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Araştırma Makalesi - Research Article

Clay-Biomass Composite: An Ecofriendly Hybrid Adsorbent for Effective Removal of Ni (II)

Kil-Biyokütle Kompoziti: Ni (II)'nin Etkin Giderimi için Çevre Dostu Hibrit Adsorban

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ABSTRACT

In this study, natural clay mineral: *Capsicum annuum* (*C. annuum*) L. seeds based composite adsorbent (CCAC) was prepared. Adsorption performance of CCAC was evaluated in terms of Ni (II) removal and adsorption capacity. Experimental conditions were optimized by investigating the initial pH of the metal solution, CCAC amount, initial metal ion concentration, and contact time parameters. The optimum conditions for Ni (II) adsorption by CCAC were pH:7.0, CCAC amount:0.06 g, and contact time:20 min. The adsorption isotherms were also analyzed by well-known models. The Langmuir isotherm model predicted a maximum monolayer adsorption capacity of 126 mg g^{-1}. Functional groups and surface morphology of CCAC were examined using FT-IR and SEM analysis, respectively. The findings indicated that the Ni (II) adsorption process was spontaneous and chemical in nature. Finally, all the results of this study revealed that CCAC, a simple to produce, cost-effective, and robust composite adsorbent, is an appropriate candidate for the treatment of waters polluted with nickel ions.

Keywords- Adsorption, Capsicum Annuum, Natural Clay, Nickel (II), Water Treatment

ÖZ

Bu çalışmada, doğal kil minerali: *Capsicumannuum* (*C. annuum*) L. çekirdekleri bazlı kompozit bir adsorban (CCAC) hazırlanmıştır. CCAC'nin adsorpsiyon performansı, Ni (II) uzaklaştırma ve adsorpsiyon kapasitesi açısından değerlendirildi. Deneysel koşullar, metal çözeltisinin başlangıç pH'ı, CCAC miktarı, başlangıç metal iyonu konsantrasyonu ve temas süresi parametreleri araştırılarak optimize edilmiştir. CCAC ile Ni (II) adsorpsiyonu için optimum pH: 7.0, CCAC miktarı: 0.06 g ve temas süresi: 20 dakika olarak bulunmuştur. Adsorpsiyon izotermleri sık kullanılan modeller ile belirlenmiştir. Langmuir izoterm modeli ile maksimum tek tabakalı adsorpsiyon kapasitesi 126mg g^{-1} olarak belirlenmiştir. CCAC'nin fonksiyonel grupları ve yüzey morfolojisi sırasıyla FT-IR ve SEM analizleri kullanılarak araştırılmıştır. Bulgular, kimyasal ve kendiliğinden gerçekleşen bir Ni(II) adsorpsiyon sürecini işaret etmiştir. Son olarak, bu çalışmadan elde edilen tüm sonuçlar, basit olarak üretilebilen, maliyeti uygun ve sağlam bir kompozit adsorban olan CCAC'nin nikel iyonları ile kirlenmiş suların arıtılması için uygun bir aday olduğunu göstermektedir.

Anahtar Kelimeler- Adsorpsiyon, Capsicum Annuum, Doğal Kil, Nikel (II), Su Arıtımı

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I. INTRODUCTION

Contamination of surface and groundwater with heavy metals has become a worldwide environmental issue due to the improper disposal of industrial effluent from various industrial uses [1]. Because heavy metals cannot be degraded or destroyed, they accumulate in living organisms, causing an increase in their concentration over time. Although nickel is one of the essential elements required for human metabolism, it has severe health impacts [2,3]. While the European Union has set a limit of 50 mg L^{-1} for drinking water, nickel levels in industrial effluent can reach 900 mg L^{-1} [4]. The World Health Organization (WHO) determined guideline and tolerated daily intake (TDI) limits as 0.07 mg L^{-1} and 12 μg^{-1} kg^{-1} body weight, respectively [5]. Therefore, Ni (II) ions in the polluted aquatic medium should be eliminated.

