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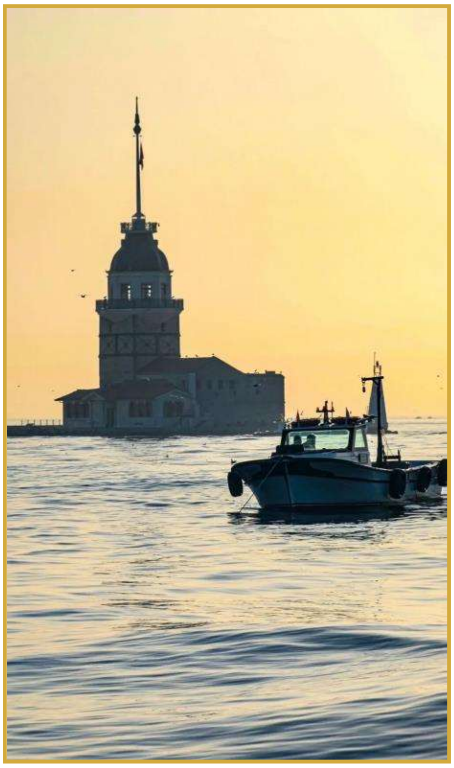

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DIPCON 2022

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EVALUATION OF HEAVY METAL SORPTION CAPACITIES OF CELLULOSE BASED ADSORBENTS WITH IONIC FUNCTIONAL GROUPS – AQUEOUS COBALT (II) ION REMOVAL –

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ABSTRACT

This study focuses on developing a novel foam material with ionic functional groups using the most abundant natural resource, cellulose, for the removal of heavy metals. Ionic functionalities were introduced to cellulose-based foam for increased affinity towards heavy metals. Based on the type of cellulose polymer used in the synthesis, four different cellulose based foam material batches were obtained, these are, activated cellulose, cellulose acetate, carboxymethyl cellulose, and acetylated carboxymethyl cellulose based foam materials. Heavy metal removal capacity of each foam material was tested using cobalt as the model heavy metal. At pH of 6.5, foam dose of 10 g/L, and initial Co^{2+} concentration of 100 mg/L, heavy metal removal capacities of the foam samples varied between 2% to 36 %, while foam material produced by cellulose acetate revealed the highest removal efficiency, 36%. Co^{2+} removal efficiency of cellulose acetate based foam increased to 50% when 15 g/L of foam sample was used under otherwise the same experimental conditions. Adsorption behavior of the cellulose acetate based foam material was also studied, which suggested Sips isotherm model as the most suitable adsorption mechanism.

Keywords: *heavy metal removal, cellulose, adsorption, cobalt, isotherm*

1. INTRODUCTION

Various industries such as battery production, tanneries, metal plating, mining, etc. employ heavy metals in production chemistry and as a result produce wastewaters including heavy metals in remarkable concentrations, which pose a vital threat to the environment. Heavy metals are toxic to humans either by direct exposure or via bioaccumulation in fresh water and marine biota, and in vegetation as a result of soil pollution (Bailey et al., 1999; Doris et al., 2000).

Electrodeposition and chemical precipitation are generally used to remove dissolved heavy metal species despite their disadvantages; the former is costly due to high electric energy consumption and the latter requires large settling tanks and produces high volumes of chemical sludge which is subject to further treatment. Therefore, numerous studies have sought low cost methods; among those, scavenging metals via adsorption has been the most abundantly investigated. If an adsorbent requires little or no pre-treatment and/or is a waste or a by-product of some process, it is usually considered as a low-cost material. For this cause, many "unusual" materials, majority of which are wastes or by-products of agriculture, even tree barks and wood dusts, ground husks of grains and shells of nuts, and brewed herbs have been employed as adsorbents (Gloaguen and Morvan, 1997; Ajmal et al., 1998; Low and Lee, 2000; Bulut and Tez, 2007; Chen et al., 2022). Separation of heavy metals from aqueous media also necessitates a further step of metal recovery and using combustible materials with low ash content as adsorbents presents a great advantage in this manner. Cellulose is a natural, and abundant polymer. Therefore, researchers within the last few decades have focused on developing cheap, eco-friendly, cellulose-based sorbents with high sorption capacity (Aniagor et al., 2021). Cellulosic adsorbent materials propose a great deal in terms of small particle size, high combustibility and low ash content. This study aims to develop a novel foam like adsorbent material with ionic functional groups using cellulose, for the removal of heavy metals.

