

COPPER ADSORPTION IN WASTE WATERS BY NOVEL ADSORBENTS POWDERED COMMON BLUE MUSSEL SHELL AND DRIED FUNGUS IN COMPARISON TO ACTIVATED CARBON

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ABSTRACT

The adsorption of Cu(II) metal ions from aqueous solutions by the adsorbents commercial activated carbon, dried fungal biomass (*Rhizopus arrhizus*) and powdered waste blue mussel shells (common mussel; *Mytilus edulis*) were compared under the same experimental conditions. Contact time (1-24 h), initial Cu(II) concentration (8.68 to 143 mg/L) and temperature (20, 30, 40 °C) were examined as the parameters of batch adsorption. The Cu(II) uptake capacities of active carbon, dried fungus and powdered waste blue mussel shells were 169.1, 169.6 and 196.4 mg/g, respectively. The maximum copper (II) removal was achieved with the powdered blue mussel shell as 100% at 20 °C. Langmuir and Freundlich adsorption models were used to describe the equilibrium isotherms and the isotherm constants were calculated for the three adsorbents. Kinetic properties were determined by pseudo-first-order and pseudo-second-order models. The results showed that the powdered blue mussel shell may be utilized as an efficient and low-cost adsorbent for the removal of Cu(II) ions from industrial effluents.

Keywords: adsorption models, activated carbon, copper, fungi, waste blue mussel shell

1. Introduction

The rapid development in industry is the major source of heavy metal contamination in the environment such as the effluents and wastes of the mining, smelting, surface finishing, electroplating, electrolysis, electric appliances and electric boards/circuits manufacturing industries as well as agricultural activities involving fertilizers and pesticides (Wang and Chen, 2009). Heavy metals including copper are non-biodegradable, and are classified as hazardous waste material with extensively studied detrimental health effects (Trivedi R. K., 1995, Dermentzis *et al.*, 2009). Especially, the levels of copper ion above 1.3 mg/L cause copper poisoning and gastrointestinal problems in humans (Ennigrou *et al.*, 2014). The exposure to most of the metals causes severe health problems such as carcinoma, organ damage, reduced growth and development, nervous system impairments and oxidative stress (Lee *et al.*, 2012). Waste streams from industries contaminated with copper may contain up to 500 mg/L copper (Dermentzis *et al.*, 2009), which must be treated before the discharge of the effluents into the environment. Several treatment processes have been suggested for the removal of copper from aqueous waste streams such as chemical precipitation (Fu and Wang, 2011), ion exchange (Cavaco *et al.*, 2007), membrane filtration (Kurniawan *et al.*, 2006), and adsorption (Kalavathy *et al.*, 2005). Among these techniques, adsorption is the most commonly utilized procedure for the treatment of heavy metal contaminated wastewater due to its high efficiency, easy handling, the availability of a variety of adsorbents, and the all over cost effectiveness (Bhattacharya *et al.*, 2006). The most commonly used adsorbent is activated carbon, due to its high metal adsorption capacity (Turan *et al.*, 2011). However, low cost adsorbent alternatives to activated carbon have been a subject of intensive research (Aksu, 2005, Sölener *et al.*, 2008). Biosorption was suggested as an alternative way to remove copper ions from Cu-contaminated wastewaters (Aksu and Işoğlu, 2005), and especially fungal biosorbents were reported as cost-effective biosorbents (Pan *et al.*,

2010). Also to the best of our knowledge direct use of waste clam shells for Cu (II) removal has not been reported in the literature. In this study the Cu(II) adsorption performances of dried fungal biomass of *Rhizopus arrhizus* and powdered waste clam shells were compared as low cost adsorbents to commercial activated carbon.

2. Materials and methods

2.1. Microorganism and growth conditions

The filamentous fungus *Rhizopus arrhizus* (RA) was obtained from the US Department of Agriculture Culture Collection. The microorganism was cultivated in a liquid medium with a composition of 17 g/L malt extract and 5.4 g/L peptone dissolved in deionized water. The initial pH of the medium was adjusted to 6.5 with 1M NaOH. The medium was autoclaved at 121°C for 15 minutes. The fungal cells were inoculated into 250 mL Erlenmeyer flasks containing 100 mL of liquid medium at 30 °C for 10 days of incubation period.

2.2. Preparation of adsorbents

After 10 days of incubation, the fungal biomass was harvested and washed with distilled water, followed by treatment with 1% formaldehyde and drying at 60 °C. The dried biomass was ground and sieved through a 80 µm sieve.

The commercial activated carbon (AC) (Sigma Aldrich, Darco type. 242233) granules were ground in a mortar and sieved through a 80 µm sieve.

Blue mussel (common mussel; *Mytilus edulis*) shell (BM) was obtained from a local sea food processing plant in Izmir, Turkey. They were obtained as washed with pressurized water. The shells were ground and sieved through a 80 µm sieve.

