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Research Article

An Investigation of Cu^{2+} Removal by Using Different Types of Modified Starch

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Abstract

In this study, Cu^{2+} removal from the aqueous solution using different types of starch was examined by the batch method. The potato starch and corn starch which were modified in different ways were examined to determine the percent removal values of Cu^{2+} by various trials. The optimum conditions of the experimental procedure were investigated from 10 to 50 mg L^{-1} as beginning concentration, 4 to 6 as pH, with 5-30 min. as shaking time. 0.15 g modified starch was added 50 mL study solution at room temperature during all different studies. The experimental results offered that thanks to the starch modification with water as an adsorbent, the percent removal values of potato starch 89.58% and corn starch 74.07% were found. Concentration, shaking time, and pH were detected with the optimum values as 20 mg L^{-1}, 20 min, and 6 respectively. Moreover, the obtained results were also evaluated according to the Freundlich adsorption isotherm and observed to be compatible with this curve.

Keywords: Corn starch, Potato starch, Freundlich adsorption isotherm, Removal, Copper.

Modifie Edilmiş Farklı Nişasta Türleri Kullanılarak Cu^{2+} Geri Kazanımının İncelenmesi

Özet

Bu çalışmada, farklı nişasta türleri kullanılarak sulu çözeltiden Cu^{2+} katyonlarının geri kazanımı batch yöntemi ile araştırıldı. Farklı prosedürlerle modifiye edilmiş patates nişastası ve mısır nişastası kullanılarak çeşitli denemeler yapıldı ve Cu^{2+}'nin geri kazanım yüzdeleri incelendi. Deneysel çalışmaların optimum parametrelerini bulabilmek amacıyla; başlangıç konsantrasyonu olarak 10 ila 50 mg L^{-1}, pH olarak 4 ila 6 değerleri, çalkalama süresi olarak 5-30 dakika kullanılarak çalışmalar yapıldı. 0,15 g modifiye nişasta, 50 mL çalışma çözeltisine oda sıcaklığında ilave edildi. Nişasta modifikasyonunun su ile yapıldığı deneysel sonuçlara göre, adsorban olarak modifie edilmiş patates nişastası kullanıldığında %89,58, mısır nişastası kullanıldığında %74,07 olarak geri kazanım değerleri bulundu. Konsantrasyon, çalkalama süresi ve pH sırasıyla 20 mg L^{-1}, 20 dakika ve 6 olarak optimum değerler tespit edildi. Ayrıca elde edilen sonuçlar, Freundlich adsorpsiyon izoterm eğrisine göre de değerlendirildi ve bu eğri ile uyumlu olduğu gözlemlendi.

Anahtar Kelimeler: Mısır nişastası, Patates nişastası, Freundlich adsorpsiyon izotermi, Geri kazanım, Bakır.

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1. Introduction

Heavy metals pose a threat to the natural environment and living life due to their toxic effects (Adeli et al., 2017; Seiler et al., 1998). The main reason for this is the adverse effects of heavy metals used in different industries on existing water resources (Singh et al., 2020). In this regard, mercury, lead, cadmium, chrome, zinc, cobalt, and copper are among the most used heavy metals. To reduce the maximum amount of risk-causing heavy metal concentrations, which can be found in wastewater, drinking water, and other water resources below the level permissible for agriculture is an obligation (Bereket et al. 1997; Gonzalez-Davila et al., 1990; Kocaoba, 2007) However, the World Health Organization data report that half of the human population is still at risk of being infected due to waterborne diseases (World Health Organization [WHO], 2018).

Although copper (Cu), which is one of the frequently used heavy metals, is one of the basic micronutrients needed for different living species (plants, animals, and humans), its excessive presence can cause biological disturbances. Besides diseases such as headaches, abdominal pain, nausea, etc., it can also cause fatal diseases, such as liver and renal failure (Gaetke and Chow, 2003). Due to these and similar harmful effects, the removal of heavy metals is gaining importance every day. Adsorption, ion exchangers, flotation, extraction, and electrolytic methods are included among the conventional methods used in practice (Dong et al., 2010; Kobya, 2004; Nassar et al., 2004). The adsorption process is one of the most frequently used among the mentioned methods due to its advantages because it has advantages such as being easily applicable to different adsorbents, being a cheap and efficient method (Schmuhl et al., 2001). Therefore, various studies that aim to reduce costs are increasing and gaining importance with each passing day (Khalil and Aly, 2001; Yin et al., 2008). Starch, which is one of the substances that can be recommended for this purpose, is defined as a polymeric hydrocarbon, and has a wide usage area in the industrial field (Carmona-Garcia et al., 2009). Fig. 1 presents the SEM images of natural corn starch granules, and Fig. 2 presents the SEM images of natural potato starch granules (Sujka and Jamroz, 2013). Furthermore, in the literature, there are studies in which the modified cellulose and modified starch compounds were used for the adsorption of different metal ions from the aqueous solution (Dong et al., 2009; Zhang et al., 2006; Xie et al., 2009).