Precipitation, flotation, adsorption, ion exchange, extraction, reverse osmosis, and membrane techniques are used to remove heavy metals contaminants from aquatic medium. Adsorption is a popular analytical technique for removing numerous organic and inorganic pollutants from wastewater. The abundance of adsorbents used in this method and their low–cost are two of the most significant advantages that led to the technique's popularity [6-10]. Clay minerals, one of the most abundant minerals, are excellent adsorbents in natural, composite, and modified forms and offer a number of advantages, including high specific surface area, nontoxicity, low–cost, and superior adsorption capabilities [11,12]. *Capsicum annuum* (*C. annuum*) type pepper seeds have also been proven to be excellent sorbent material for eliminating pollutants from aquatic environments[13-16]. The industrial manufacture of such products generates a significant volume of waste seeds. As a result, employing this material as a possible feedstock for the development of an adsorbent is a waste evaluation procedure [17].

Researchers have recently prepared clay composites with various agents (chitosan, alginate, cellulose, magnetic iron oxide, ethylene glycol, and biomass) for more effective removal of multiple contaminants in an aqueous solution. Compared with the natural adsorbents, a composite adsorbent becomes more effective due to its enhanced mechanical strength, surface area, pore size, robustness, and ion exchange capacity. A clay-biomass hybrid composite is a potential approach for achieving more effective and reliable goals in adsorbent characteristics [7]. Such adsorbents are also five times less expensive than activated carbons [18]. *Sapindus* seed-activated carbon-clay [19], papaya seed-clay and pine cone-clay [18, 20, 21], cassava peel-clay [22], bamboo powder-clay [23], durian shells-clay [24], corn cob-clay [25], bamboo-clay [26], and cauliflower leaves [27] composites are few examples of clay-biomass composite materials in recent literature.

In this paper, *C. annuum* L. seeds and clay minerals, abundant in nature and readily available materials, were combined to make a composite adsorbent (CCAC) that was successfully employed to separate nickel (II) ions from the aquatic environment. To our knowledge, no previous research on the heavy metal removal ability of the prepared clay-biomass composite adsorbent has been reported. Preparation, characterization (SEM and IR), and optimization of each batch parameter (initial pH, CCAC amount, contact time, and initial pollutant concentration) were presented. The kinetic and equilibrium aspects of the Ni (II) treatment were also considered.

II.MATERIALS AND METHODS

A. *Preparation of Clay-Biomass Composite*

The composite adsorbent used in this study was prepared by mixing natural montmorillonite clay and *C. annuum* L. seeds in a mass ratio of 1:1. The powder mixture was moistened with a small amount of water and mixed well. The paste-like mixture was dried for 24 hours at 70 °C in an oven. Then, the prepared adsorbent was sieved and stored in a dark-colored bottle for use in adsorption experiments.

B. *Apparatus and Adsorption Studies*

The working solutions of Ni (II) were obtained by serial dilutions of 1000 mg L^{-1} Ni (II) stock solution prepared from Ni $(NO_3)_2 \cdot 6H_2O$ (Merck, 99.0 - 102.0%). Batch adsorption trials were carried out with 50 mL of 100 mg L^{-1} Ni (II) solutions on a multi-point magnetic stirrer (Variomag Multipoint 15) with a stirring speed of 200 rpm at room temperature. Appropriate concentrations of HCl or NaOH solutions were used to adjust the initial pH of the metal ion solutions. A pH meter (WTW, pH 7110) was used to measure the pH of the Ni (II) solutions. Parameters affecting the adsorption process such as initial pH (3-8), CCAC amount (0.02-0.20 g), agitation time (5-120 min), and initial Ni (II) concentration (70-830 mg L^{-1}) were examined. At the defined time intervals, the suspensions were centrifuged (5000 rpm, 5 min), and supernatants were analyzed with a flame-atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 400). The following equations were used to quantify the experimental results in terms of adsorption efficiency (E, %) and adsorption capacity (q_e, mg g^{-1}):

$$E = \frac{C_i – C_e}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{C_i – C_e}{m} \times V \tag{2}$$

where m(g) is the mass of CCAC, V (mL) is the volume of Ni (II) solution, C_i is initial, and C_e is the equilibrium concentrations of contaminant (mg L^{-1}), respectively.

