Artificial neural network model for removal of copper ions from pollutant solutions by olives seeds powder

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Abstract. Artificial Neural Network (ANNs) model was done to develop and to predict the Pollutant Removal Efficiency (PRE) of Copper Cu (II) ions from polluted solution by olives seeds powder. Five model variables as Adsorbent dosage, the initial concentration, initial pH, agitation speed, and contact time was studied to optimize the conditions for maximum removal efficiency of Cu (II) ions. Perceptron Multilayer Networks (PMN), with a back-propagation algorithm where the sigmoid axon transforms function for input and output layers is adopted. The PMN model is systematically trained with 425 data points and is validated with data points from the database. The optimum values of learning parameters that are giving encouraging and satisfactory with a correlation coefficient of about 0.983 at training and 0.987 at verification for variables used in this study. The model results showed that the major important parameter influencing on the removal efficiency is the initial copper concentration 37.3%, olive seeds dosage 23.53%, the agitation speed 21%, the pH 10.38%, and smallest influence has the contact time 7.77%. The results showed a good agreement between the ANN model result and the experimental result.

Keywords: Artificial neural networks, Adsorption, Modeling, Olive seeds, Cu (II) removal.

1. Introduction
Pollution of industrial wastes, which use heavy metals and their applications, is a problem of the modern environment. In a short time, minerals became a source from causes of environmental pollution that threaten human, animal health and the surrounding environment. Heavy materials are classified into three types: Toxic metals such as Hg, Cr, Pb, Zn, Cu, Precious metals such as Pd, Pt, Ag, and Radiation emitters such as Ra, Am and others [1, 2, and 3]. Heavy materials usually present in the environment from different activities like Industry, Agriculture, and Waste disposal. [4]
Recommended the maximum permissible concentration of copper Cu (II) in drinking water as (1 mg L\(^{-1}\)) while Environmental Protection Agency (EPA) recommended as (1.3 mg L\(^{-1}\))\(^{[5]}\). Heavy metal can be removed from the aqueous solution through Sorption, precipitation and Degradation. Adsorption is the low cost and powerful technique for contaminant removal from solution with using absorption and ion exchange to the reactive media. The biomass has the ability to capture minerals and reduce the quantity of heavy metal ions concentration in the liquid from p.p.m to p.p.t. It can hold the dissolved metal ions from complex and extended solutions quickly and effectively. Recent literature highlighted the extensive use of activated carbon in the field of wastewater treatment.\(^{[6,7,8]}\) studied ion exchange characteristics of Cu\(^{2+}\) on the natural zeolite at 2 and 22 °C to treat heavy-metal contaminated water. Because of the complexity mechanism of biosorption and the difficulty to model using mathematical modeling due to interaction of more number of sorption procedure variables, Besides, the result relations are extremely nonlinear \(^{[9]}\). Therefore, in recent years, ANN has become a popular choice among engineers and scientists as one of the powerful tools for predicting contamination and simulates operation condition of different effluents in drinking water, wastewater and aquifers. Many authors have described the structure and operation of Artificial Neural Networks ANN. A single-layer ANN model was developed by \(^{[10]}\) to forecast the removal efficiency of Cd (II) ions from aqueous solution using agricultural waste. The ANN model was designed by combining Back Propagation (BP) with principal component analysis. The researcher demonstrates the successful removal of Cadmium ions from the waste water without requiring a big amount of precise experimental data.\(^{[11]}\) Was established a three-layer ANN model to forecast the removal efficiency of Copper ions from simulated wastewater by fungal biomass. The results indicated that the primary pH of the simulated wastewater with a comparative importance of 22.1% seemed to be the maximum important factor in the Cu (II) removal, shadowed by dosage, agitation speed, temperature, time, and concentration.

Biomaterials such as agricultural waste which could be adsorbed heavy metals is called Biomass. Recently, they are widely used for heavy metal removal from aqueous media such as olive seeds biomass due to their large available quantities, low cost and good performance \(^{[12]}\). Olive seeds or pits are an important byproduct generated in the olive oil industries. It is accounts for a large percentage of the fruits’ weight (20-28%) and is equivalent to a hard wood. It is consists of a thick, highly lignified wall (29-32%), rich in cellulose (27-28%), hemicellulose (24-35%) , poor in salts (0.6-0.8%), carbohydrates account for 52% of the pit weight \(^{[13]}\).