2. MATERIAL AND METHODS

Synthesis of foam samples

2.1.1. Synthesis of activated cellulose foam sample (AC)

1,4-phenylene diisocyanate (1g) was added to the gel produced from activated cellulose, followed by the addition of THF (0.5 mL) and catalytic amount of diisopropyl amine (2 drops). The mixture was stirred at room temperature for an hour, then few drops of water were added. The resulting foam was washed with distilled water (100.0 mL) several times, filtered and dried at 60°C for an hr.

2.1.2. Synthesis of carboxymethyl cellulose (CMC)

CMC was produced from cellulose by the addition the of 50% NaOH dropwise, and a suspension of sodium chloroacetate. 1 g of produced CMC and 1 mL distilled water were stirred in a beaker until a clear gel was obtained. 10 mL N, N-dimethyl acetamide (DMAc) were added to the gel followed by addition of catalytic amount of diisopropyl amine (2 drops). Excess amount of 1,6-hexamethylene diisocyanate was then added. The mixture was stirred at room temperature for an hour. The resulting foam was washed with distilled water several times, filtered and dried at 60°C for an hour.

2.1.3. Synthesis of acetylated carboxymethyl cellulose based foam (AcCMC)

CMC was firstly acetylated by the addition of acetic acid, and H_2SO_4 under nitrogen. Then, in a 200 mL beaker, acetylated CMC (0.2 g) was mixed with 1,6-hexamethylene diisocyanate (3.0mL), followed by the addition of THF (0.5 mL) and catalytic amount of diisopropyl amine (6 drops). The mixture was stirred at room temperature for an hour. The resulting foam was washed with distilled water several times, filtered and dried at 60°C for an hour.

2.1.4. Synthesis of cellulose acetate based foam (CAc)

A clear gel was obtained from cellulose acetate by dissolving in DMAc. 1,4-phenylene diisocyanate (1g) was added to the produced gel, followed by the addition of THF (0.5 mL) and catalytic amount of diisopropyl amine (6 drops). The mixture was stirred at room temperature for an hour. The resulting foam was washed with distilled water several times, filtered and dried at 60°C for an hour.

Determination of Heavy Metal Removal Capacities

Aqueous solutions of cobalt were prepared at 100 mg/L initial concentration. 0.1 g of each adsorbent material, was added into a flask containing 10 ml aqueous Co solution. The pH of all test solutions were 6.5. Adsorption experiments were carried out in a temperature controlled shaker (IKA, Germany) in batch mode at 25 ºC for 24 hours with a mixing speed of 200 rpm. After the adsorption process, the samples were filtered with 0.2 µm PTFE filter. Then, the remaining cobalt concentrations were measured by atomic absorption spectroscopy using a Perkin Elmer AAnalyst 400 spectrometer. In order to assess the adsorption capacity, mass of Co adsorbed per unit mass of foam material was calculated using Equation 1.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

In Equation 1, C_0 and C_e are the initial and equilibrium concentrations of heavy metals (mg/L), q_e is the mass of pollutant adsorbed per unit mass of adsorbent (mg/g), V is the solution volume (L) and m is the adsorbent mass (g).

The percent (%) removal efficiency was calculated using Equation 2

$$Re\% = \frac{(C_0 - C_e)}{C_0} \text{x}100\% \tag{2}$$

where Re% is the percent removal efficiency.