The structure of natural clay, *C. annuum* L. seeds, and CCAC were also investigated by FTIR (Bruker–Tensor 27), SEM(JEOL–560–LV), and EDX analyses.

C. Adsorption Isotherm

Isotherm modeling of adsorption data was important to describe the adsorption mechanism between CCAC and Ni (II). The adsorption data in this study were examined using linearized Langmuir [28], Freundlich [29], and Dubinin–Radushkevich (D–R) [30]isotherm models in Eqs. 3, 4 and 6, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right) \times \frac{1}{C_e} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \times \ln C_e \tag{4}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

$$\ln q_e = \ln q_m - \beta\ \varepsilon^2 \tag{6}$$

$$E = 1/\sqrt{2\beta} \tag{7}$$

where, C_e is the remaining Ni (II) concentration in solution (mol L^{-1}), q_e is the amount of Ni (II) adsorbed on the clay composite adsorbent (mol g^{-1}), and q_m is the maximum calculated Ni (II) adsorption capacity of CCAC (mol g^{-1}). K_L (L mol^{-1}), K_F and β (mol^2 J^{-2}) are Langmuir, Freundlich, and D-R isotherm constants, respectively. 1/n is the adsorption intensity factor (dimensionless), R is the ideal gas constant (8.314 kJ mol^{-1}), E is the mean free energy calculated from Eq. 7 (kJ mol^{-1}), and T is the absolute temperature (K).

III. RESULTS AND DISCUSSION

A. Characterization

The FT–IR spectra of CCAC and metal ion-loaded CCAC are given in Figure 1. Natural clay has various absorption bands at 3588, 3433, 2931, 2857, 1635, 773, 729, and 686 cm^{-1}. The same absorption bands were also found in the spectrum of CCAC in addition to the peaks at 1409, 1013, 649, and 443 cm^{-1}, which indicate complex surface characteristics and rich in C, O, and H elements [31]. The peaks at 3310, 2927, 2855, 1747, 1657, 1548, 1461, 1391, and 1100 cm^{-1} are the major bands of the functional groups present on the *C. annuum* seeds [32]. The absorption bands in the spectrum of CCAC at 3588 and 3433 cm^{-1} (–NH or –OH) shifted to 3608 and 3422 cm^{-1}, respectively, and the strength of the band at 3588 cm^{-1} also decreased after an interaction with Ni (II) ions. The peak at 1635 cm^{-1} (–OH stretching/bending vibrations of water) [33] was relocated to 1632 cm^{-1}. The intensity of this absorption band also enhanced after Ni (II) adsorption onto CCAC. A weak peak at 1409 cm^{-1} (C–H bending vibration) shifted to 1384 cm^{-1} with an increase in the band intensity after Ni (II) adsorption process (Figure 1b) [34]. Si–O symmetrical vibration band (1013 cm^{-1}) also slightly weakened after Ni (II) exposure. The observed bands of the CCAC at 772, 686, 649, and 443 cm^{-1} were minimally affected by Ni (II) adsorption. Similar results can also be shown in previous studies using clay minerals [35, 36]. These findings might be strong evidence for Ni (II) adsorption via different binding sites on the composite clay surface.