Accordingly, the objectives of this study is characterization the efficiency of copper removal from simulated wastewater using olive seeds biomass by applies and verifies the use of artificial neural network in contrast with batch investigational results by experimental work and clarify the influences of different working conditions.

2. INGREDIENTS AND METHODS

2.1. Biosorbent preparation.

The olive seeds were poised from kitchen unused. This material first washed with distilled water to remove dust and soluble impurities. Thereafter, it was dried up in an oven at 100 °C for 24 hours, crushed well into a fine powder, sieved with average particle size of approximately a 1 mm and stored in plastic bags for further use.

2.2. Reagents and experimental procedure.

Aqueous solutions of copper were selected as a illustrative of heavy metal pollutants in the water. CuSO\(_4\)·5H\(_2\)O solution was prepared as required concentration by dissolving of CuSO\(_4\)·5H\(_2\)O (manufactured by Germany) in double-distilled water in a 1000 mL volumetric flask. The pH of the solution was attuned by adding 0.1 M HNO\(_3\) or 0.1 M NaOH as obligatory solutions by using pH electrode.
2.3. Batch tests

Batch study based on 85 experimental sets was obtained in a laboratory. Batch tests are usually faster, cheaper, and simpler to set up than columns, allow rapid comparison of varied parameters on the experimental results, and specify the best conditions [14]. Batch experiments carried out as a function of biomass dosage, contact time, copper concentration, initial pH of the solution and agitation speed. A 250 mL conical flask in a temperature-controlled an orbital shaker (Edmund Buhler SM25, German) was used. At the end of predetermined time the content was filtered. The initial concentrations of the copper, and the corresponding concentrations after fixed the time periods, were measured by an atomic adsorption spectrophotometer (AAS) (Norwalk, Connecticut (USA). From the best experimental results, the efficiency of adsorption (Re, %) was calculated as follows:

\[ Re\% = \frac{Co - Ce}{Co} \]  

Where Co = the initial concentrations of the copper in the solution (mg/l), and  
Ce = the equilibrium Cu (II) concentrations of the copper in the solution (mg/l)

3. Results and Discussion

3.1. Optimize the Best Conditions

Sorption experiments led to the standardization of the optimum conditions as biomass dosage 0.9 g, Cu (II) concentration 45 mg/l for volume 50 ml, agitation speed 250 rpm at pH 6.5 and a contact time of 70 min, for maximum Cu (II) removal approximately (90 %). The results indicate that the olive seeds have considerable potential to be used as biosorbent for metal removal from waste water.

3.2. Evolving and Optimization of the ANN Model

The ANN model of MATLAB mathematical software was used to develop a design formula to calculate the adsorption efficiency Re% by using Multi-Layer Perceptions (MLP). The model has five inputs parameters representing the adsorbent dosage, initial concentration of Cu (II) ions, initial pH, agitation speed, and contact time. All the statistics parameters and their values are listed in Table 1.

| parameter                  | Range     | Mean and S.D       |
|----------------------------|-----------|--------------------|
| Initial con. (mg/l)        | 0 - 50    | 27.231 ± 13.367    |
| PH                         | 3-7       | 5 ± 1              |
| Contact time (min)         | 0 - 120   | 59.107 ± 34.84     |
| Adsorbent dose (gm)        | 0 - 1     | 0.484 ± 0.319      |
| Agitation speed (rpm)      | 0 - 250   | 140 ± 70,661       |

The data collected from 85 sets experimental data are divided in two groups. The first group consist of 385 data are used for the training of the neural network and the other data group consist of 40 data are used for the testing obtained data of the neural network. The multi-layer feed forward back-propagation technique is implemented to develop and train the neural network and the sigmoid transform function is adopted. The basic ANN architecture consists of five types of layers input, four nodes in hidden and one output layer. The selection of the number of neuron in a hidden layer is an important decision [15]. The structure of the optimal ANN model is shown in Fig.1.
3.3. Impact of Contact Time and Initial pH