Isotherm studies

10 mL of aqueous solutions at 20, 40, 60, 80, and100 mg/L initial concentrations were transferred into flasks. 0.15 g of cellulose acetate based foam material, was added into each flask containing 10 ml aqueous Co solution. The pH of all test solutions were 6.5. Adsorption experiments were carried out in a temperature controlled shaker (IKA, Germany) in batch mode at 25 ^oC for 24 hours with a mixing speed of 200 rpm. After the adsorption process, the samples were filtered with 0.2 µm PTFE filter. Then, the remaining heavy metal concentrations were measured by atomic absorption spectroscopy using a Perkin Elmer AAnalyst 400 spectrometer.

Isotherm models

The isotherm models Langmuir, Freundlich, Sips and Dubinin-Astakhov were tested since they are the most commonly used isotherms in the aqueous phase adsorption studies. The parameters of the isotherm models were determined by nonlinear optimization technique using Microsoft Office Excel software (Microsoft Corp., USA) as described by a Tran et al., 2017. The obtained models were evaluated according to Chi square (χ^2), correlation coefficient (R^2) and normalized root mean square error (NRMSE).

3. RESULTS AND DISCUSSIONS

Heavy Metal Removal Capacities of Cellulose Based Adsorbents

As can be seen in Figure 1, Co removal capacities of the foam samples varied between 2% to 36 %. While the foam produced by activated cellulose had the lowest Co removal efficiency (<1%), foam material produced by cellulose acetate revealed the highest removal efficiency, 36%. Solid phase concentrations of Co, as represented by the q values, varied between 0.05 and 3.84 mg/g.

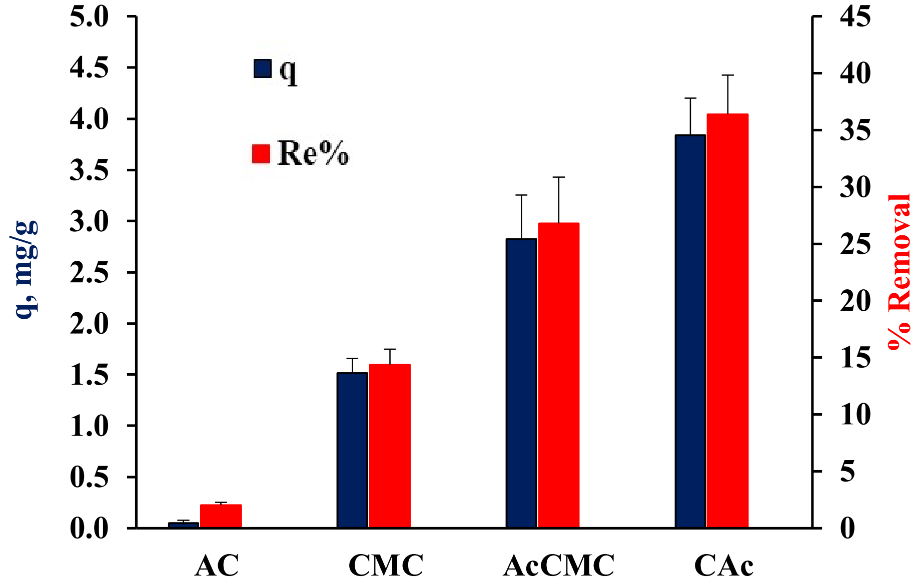

Figure1. Co^{2+} adsorption capacities of cellulose based foam samples (Initial Co^{2+} concentration 100 mg/L, contact time 24 h, adsorbent dosage 10 g/L, pH 6.5)

Equilibrium Study of Co^{2+} Adsorption onto CAc

24-hour equilibrium studies were conducted at 25 ºC, and pH 6.5, using 15 g/L CAc, and varying the initial concentration of Co^{2+} between 20–100 mg/L. The results are given in Figure 2. As can be seen in Figure 2, q values vary between 1-3.23 mg/g. The highest removal efficiency, 96.7%, was obtained for initial Co^{2+} concentration of 20 mg/L. Percent removal efficiencies gradually decreased when the initial Co^{2+} concentration in solution increased. For 100 mg/L initial Co^{2+} concentration, percent removal was as low as 49.6%.