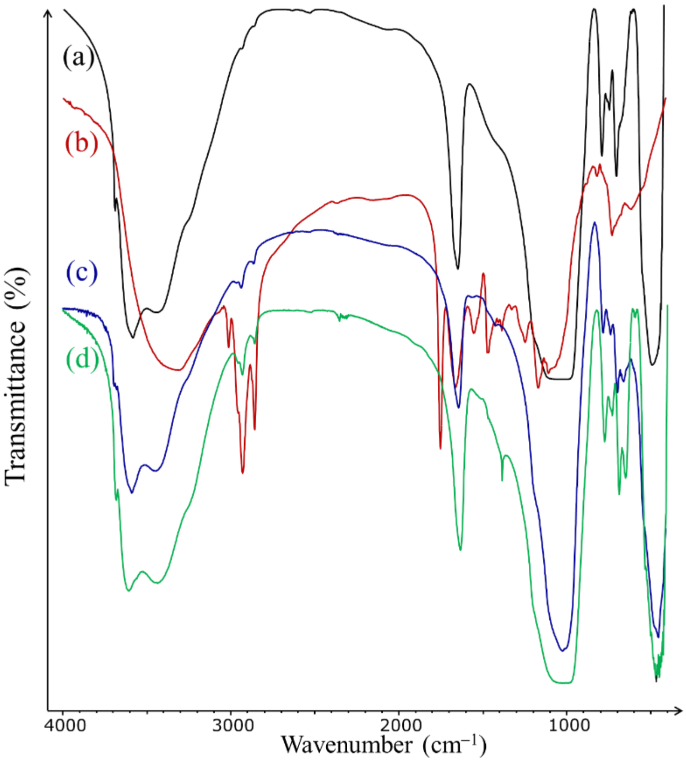

Figure 1. IR spectra of clay**(a)**, *C. annuum***(b)**, CCAC**(c)**, and Ni (II) loaded CCAC**(d)**.

SEM analysis was utilized to characterize the surface morphologies of the clay, *C. annuum*, CCAC and Ni (II) loaded CCAC and SEM micrographs at ×3000 magnification are shown in Figure 2. The surface of natural montmorillonite clay has a rough and porous surface (Figure 2a). SEM micrograph of *C. annuum* also indicated its rough, irregular, and porous structure (Figure 2b). CCAC revealed a more heterogeneous and relatively porous microstructure and had a rough surface (Figure 2c). Partial pores on the sorbent surface of CCAC were detected, and these served as binding sites for Ni (II) ions and enhanced their diffusion. It can be observed from these figures that the adsorption process affected the morphology of the composite adsorbent (Figure 2d). The interlayer gaps were minimized after Ni (II) adsorption, and the adsorbent surface appeared smoother and more uniform than CCAC.

EDX spectrums of the CCAC and Ni (II) loaded CCAC were also examined to validate the interaction of Ni (II) ions with composite adsorbent. While the different peaks of Ni (II) ions were not apparent in the EDX spectrum of CCAC (Figure 3a), they were visible in the EDX spectrum of Ni (II) adsorbed composite adsorbent (Figure 3b), which was an indicator of Ni (II) adsorption onto CCAC.

