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CONFERENCE PAPER

Removal of Cu (II) from wastewater of metal coating process by borax sludge

Esma Burcu Rona[1], Meral Yildirim[2], Emek Moroydor Derun[*,2]

[1]Istanbul Water and Sewerage Administration (ISKI) 34060 Eyup/Istanbul, TURKEY
[2]Yildiz Technical University Chemical Engineering Department, 34220 Esenler, Istanbul, TURKEY

ABSTRACT

The aim of this study is to determine the adsorption behavior of borax sludge for removal of copper from industrial wastewater. The borax sludge was generated during borax production and used for treatment of wastewater of metal coating process. The parameters of pH, concentration and contact time were investigated in batch experiments to determine the efficiency of adsorption. Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to calculate the reduced amount of Cu (II). The results were applied to various kinetic models and adsorption isotherms. The pseudo second order model was successful to fit the adsorption process in the kinetic study because the regression coefficient values (R^2) were changed between 0.9995 and 0.9978. Langmuir (R^2=0.9985) and Temkin (R^2=0.9985) isotherms models were the best to explain the process.

Keywords: Adsorption, borax sludge, heavy metal, wastewater treatment

1. INTRODUCTION

Heavy metal ions in the exit water of different industries like electroplating, smelting, mining, petroleum and chemical industries cause soil and water related pollution effects to the environment. Even if they found in low amounts in the ecosystem, they cause severe damages [1]. In order to prevent industrial heavy metal contamination, the wastewater must be treated before being discharged to the receiving environment and the heavy metal concentrations contained in the contents must be reduced to the discharge limits specified in the laws and regulations. Heavy metal removal from industrial wastewater at high concentration levels is mainly carried out using purification methods such as chemical precipitation, reduction/oxidation, reverse osmosis, membrane filtration, ion exchange, neutralization, evaporation and adsorption [2-4].

Copper is one of the threatening heavy metal that excessive intake of it leads to serious toxicological consequences such as vomiting, cramps, convulsions and death in living bodies [5]. To remove of copper ions from aqueous solution effectively, precipitation [6], ion exchange [7], electrochemical separation [8] and adsorption methods [9] have been used. Compared to the other methods adsorption has many advantages that needs very low concentrations, easy handling and has continuous processes with the possibility of regeneration [10], while the others need excessive time requirements, high cost and high energy consumption [11].

In literature there are many studies about removal of copper from aqueous solutions among many low cost adsorbents like montmorillonite [12], kaolinite [13], illite [14], palygorskite, sepiolite [15], dolomite [16] and calcite [17].

As studies going on finding low cost adsorbents; using waste materials as adsorbents has also extra advantages on removal of heavy metals. For instance in Turkey 600.000 tons of boron waste causes an important waste problem [18]. As the consumption of boron increase, the waste boron amount will also increase in the future. Thus, using waste boron for waste removal is a unique approach. In published literature, boron waste has been used as an adsorbent in adsorption studies for dye, cadmium (II), zinc (II) [19-20] and chromium [18]. Although there are studies on copper adsorption with different

Corresponding Author: moroydor@yildiz.edu.tr (Emek Moroydor Derun)
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adsorbents, adsorption using boron waste has not been studied yet.

The aim of this work is to research the feasibility of using borax sludge as a low cost adsorbent for copper adsorption. The adsorption behavior of borax sludge was examined with various parameters such as pH, contact time and initial Cu (II) concentration and experimental data has been applied to different kinetic and isotherm models.

2. MATERIALS AND METHOD

2.1. Raw Material Preparation

Borax sludge was taken from Eti Mine Bandırma Boron Works (Balıkesir, Turkey). Before the sludge was used in experimental runs, in order to decrease the moisture content, it was dried at 105 °C for 2 hours in an incubator (Ecocell 111, Germany). The dried adsorbent was milled with an agate mortar and sieved with a vibrating screen- shaker (Fritsch, Germany) so its particle size was decreased below 90 µm. The XRD pattern of the borax sludge (Fig 1) showed the main components were dolomite ($CaMg(CO_3)_2$) and tincalconite ($Na_2B_4O_7{\cdot}5H_2O$) with powder diffraction file (pdf) numbers of 00-005-0622 and 00-008-0049.The BET surface area of borax sludge was 5.54 $m^2\ g^{-1}$ [18].