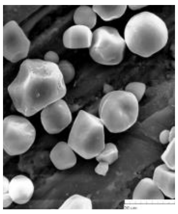

Figure1. *SEM micrographs of natural corn starch granules.*

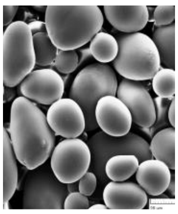

Figure 2. *SEM micrographs of natural potato starch granules.*

For example, the adsorption of Pb^{2+} and Cu^{2+} was examined using adsorbents o btained by a cross-linked starch modification study (Zhang and Chen, 2002). Heavy metal adsorption from the aqueous solution with carboxymethyl cross-linked adsorbents by using corn starch was evaluated (Kim and Lim, 1999). In another study, Cu^{2+} adsorption capacity was tried to be found using modified starch (Li et al., 2004). Furthermore, by using modified starch the removal of some heavy metals from wastewater was applied successfully (Kim and Lim, 1999; Kweon et al., 2001).

The removal of Cu^{2+} from the aqueous solution by using potato starch and corn starch, which are cheap adsorbents, wereexamined in offered study. The adsorption capacity of both starches obtained modified form with water and NaOH were compared, and the collected data were evaluated in terms of the Freundlich adsorption isotherm curve.

2. Material and Method

2.1. Materials and Reagents

Corn and potato starch used during the study of Cu^{2+} adsorption from the aqueous solution were purchased from Sigma-Aldrich. Solutions of 0.1 M NaOH, 0.1 M HCl, and 100 mgL^{-1} Cu^{2+} (from $CuSO_4.5H_2O$) with analytical purity used in experimental studies were obtained from Merck, Germany. The water used during all experimental studies was supplied from the Milli-Q (Millipore, USA) purification system.

2.2. Preparation of Adsorbents

The starch solution was prepared as an aqueous suspension from corn starch and potato starch at a concentration of 30% (w/v) separately. It was heated by stirring at 75 ± 2 °C for 20 minutes. Then, it was centrifuged at 4000 rpm for 15 minutes. The solution portion was separated by decantation, and the residue was dried in the oven at 130 ± 2 °C for 55 minutes. The same process was repeated using 0.1 M NaOH solution instead of water.

2.3. The Adsorption of Cu^{2+}

Adsorption experiments were carried out using the batch method. To this end, Cu^{2+} solutions with initial concentrations of 10, 20, 30, 40, and 50 mgL^{-1} were prepared. 50 mL of Cu^{2+} solution was added to 0.15 g dried modified starch, the working pH value was determined to be 5, and it was shaken on a magnetic shaker at 25 °C for 20 minutes using a platform shaker. The samples taken at the end of the shaking process were passed through a 0.45 µm microporous membrane filter. Then, quantification was performed using the atomic absorption spectrophotometry (Varian Spect AA 220) device.

The amount of Cu^{2+} adsorbed per unit mass (Q_e) was found by using Formula 1.

$$Q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

According to formula 1; C_0 and C_e (mequiv./L) refer to the initial and final Cu^{2+} concentrations. Furthermore, V demonstrates the solution volume (L), and m denotes the amount of adsorbent used (g) (Kocaoba, 2007).

2.4. Adsorption Isotherms of Cu^{2+}

Although many different models have been proposed to explain the adsorption process, the Freundlich model is the most frequently used method in terms of its applicability. In adsorption experiments carried out from water and wastewater, this model is frequently used to explain the adsorption kinetics (Donat et al., 2005; Gupta and Bhattacharyya, 2006; Naseem and Tahir, 2001; Patel et al., 2006). We can calculate the Freundlich equation as in Formula 2 and Formula 3 (Kocaoba, 2007).

$$Q_e = K_f C_e^n \qquad \text{(non-linear form)} \qquad (2)$$

$$\log Q_e = \log K_f + \qquad \text{(linear form)} \qquad (3)$$

In the Formula 2, Q_e indicates the amount of Cu^{2+} absorbed per unit mass (mequiv./g); C_e solute amount of Cu^{2+} in the bulk solution (mequiv./L); K_f is a constant that showing the relative adsorption capability (mequiv./g); n represents the constant which belongs to the intensity of the adsorption. If the value of n is in the range between 0 and 1, it can be decided that the adsorption process is favorable under these operating conditions.