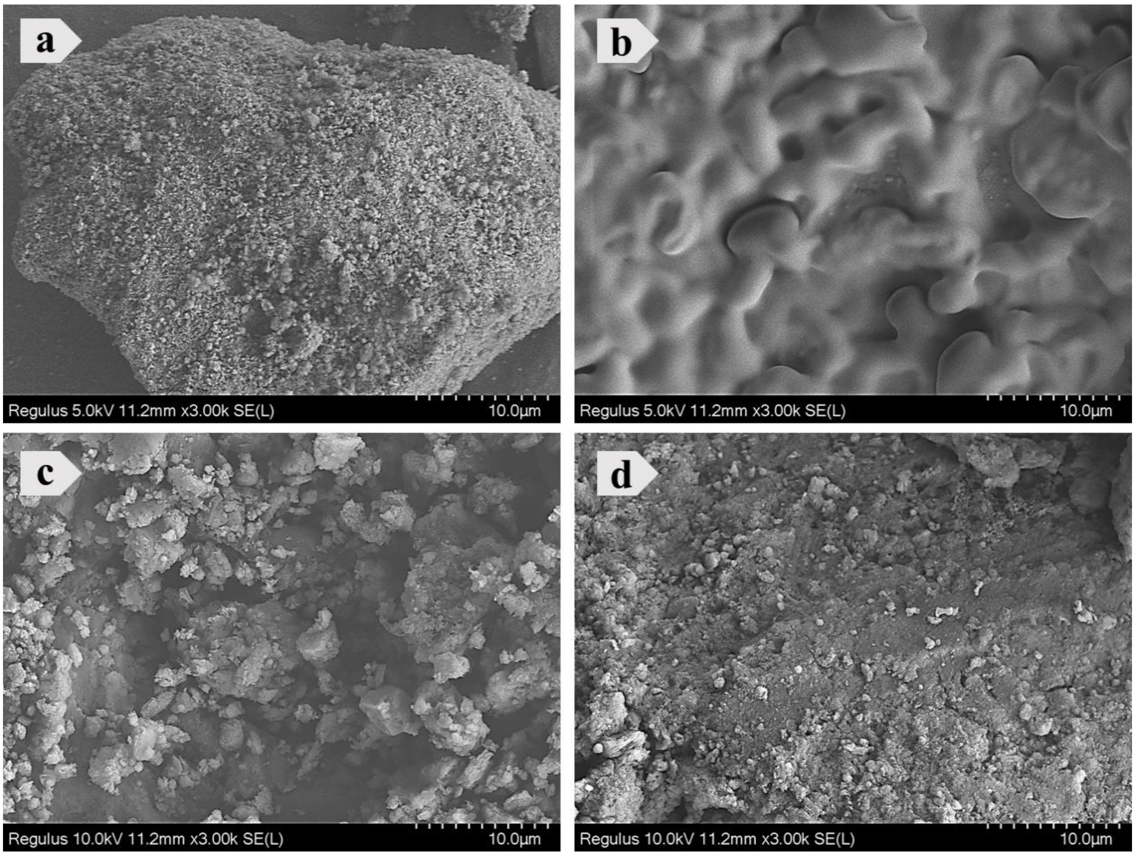

Figure 2. SEM micrographs of natural montmorillonite clay (**a**), *C. annuum* L. seeds (**b**), CCAC (**c**) and Ni (II) loaded CCAC (**d**).

B. Effect of pH on CCAC Adsorption

The initial pH value is an essential factor affecting the adsorption process. The pH of the solution affects the solution chemistry of the contaminants, the activity of binding sites in adsorbents, and the competition with other ions in the sorption medium.

The influence of pH on CCAC's adsorptive efficacy was evaluated at various pH values (3.0–8.0) at ambient temperature, and the findings are shown in Figure 4. Due to the possibility of nickel precipitation in the hydroxide form after pH 8, studies at higher pH values were not carried out. The figure demonstrated that the initial pH had a significant impact on the adsorption process of Ni (II) by CCAC up to 7.0 and that at lower pH values, competition for binding to active sites between Ni (II) and hydronium ions increased, resulting in reduced Ni (II) adsorption on the CCAC's surface [9]. The adsorption capacity of Ni (II) rose from 14.5 to 32.1 mg g^{-1} with increasing pH values from 3.0 to 7.0 and then remained constant at pH 7.0 ($p > 0.05$). Based on these findings, the pH value of 7.0 was determined to be the optimal value.

C. Effect of CCAC Quantity

Optimization of the adsorbent quantity is also an important stage of the adsorption process. When the adsorbent quantity is increased, the amount of adsorbed contaminant per unit weight of absorbent generally decreases while the percentage efficacy increases [37, 38]. The impact of adsorbent quantity was investigated by varying the amount of CCAC from 0.02 to 0.20 g using 100 mg L^{-1} Ni (II) solution (pH 7.0) at ambient temperature. Figure 5 showed that increasing the adsorbent dosage lead to an increase in the available active sites, resulting in increased adsorption yield for Ni (II) removal [39]. The percentage of Ni (II) removal increased from 8.5 to 97.5% when the CCAC dosage was increased from 0.02 to 0.20 g. The adsorption capacity also increased from 24.4to 41.3 mg g^{-1} by increasing CCAC dosage from 0.02 to 0.06 g and decreased with a further increase. The optimal CCAC dose was determined to be 0.06 g, and further studies were performed using 0.06 g CCAC.