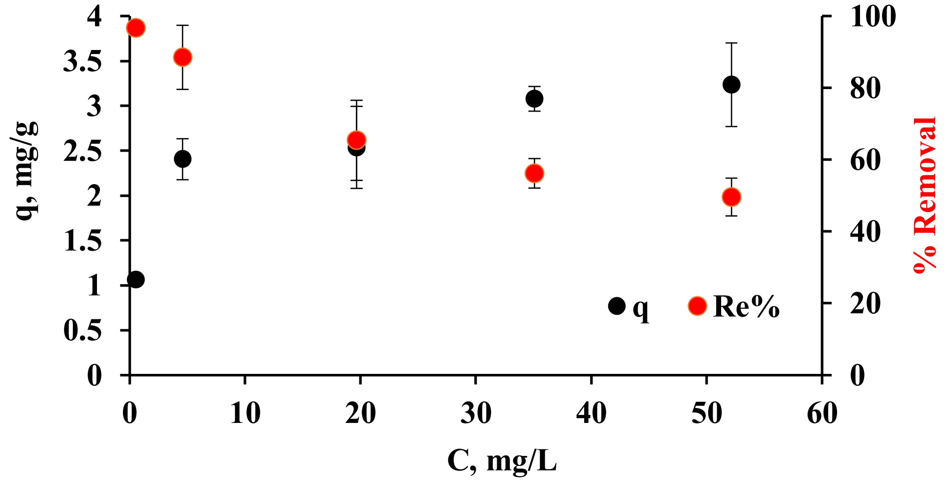

Figure 2. Equilibrium data for Co^{2+} adsorption onto CAc

Adsorption equilibrium data for the removal of Co^{2+} ions from aqueous solutions by cellulose acetate based foam were analyzed using the two-parameter models, Langmuir, and Freundlich, and three-parameter models, and Dubinin-Astakhov, and Sips.

Figure 3 shows the fit of the isotherm models to the experimental data for the adsorption of Co^{2+} ions from aqueous solutions by CAc. Calculated parameters of the tested isotherm models, and their goodness of fit measures are presented in Table 1. In Table 1, R^2 is the correlation coefficient, χ^2 represents Chi square, and NRMSE is the normalized root mean square error. NRMSE and χ^2 values close to zero, and R^2 value close to unity demonstrate that the model is effective at estimating the experimental results. Among the applied models, Langmuir, Freundlich, Sips and Dubinin-Astakhov showed good performances with high R^2 values, but Sips isotherm had a slightly better fit to the experimental data with the smallest NRMSE value, and the highest R^2 value. The maximum adsorption capacity calculated by Sips model was found to be 84.5 mg/g (at 298 K). Sips isotherm is a combination of both Langmuir and Freundlich isotherm models (Sips, 1948). As such, it is a hybrid model. This three-parametric isotherm is highly valid for predicting monolayer adsorption in homogenous and heterogeneous systems (Wang and Guo, 2020). Metal adsorbents generally fit Sips model (Chen et al., 2022).