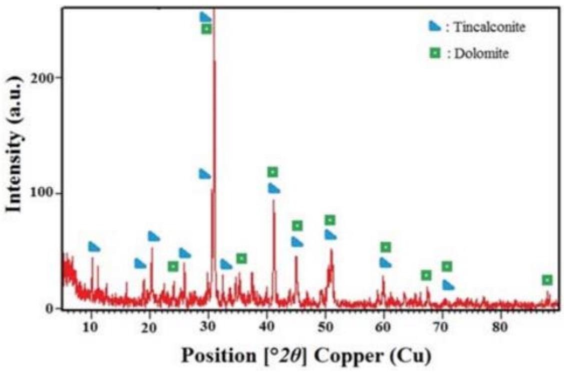

Fig 1. XRD pattern of borax sludge [18]

The wastewater was taken from the inlet water line of a wastewater treatment facility in the Ikitelli Organized Industrial Zone where wastewater from metal coating industries' is collected. The heavy metal content of the wastewater was Cu, Cr, Ni, Al, Cd, Zn, Pb etc. In this study, only removal of Cu was taken into account. Sodium hydroxide (NaOH), which was used to adjust the pH, was supplied Merck Chemicals.

2.1 Adsorption Experiments

The experiments were done with different pH values, initial Cu (II) concentrations and adsorption times at room temperature. Firstly, adsorption experiments were done with various pH values (pH 3, pH 5, pH 7 and pH 9) to determine the effect of pH on the adsorption.0.2 g borax sludge was added at each 100 mL wastewater and stirred with the speed of 200 rpm. After determination the optimum pH value, for the isotherm studies the same amount of borax sludge was added to the same amounts of wastewater with 3 different concentrations (75, 50 and 45 ppm Cu (II) containing) and the experiments were carried out for 6 different contact times (15-120 min). At the end of each adsorption period, the adsorbents were filtered through 110 mm Ø filter paper (Blue ribbon, Chmlab) and the residual Cu (II) concentration was analyzed by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Optima DV 2100, Perkin Elmer, USA).

Amount of Cu (II) removed from the solutions by the borax sludge was calculated from the decrease of metal concentration in the solutions by using the expression in Eq. 1:

$$q = \frac{C_i - C_f}{\mathrm{m}} \times \mathrm{V} \tag{1}$$

where q is the removal capacity of the adsorbent at equilibrium (mg g^{-1}), V is the volume of the suspension (mL), m is the weight of adsorbents (g), C_i and C_f are the initial and final concentrations of Cu (II)(mg L^{-1}), respectively [18].

2.2. Kinetic Models

Parameters from two kinetic models, pseudo first-order (Eq. 2) and pseudo second-order (Eq. 3), were fitted to experimental data to examine the kinetics of copper uptake by the samples. The pseudo first-order model [18] equation is given as follow:

$$\mathrm{q_t} = \mathrm{q_e}\,(1 - \exp(-\mathrm{k_1}\,\mathrm{t})) \tag{2}$$

The pseudo-second-order model [21] equation is given as:

$$\mathrm{q_t} = \frac{\mathrm{k_2\,q_e^2\,t}}{1 + \mathrm{k_2\,q_e t}} \tag{3}$$

where, q_t is the removal capacities (mg g^{-1}) at time t, k_1 is the pseudo first-order model rate constant in min^{-1} and k_2 is the pseudo-second order adsorption rate constant in g mg^{-1} min^{-1}.