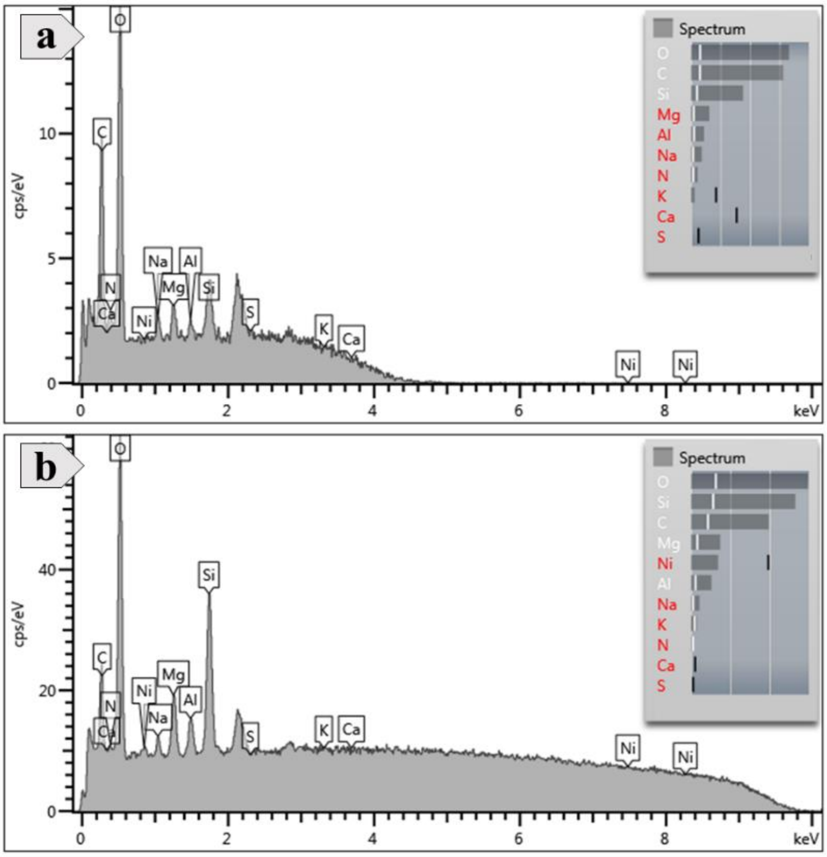

Figure 3. EDX spectra of CCAC (a) and Ni (II) loaded CCAC (b).

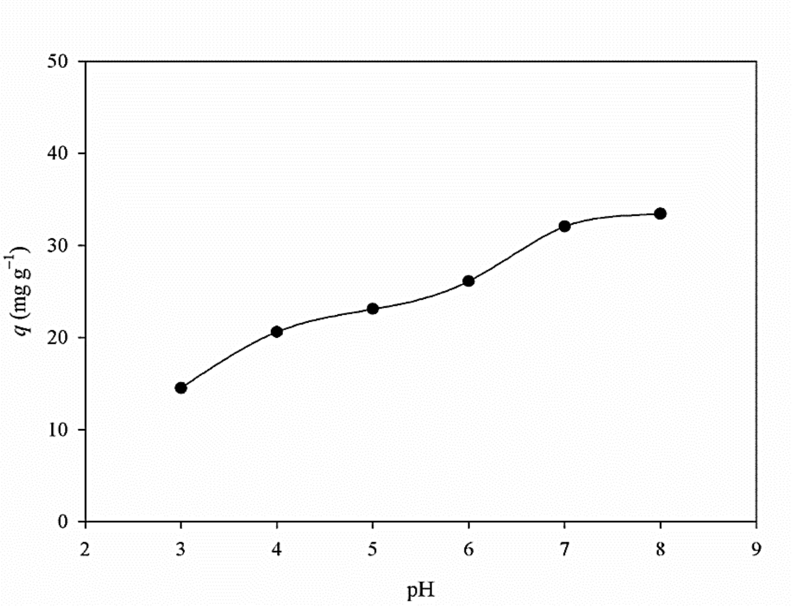

Figure 4. Impact of pH on the Ni (II) adsorption onto CCAC.