The pH is the most important factor affecting on the equilibrium and the sorption process. Only the range (3–7) of pH values were carried in experimental adsorption tests because the precipitation of copper is occurred at pH greater than 7. Fig.3 shown the removal efficiency (Re%) increases with an increase in pH value. This occurs due to decrease in competition between proton and metal species on the surface sites and the decrease in the positive surface charge, which leads to a lower columbia repulsion of the sorbing metal [16]. On the other hand, the removal efficiency became bigger with increased time at the beginning and

The (Re%) is less percentage increasing with increased time up to 70 min. This mean that the contact time of 70 min was adequate to realize equilibrium and the sorption did not variation significantly with
additional increase in contact time. This occurs because of the occurrence of big number of adsorbent places existing for the adsorption [17, 18].

![Graph showing variation of removal efficiency with time and pH](image)

**Fig. 3.** Variation of the removal efficiency with time and pH at Dose = 0.9, Co = 50 mg/L, AS = 250 rpm and T = 20 °C

### 3.4. Impact of Olive Seeds Dosage

Fig. 4 shows the ANN model predictions as a function of adsorbent dosage. The results of the ANN showed little change in removal efficiency value with dose change from 0.5 to 0.9 gm. For all range of dosage used, the percentage of Cu (II) particles expelled likewise expanded from 16 to 70 % for expanded contact time. This can be ascribed to the way that the quantity of adsorption locales or surface zone increments with the heaviness of adsorbent, bringing about a higher percent metal expulsion at a high dose [19].
Fig. 4. Variation of the removal efficiency with time and dose at pH = 6.5, Co = 50 mg/L, AS = 250 rpm and T = 20 ºC

3.5. Impact of Initial Copper Concentration

Fig. (5) clarifies that the removal efficiency of Cu (II) increased to 75 % with increasing the initial concentration to 45 mg/L. The larger percentage in removal efficiency value (Re %) occur at the begin time until reach to equilibrium time [20].

Fig.5. Variation of the removal efficiency with time and Co at pH = 6.5, Dose = 0.9 gm, AS = 250 rpm and T = 20 ºC

3.6. Impact of Agitation Speed

Fig. 6 displays that about 70 % of the Cu (II) was removed before shaking (agitation speed = zero). Also, an increase the removal efficiency of Cu (II) as the agitation speed was increased from zero to 250 rpm at reach maximum about 80 %. This can be able to improving the dispersion of particles towards the outside of the responsive media and great contact between particles in the arrangement and restricting locales [21].
Fig. 6. Variation of the removal efficiency with time and AS at pH = 6.5, Co = 50 mg/L, dose = 0.9 gm and T = 20 °C

4. Importance Degree of variables
The method which proposed by [22] and adopted by [23], was conducted to determine the degree of importance of variables. The major important parameter influencing the removal efficiency is the initial Copper concentration 37.3% following by the olive seeds dosage 23.53%. Thereafter follow the agitation speed 21%. The pH has a little effect 10.38%, and smallest influence has the contact time 7.77%. All the result shown in Fig. (7).

Fig. 7. Importance Geometry Factors of Parameters
5. Conclusion

The batch experiments results proved that an Olive seeds as low cost materials has suitable adsorption capacity to about 80% for removal of copper ions from simulated waste water. The best operating conditions were originate to be enough to realize equilibrium as initial pH of 6.5, an adsorbent dosage of 0.9 g/ 50 mL, an initial Cu (II) concentration of 45 mg/L, an agitation speed of 250 rpm and a contact time of 70 min.

Artificial Neural Network model showed a precise and an effective prediction of the investigational data by experimental work with a high correlation coefficient of greater than 0.98 for five operating variables. The initial concentration of the copper with a comparative importance of 37.3% seemed to be the greatest important parameter in the removal efficiency. This substance can be used as a permeable reactive barrier in the remediation of contaminated groundwater and may be useful in designing treatment plants for metal removal from wastewaters.

Acknowledgments

The authors would like to thank Mustansiriyah University, (www.uomustansiriyah.edu.iq) Baghdad-Iraq.

6. Reference

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