2.3. Adsorption studies

Adsorption studies were done by a batch technique in 250 mL Erlenmeyer flasks containing 200 mL of Cu(II) solutions of known initial concentrations. The stock solution of Cu(II) was prepared by the dissolution of CuSO₄ (Merck) to a final concentration of 1 g/L. Appropriate concentrations were prepared by the dilution of the stock solution. The flasks were continuously shaken in a constant temperature bath shaker at 100-rpm for a series of contact times ranging from 1 to 24 hours. Aliquots of 2 mL were taken at the appropriate contact times to determine the Cu(II) concentrations. Three parallel series of 0.1 g of each of the adsorbents AC, RA, and BM were added to the 200 mL of Cu(II) (0.5 g adsorbent/L adsorbate solution). The initial concentrations of a series of Cu(II) solutions were 8.68, 15.46, 22.51, 28.48, 36.90, 60.46, 76.83 and 142.58 mg/L at 20°C with pH equals 4. The temperature effects were determined with a Cu(II) solution of 36.90 mg/L at 20, 30 and 40°C. Cu(II) solutions with the former concentration range without adsorbent were used as controls. The samples (2 mL) taken at 2 hr intervals were centrifuged at 5000 rpm for 5 min (Hettich EBA12). The Cu(II) concentration in the supernatant was determined by atomic absorption.

2.4. Analytical methods

A Cu(II) concentrations from the adsorption were determined by atomic absorption spectrometry (GBC 932 AA). Measurements were conducted in triplicate and the results were reported as the average. The percentage removal (R%) and uptake capacity (q_m , mg/g) were calculated by Equations 1 and 2, respectively.

$$R\% = ((C_{\text{initial}} - C_{\text{final}})/C_{\text{initial}}) \times 100 \quad (1)$$

$$q_m = (C_{\text{initial}} - C_{\text{final}})V_{\text{solution}}/W_{\text{adsorbent}} \quad (2)$$

where, C_{initial} (mg/L) and C_{final} (mg/L) are the Cu(II) ions initial and residual concentrations, respectively. V_{solution} (L) and $W_{\text{adsorbent}}$ (g) are the solution volume and the dosage of adsorbent, respectively.

2.5. Adsorption isotherms and kinetics

The adsorption data were plotted to fit Langmuir and Freundlich isotherms, and the isotherms parameters were calculated by Equation 3 and 4, respectively. The adsorption kinetics was represented by the pseudo-first order kinetic model given by the Lagergren equation (Eq 5), and pseudo-second order kinetics (Eq 6).

$$\text{Langmuir isotherm} \quad \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (3)$$

$$\text{Freundlich isotherm} \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

In these equations q_e is the amount of Cu(II) adsorbed per unit weight of adsorbent at equilibrium (mg/g), q_m is the maximum Cu(II) uptake per unit mass of adsorbent (mg/g), K_L is the Langmuir constant (L mg/g) related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate, and C_e is the equilibrium concentration of adsorbate (L/mg). K_f is the Freundlich isotherm constant (L g⁻¹) and $1/n$ is the heterogeneity factor. The values of q_m and K_L were calculated from the slope and intercept of the $1/q_e$ versus $1/C_e$ plots. The values of n and K_f were calculated for each of the three adsorbents from the slope and intercept of the $\log q_e$ versus $\log C_e$ plots.

The pseudo-first order and pseudo-second order model equations are given by

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where, q_t and q_e are the amounts of Cu(II) adsorbed (mg g⁻¹) at time t , and at equilibrium, respectively, k_1 is the rate constant of pseudo-first-order equation (min⁻¹). The slope and intercept of the graph of $\log(q_e - q_t)$ versus t corresponds to the value of constants k_1 and q_e respectively. k_2 is the rate constant of pseudo-second-order equation.

3. Results and discussion

3.1. The effect of contact time

The effect of contact time on the Cu(II) removal at pH 4 is given in Fig. 1(a). The maximum metal removal for all of the adsorbents occurred at the maximum contact duration of 24 hours. The metal removal by blue mussel shell reached the maximum value of 98.5% at and above 8 hours.

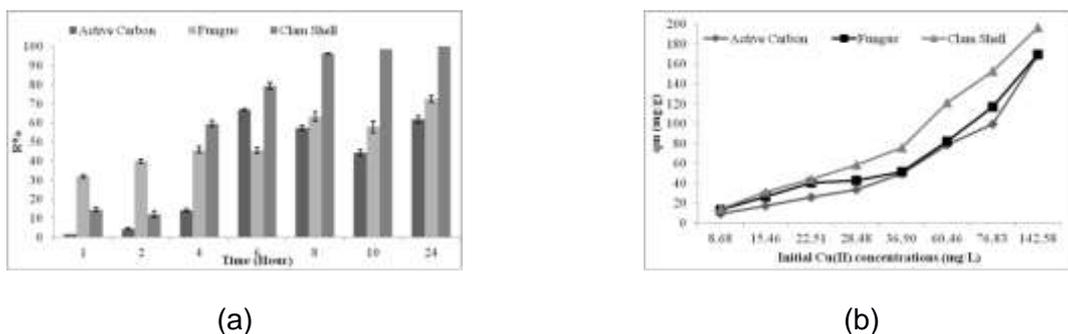


Figure 1: (a) The effect of contact time on Cu(II) removal (R%) ($C_0 = 36.90$ mg/L, $T = 20^\circ\text{C}$)

(b) the effect of initial Cu(II) concentrations on Cu(II) removal capacities (q_m) ($T = 20^\circ\text{C}$; contact time = 24 hours)

The blue mussel shell proved to be the most effective adsorbent, removing the highest amounts of Cu(II) ions as compared to other adsorbents. The effect of initial Cu(II) concentrations from 8.68 to 142.58 mg/L on adsorption capacity (q_m) of active carbon, fungus and blue mussel shell

are shown in Fig. 1(b). Increasing Cu(II) concentrations resulted in an increase of the adsorption capacity. Maximum adsorption capacity was 196.72 mg/g of the blue mussel shell.