3. Results and Discussion

3.1. Effect of Different Shaking Time on Removal of Cu^{2+}

To determine the effect of different types of starch, 0.15 g potato starch that was modified with water was added as an adsorbent to 50 mL of the solution containing 20 mgL^{-1} Cu^{2+} at room temperature. Samples were taken from the solutions prepared in a series by performing the shaking process in an interval between 5 and 30 minutes, and the amount of Cu^{2+} was determined. The same studies were carried out for corn starch. As can be seen in Fig. 3, not much change is observed in removal value for both potato and corn starch after the 20th minute. Therefore, ongoing studies were carried out for 20 minutes. Furthermore, the percent removal was found to be a maximum of 70.43 for water-modified potato starch and 62.74 for corn starch.

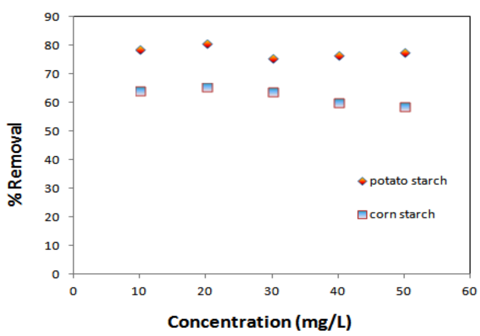

Figure 3. *Effect of shaking time for removal of Cu^{2+}(pH 5, 0.15 g, 20 mgL^{-1}).*

3.2. Effect of Different Modifications on Removal of Cu^{2+}

To determine the effect of different starch modifications, 0.15 g potato starch that was modified with water added as an adsorbent to 50 mL of the solution containing 20 mgL^{-1} Cu^{2+}. After shaking for 20 minutes, quantification was performed, and the percent removal was calculated. The same trials were done by using potato starch modified with NaOH, corn starch modified with water and corn starch modified with NaOH. As shown in Fig. 4 the removal values of potato and corn starches modified with water were found to be 68.27 and 49.71, respectively. The removal values for both types of starch are higher compared to those modified with NaOH.

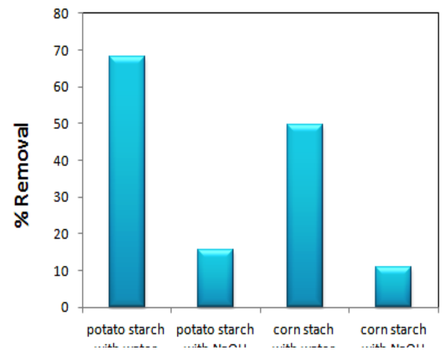

Figure 4. *Effect of modification types to removal of Cu^{2+} (0.15 g, 20 mgL^{-1}, 20 min.).*

3.3. Effect of Different Beginning Concentrations on Removal of Cu^{2+}

The studies were repeated using Cu^{2+} solutions at different concentrations. To this end, 50 ml solutions with different concentrations in the range of 10-50 mgL^{-1} were taken. Again, 0.15 g potato starch modified with water was added, and after shaking for 20 minutes, quantification was performed. The same processes were repeated for corn starch modified with water. The results are presented in Fig. 5. Accordingly, the removal percentages of the solution containing 20 mgL^{-1} Cu^{2+} were found to be 89.58% and 74.07%, respectively, for potato and corn starch.

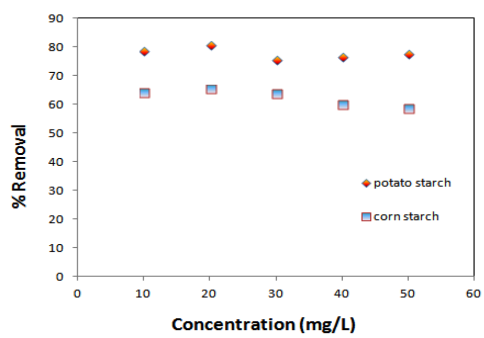

Figure 5. *Effect of different beginig concentration of Cu^{2+}(pH 5, 0.15 g, 20 min.).*

3.4. Effect of Different pH on Removal of Cu^{2+} from the Aqueous Solution

To determine the effect of different pH, 0.15 g potato starch that was modified with water added as an adsorbent to 50 mL of the solution containing 20 mgL^{-1} Cu^{2+} and pH was adjusted 4 by using 0.1 M HCl or 0.1 M NaOH. After shaking for 20 minutes, quantification was performed, and the percent removal was calculateed. The same trials were done in pH 5 and pH 6. After same experiments were repeated with corn starch modified with water as adsorbant. Fig. 6 had showed us the pH 5 results 72.3% and 65.83%, respectively, for potato and corn starch.