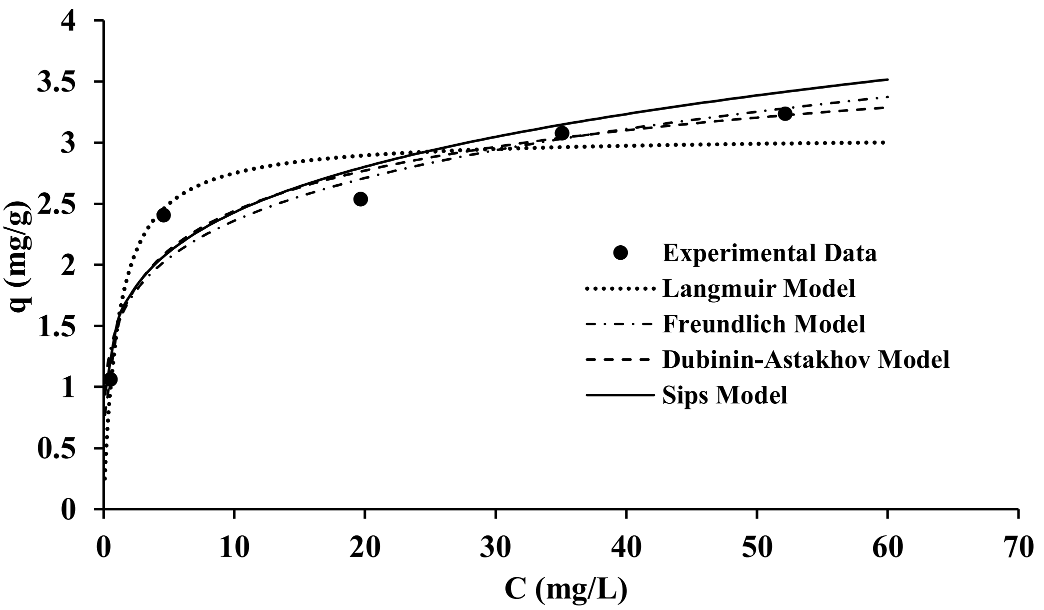

Figure 3. Model fit of adsorption isotherm of Co^{2+} adsorption onto CAc (Initial Co^{2+} concentration 20–100 mg/L, contact time 24 h, CAc dosage 15 g/L, pH 6.5)

Table 1. Isotherm model parameters and goodness of fit measures

Model	Equation	Model Parameters	Goodness of fit measures
Langmuir	$q_e = \frac{Q^o_{max} K_L C_e}{1 + K_L C_e}$	Q_{max} (mg/g) = 3.1 K_L (L/mg) = 0.893	R^2 = 0.929 χ^2 = 0.076 NRMSE = 0.094
Freundlich	$q_e = K_F C_e^n$	K_F ((mg/g)/(mg/L)^n) = 1.491 n = 0.1994	R^2 = 0.918 χ^2 = 0.132 NRMSE = 0.101
Sips	$q_e = \frac{q^S_m K_S C_e^{1/n_S}}{1 + K_S C_e^{1/n_S}}$	q^S_m (mg/g) = 84.5 K_S (mg/L)$^{-1/nS}$ = 0.018 $1/n_S$ = 0.207	R^2 = 0.936 χ^2 = 0.094 NRMSE = 0.089
Dubinin-Astakhov	$q_e = q_{DA\,(max)} \cdot \exp\left\{-K_{DA}\left[RT\ln\left(\frac{C_S}{C_e}\right)\right]^{n_{DA}}\right\}$	$q_{DA\,(max)}$ (mg/g) = 3.95 K_{DA} ((mol/kJ)^{nDA}) = 0.0004 n_{DA} = 1.569	R^2 = 0.919 χ^2 =0.130 NRMSE = 0.101

4. CONCLUSIONS

This study investigated the synthesis and use of novel cellulose based adsorbents for the removal of heavy metals from aqueous solutions. Co^{2+} was selected as the target heavy metal and different cellulose based materials (i.e., activated cellulose, carboxymethyl cellulose, acetylated carboxymethyl cellulose and cellulose acetate based foams) were synthesized. The comparative adsorption studies showed that among the synthesized materials, cellulose acetate based foam exhibited the highest adsorption capacity and percent removal efficiency for Co^{2+} ions. Using this adsorbent material, equilibrium adsorption studies were conducted. Isotherm models including Langmuir, Freundlich, Sips and Dubinin-Astakhov models were used to describe the experimental data, where Sips isotherm model provided the best fit. The maximum adsorption capacity by Sips model was calculated as 84.5 mg/g and the highest percent removal efficiency (experimental) was 96.7%. The results of this study are expected to contribute to developing insights on the design and synthesis of novel adsorbent materials for the removal of heavy metals from aqueous solutions.

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