Table 1: Comparison the Cu (II) removal (R%) by active carbon, fungus and blue mussel shell (T=20°C, contact time=24 hr).

Initial Cu(II) concentrations (mg/L)	Active carbon R %	Fungus R %	Blue mussel shell R %
8.68	49.9	79.748	77.56
15.46	56.605	87.404	96.733
22.51	56.948	89.762	96.32
28.48	61.859	72.474	100
36.90	67.51	70.988	99.677
60.46	64.994	68.516	98.956
76.83	62.167	78.792	99.317
142.58	59.32	60.778	67.363

The comparison of Cu (II) removal (R%) by active carbon, fungus and blue mussel shell was given in Table 1. Maximum Cu(II) removal by active carbon was observed at 36.90 mg/L initial Cu(II) concentration as 67.51%. The dried fungus *R. arrhizus* removed 89.762% of 22.51 mg/L Cu(II) maximally. The removal of 28.48 mg/L Cu(II) by blue mussel shells was 100%. Powdered blue mussel shell proved to be by far the superior adsorbent.

3.2. The effect of temperature

The adsorption isotherms were determined by measurements carried out at 20, 30, and 40°C The maximum Cu(II) adsorption was obtained at 20°C for all adsorbents as given in Table 2.

Table 2: The effect of temperature on Cu(II) removal (R%) by active carbon, fungus (*R. arrhizus* biomass) and waste blue mussel shell (C₀=36.90 mg/L)

Temperature	20°C R%	30°C R%	40°C R%
Active carbon	67.51	19.891	10.53
Fungus	70.988	70.185	57.51
Blue mussel shell	99.677	79.503	95.898

3.3. Adsorption isotherms and kinetics

Langmuir and Freundlich adsorption models were used to describe the equilibrium isotherms and the isotherm constants were calculated for the three adsorbents, and the values are given in Table 3.

Table 3: Langmuir and Freundlich isotherm parameters for Cu(II) adsorption.

Adsorbent	Langmuir			Freundlich		
	q _m (mg/g)	K _L (L/mg)	R ²	K _f	n	R ²
Active carbon	-----	-----	-----	2.1038	0.8810	0.957
Rhizopus arrhizus	250	0.0377	0.732	15.205	1.6556	0.851
Blue mussel shell	200	1.000	0.994	85.114	5.494	0.256

The correlation coefficients (R²) of Freundlich equation were 0.957 and 0.851 for active carbon and Rhizopus arrhizus, respectively. These values shows that the Freundlich model satisfactorily describes the Cu(II) adsorption on active carbon and Rhizopus arrhizus. For the blue mussel shells, a correlation coefficients of 0.994 shows that the data fits better to Langmuir equation, indicating the Cu(II) adsorption follows the Langmuir adsorption isotherm. The applicability of two

kinetic models, namely, pseudo-first order model (Lagergren equation) and pseudo-second order model was assessed. The results are given in Table 4.

Table 4: Kinetic parameters for the active carbon and *Rhizopus arrhizus* adsorption of Cu(II)

	Pseudo first order model			Pseudo second order model		
	q _{ecal}	k ₁	R ²	q _{ecal}	k ₂	R ²
Active carbon	77.61	1.772x10 ⁻³	0.592	52.63	1.580x10 ⁻⁴	0.456
<i>Rhizopus arrhizus</i>	56.75	2.247x10 ⁻³	0.903	71.43	1.631x10 ⁻⁴	0.770

Cu(II) adsorption of *rhizopus arrhizus* seems to follow the first order kinetics, however, the kinetics of Cu(II) adsorption of active carbon does not fit to neither kinetic model as indicated by the R² values.

4. Conclusions

In this study, the copper ion removal efficiencies of dried fungal biomass and powdered waste common blue mussel shells by adsorption were compared to that of commercial activated carbon, and blue mussel shell was determined to be a far superior adsorbent for Cu(II) ions in aqueous solutions, while the adsorption efficiency of dried *rhizopus arrhizus* was nearly the same as the activated carbon. The maximum Cu(II) uptake efficiency of the blue mussel shell was determined to be as 196.72 mg/g for initial Cu(II) concentration of 142.58 mg/L and at 20°C. The Cu(II) adsorption of the activated carbon and *rhizopus arrhizus* could be described by Freundlich isotherms, while the Cu(II) adsorption of the blue mussel shell followed Langmuir isotherm equation. *Rhizopus arrhizus* adsorption kinetics fitted to the first order Lagergren model.

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