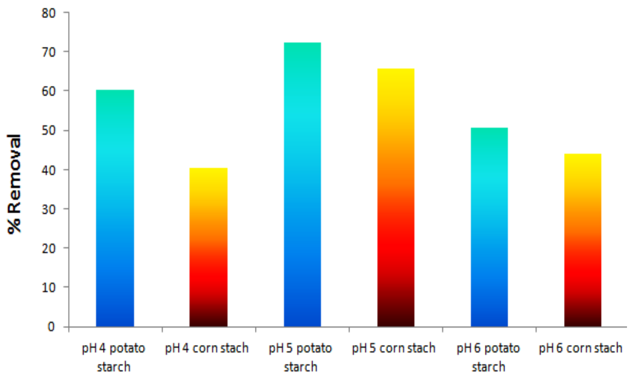

Figure 6. *Effect of different pH for removal (0.15 g, 20 mgL^{-1}, 20 min.).*

3.5. Examination of Adsorption Isotherms

The Freundlich adsorption isotherm gives the surface heterogeneity and the exponential distribution and energy of active species. In the Fig. 7, the values of log Q_e versus log C_e give a straight line following the Freundlich isotherm equation. Both K_f and n values are empirical constants and indicator of the amount of adsorption, the degree of linearity between the solution and concentration.

The specified Cu^{2+} adsorption process was evaluated in terms of the Freundlich adsorption isotherm. Experimental results obtained at the end of the calculations are presented in Fig. 7 (for potato starch), Fig. 8 (for corn starch) and Table 1.

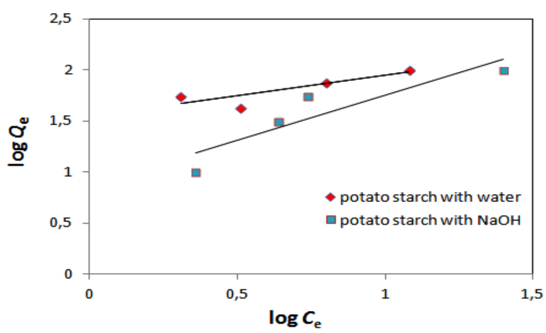

Figure 7.*The sorption isoterm of Freundlich which belongs to Cu^{2+} ions by using different modification types of potato starch.*

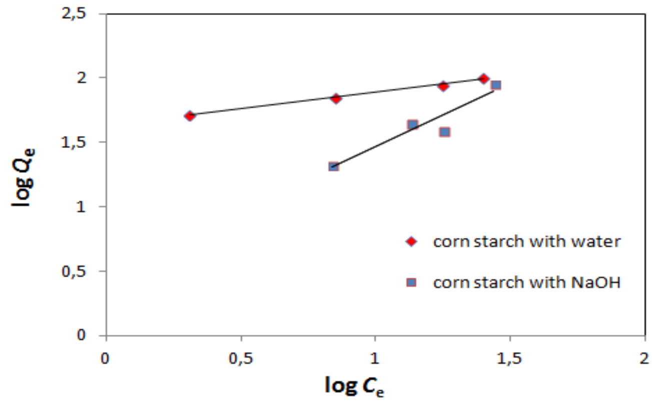

Figure 8. *The sorption isoterm of Freundlich which belongs to Cu^{2+} ions by using different modification types of corn starch.*

Table 1. *Parameters of Freundlich isotherm for sorption of Cu^{2+} ion on different modification type of potato starch and corn starch.*

Modified type of starch	Freundlich isotherm method	
	K_f	n
Potato starch modified with water	0.8762	0.8743
Potato starch modified with NaOH	1.5425	0.4037
Corn starch modified with water	1.6387	0.2533
Corn starch modified with NaOH	0.4935	0.9734

4. Conclusions and Recommendations

Studies on the removal of Cu^{2+}, one of the heavy metals frequently used in the industrial field, from aqueous solutions were carried out. During the trials, different types of starch (potato-corn) and modified starch obtained by applying different methods (water modification-NaOH modification) were used as adsorbents. According to the examination of % removal data, when 0.15 g of the adsorbent substance was used, it was determined that the optimum application time 20 minutes, and potato starch modified with water was more advantageous than corn starch. With its removal value of 89.58%, potato starch modified with water having an initial concentration of 20 mg L^{-1} can be recommended as an economical adsorbent that can be used in the removal of Cu^{2+} from aqueous solutions. Another result of the experimental data was shown that the pH 5 was the most favorable one. Moreover, the adsorption process was supported by the Freundlich isotherm curve, and the adsorption coefficients were observed to be compatible because of n values were between 0.2533 and 0.9734.

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