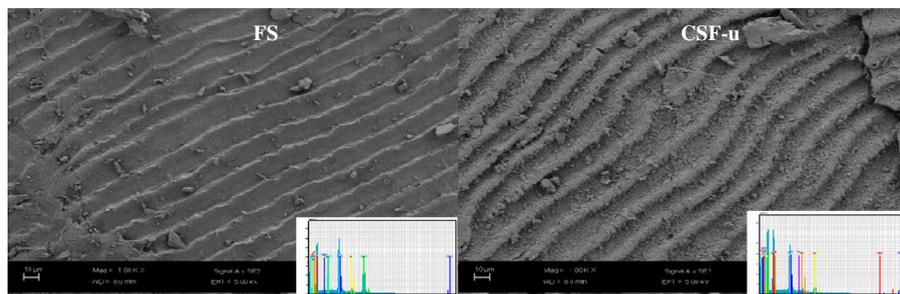


Fig. 3. SEM images of fish scales before (FS) and after (Cu-FS) adsorption.

groups [12]. In this regard, the three sharp peaks between 700 and 520 cm^{-1} correspond to the triple bending vibrations of phosphate in FS, and also the one peak at 1,043 represents the phosphate groups in FS. Besides, the bands at 1,452 and 1,420 cm^{-1} are derived from carbonate groups. Moreover, FTIR analysis showed that adsorption of Cu(II) onto FS occurred by ion exchange (shifted peaks) and chemisorption (new peaks) between amide, phosphate and carbonate groups of FS, and Cu(II) ions. Furthermore, the percentage by mass of Cu(II) was determined as 23.62% after adsorption by EDX analysis; and also, a rougher surface was observed by SEM analysis after adsorption (Fig. 3). These findings confirmed the binding of the Cu(II) ions to FS.

Consequently, fish (*D. labrax*) scales, low-cost and environment-friendly adsorbent could be considered as favorable adsorbent for the removal of Cu(II) from waters and wastewaters.

Nomenclature

b	— a constant related to the affinity of the binding sites (L mg^{-1})
C_{ad}	— adsorbed Cu(II) concentration at equilibrium (mg L^{-1})
C_e	— unadsorbed Cu(II) concentration at equilibrium (mg L^{-1})
C_o	— initial Cu(II) concentration (mg L^{-1})
K_F	— Freundlich constant indicating adsorption capacity ($(\text{mg/g})/(\text{L/mg})^{1/n}$)
K_i	— intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$)
k_1	— pseudo-first-order kinetic rate constant (min^{-1})
k_2	— pseudo-second-order kinetic rate constant ($\text{g mg}^{-1} \text{min}^{-1}$)
T	— temperature ($^{\circ}\text{C}$)
q_e	— adsorbed amount per unit mass of adsorbent (mg g^{-1})
$q_{e,\text{cal}}$	— calculated adsorbed amount per unit mass of adsorbent (mg g^{-1})
$q_{e,\text{exp}}$	— experimental adsorbed amount per unit mass of adsorbent (mg g^{-1})
q_t	— adsorbed amount per unit mass of adsorbent at any time (mg g^{-1})
Q°	— maximum monolayer coverage capacity of adsorbent (mg g^{-1})
X_o	— adsorbent concentration (g L^{-1})
$1/n$	— Freundlich constant indicating adsorption intensity

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