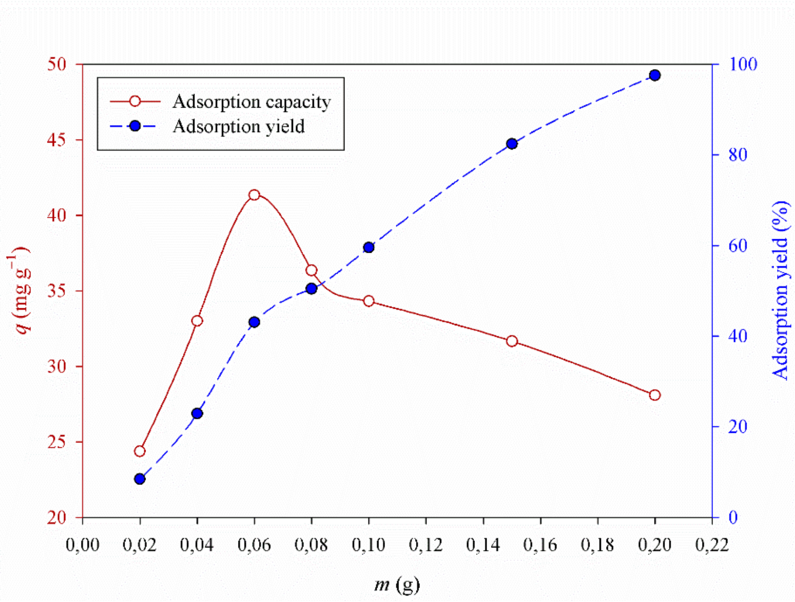

Figure 5. Impact of CCAC dosage on the Ni (II) adsorption onto CCAC.

D. *Effect of Contact Time*

Determining the time required for the adsorption critical for keeping energy and workforce to a minimum. The adsorption capacity reached 37.3 mg g^{-1} in the first 5 min, increased up to 51.5 mg g^{-1} in 20 min and then reached an equilibrium (Figure 6). This quick nickel extraction efficiency was a significant aspect of the suggested composite adsorbents for practical use in water purification systems.

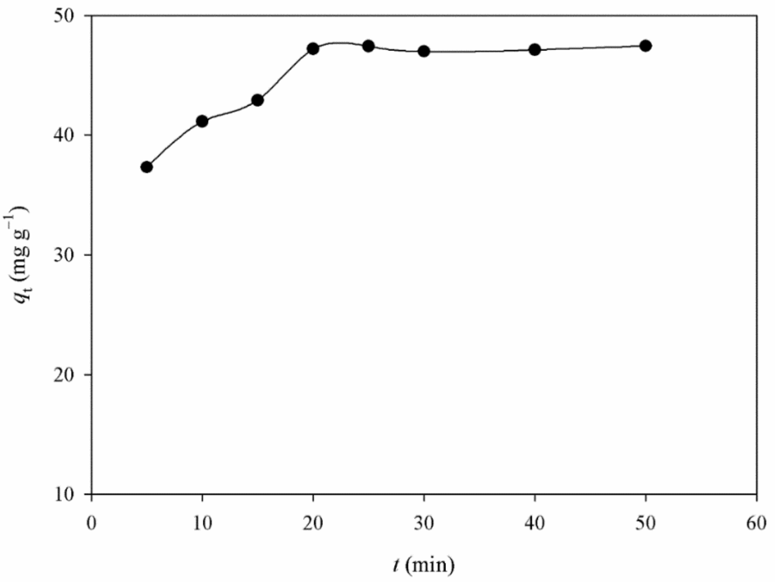

Figure 6. Impact of contact time on the Ni (II) adsorption onto CCAC.