2.2 Isothermal Models

The Langmuir isotherm considers that the adsorption takes place on homogenous surfaces with negligible interaction between adsorbed molecules. The linear form of the Langmuir isotherm model [22] is described as (Eq. 4):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

where q_e (mg g^{-1}) is the adsorbed Cu(II) per unit mass of adsorbent, q_{max} is the maximum adsorption capacity of adsorbent (mg g^{-1}), C_e is the equilibrium concentration of Cu(II) (mg L^{-1}) and K_L is the Langmuir constant related to the affinity of the binding sites.

The Temkin isotherm model (Eq. 5 and Eq. 6) that explains the influences of some indirect interactions between adsorbent and adsorbate is represented as;

$$\mathrm{q_e} = \mathrm{B_T} \ln \mathrm{A_T} + \mathrm{B_T} \ln \mathrm{C_e} \tag{5}$$

$$\mathrm{B_T} = \frac{\mathrm{RT}}{\mathrm{b_T}} \tag{6}$$

where B_T is the Temkin constant related to the heat of adsorption(Kj mol^{-1}), A_T is the equilibrium binding constant, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and b_T is the Temkin isotherm constant [18].

Harkins-Jura isotherm model explains the possibility of multilayer adsorption with the existence of heterogeneous pore distribution. The Harkins-Jura isotherm model can be expressed by Eq. (7) where B_H and A_H are the Harkins-Jura constants [23].

$$q_e = \sqrt{\frac{A_H}{\log C_e + B_H}} \qquad (7)$$

3. RESULTS & DISCUSSION

The adsorption experiments were carried out with different pH values to decide the best pH value for the further experiments. Because pH directly affects the surface charge of the adsorbent. Results showed that the adsorption of Cu (II) ions onto borax sludge is pH dependent and suggested that highest removal efficiency was observed at pH range of 7-9 (Fig 2). Depend on the obtained results, pH=7 was chosen for all the experiments.

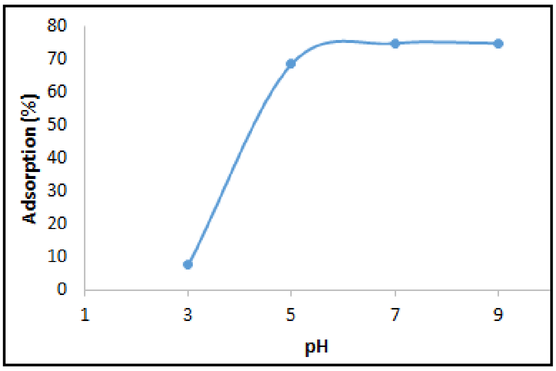

Fig 2. Adsorption percentage of Cu (II) ions for different pH values

Fig 3 shows the effects of contact time the adsorption of Cu (II) ions. As seen in the Fig 3, Cu (II) ions were adsorbed onto the borax sludge very rapidly within the first 15 min and the equilibrium was attained after 30 min.

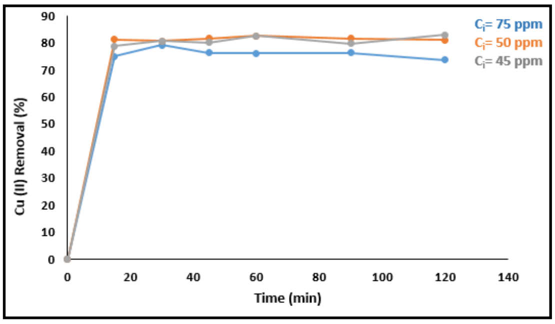

Fig 3. Removal percentage of Cu (II) ions for different contact times

Langmuir, Temkin and Harkins-Jura models were employed to describe the experimental data and results are revealed in Table 1. It is apparent from Table 1 that all the isotherms provide a good fit to the experimental results. The applicability of the all the applied isotherm models can be reasoned by the complex adsorption process between Cu (II) and borax sludge which can involve more than one mechanism.

Table 1. Isotherm parameters for Cu (II) removal by borax sludge

Isotherms	Parameters	R^2
Langmuir	K_L= 0.0337 q_{max}= 90.90 mg/g R_L= 0.2829	0.9985
Temkin	B_T= 24.528 A_T= 0.1131 b_T= 101.01	0.9985
Harkins-Jura	B_H= 1.3621 A_H= 172.414	0.9817

The essential characteristics of Langmuir isotherm can be explained by the constant separation factor (R_L) which was calculated according to Eq. (8).

$$R_L = \frac{1}{1+K_L C_i} \qquad (8)$$

In the present study, R_L value was found as 0.2829 which was between $0<R_L<1$ and showed that adsorption process was favourable and borax sludge exhibited a good potential for Cu (II) removal. Also, the maximum Cu (II) adsorption capacity of borax sludge was found as 90.90 mg g^{-1}.

In Table 2, the comparison of maximum adsorption capacity (q_{max}) of Cu (II) for Langmuir model of previous studies in literature is given. As seen in Table 2, various low cost adsorbents and their activated forms were used for Cu (II) removal. When the borax sludge was compared with other adsorbents given in Table 2, it clearly seen that satisfying q_{max} value was obtained for borax sludge which was an industrial waste and not processed by an activation method.

Table 2. Previous studies using different adsorbents for removal of Cu (II)

Adsorbent	q_{max} (mg g^{-1})	References
CH_3COONa-intercalated halloysite	52.3	[24]
Chitosan-clay nanocomposites	181.5	[25]
Cationic surfactant modified bentonite	50.76	[26]
Sugarcane Bagasse (Citric Acid activated)	96.90	[27]
Bentonite	33.44	[28]
Acid activated bentonite	38.31	[28]
Borax sludge	90.90	present study

Different kinetic models were applied to the experimental data and the highest regression coefficients (R^2) were obtained for pseudo second order kinetics which indicated the applicability of this kinetic model. Depend on the pseudo-second order kinetic equation, this adsorption is mainly controlled by the surface [18]. Fig 4 shows the pseudo second order plots for the experimental sets in which different initial Cu (II) concentrations were used. The pseudo-second-order rate constant (k_2), the calculated and experimental q_e values are given in Table 3. It was observed that the rate constant showed irregular change by increasing initial concentration. Also, the calculated and experimental qe values were showed similarity which indicated that the pseudo-second-order model can be applied to the Cu (II) removal by borax sludge [29].

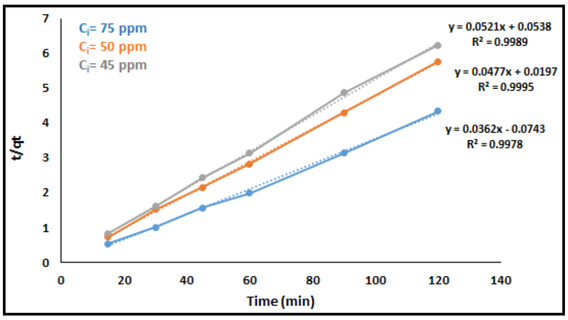

Fig 4. Adsorption kinetics of Cu (II) onto borax sludge for pseudo second-order kinetic model

Table 3. The second-order rate constants and q_e values

C_i (ppm)	q_e (mg g^{-1}) (experimental)	q_e (mg g^{-1}) (calculated)	k_2
75	30.14	27.62	0.01764
50	21.19	20.96	0.1155
45	19.14	19.19	0.0505

4. CONCLUSIONS

An industrial waste of borax sludge was used to remove Cu (II) ions from wastewater of metal coating process. Various experimental parameters such as pH, contact time and initial metal concentration were studied at a constant temperature of 25 °C. According to studies, the optimum pH was determined as 7. Many adsorption isotherms and kinetic models were applied to the obtained results. Experimental results are in good agreement with Langmuir, Temkin, and Harkins-Jura adsorption isotherm models. The adsorption of Cu (II) was fitted to pseudo-second order equation with good correlation. In conclusion, borax sludge can be an effective adsorbent for wastewater treatment with the Cu (II) adsorption capacity of 90.90 mg g-1.

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