E. *Adsorption Isotherm Models*

A relationship between adsorption capacity and metal ion concentration was given in Figure 7. Metal ions were adsorbed on the particular functional groups at lower Ni (II) concentrations. The adsorption rate decreased at later stages as the Ni (II) concentration increased because these sites became occupied. The maximum adsorption capacity of CCAC was calculated as 115 mg g^{-1} using 730 mg L^{-1} initial Ni (II) concentrations.

The Langmuir (Figure 8), Freundlich (Figure 9), and D-R (Figure 10) isotherm model curves derived from the linearized plots were tabulated in Table 1. Figure 8 and Table 1 showed that Ni (II) adsorption better fits the Langmuir isotherm model. This result indicated the generation of a monolayer surface coating of Ni (II) ions on the CCAC's surface. A maximum monolayer sorption capacity of 126 mg g^{-1} was predicted from the Langmuir isotherm model. The *n* value calculated from the Freundlich isotherm model and the adsorption energy predicted from the D–R isotherm model indicated spontaneous adsorption and the chemical ion-exchange adsorption mechanisms, respectively [39-42].

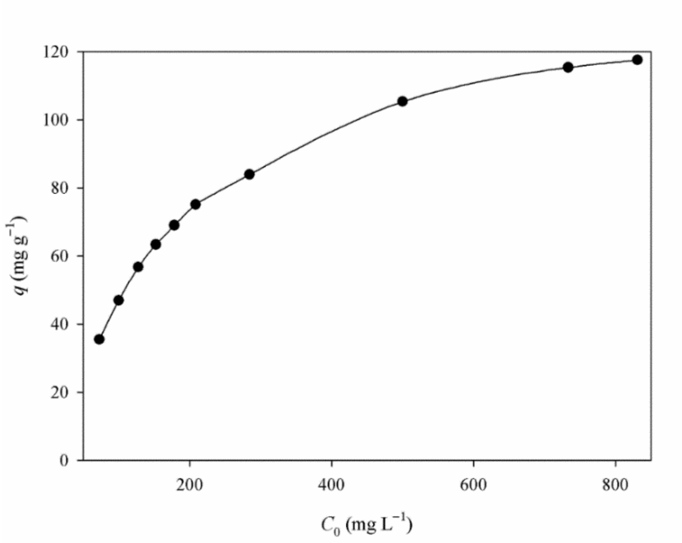

Figure 7. Impact of initial Ni (II) ion concentration on adsorption capacity of CCAC.

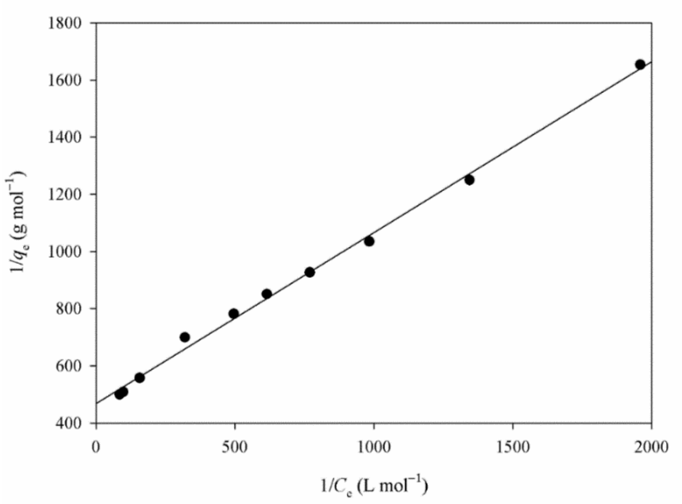

Figure 8. Linearized Langmuir isotherm plots for the adsorption of Ni (II) onto CCAC.

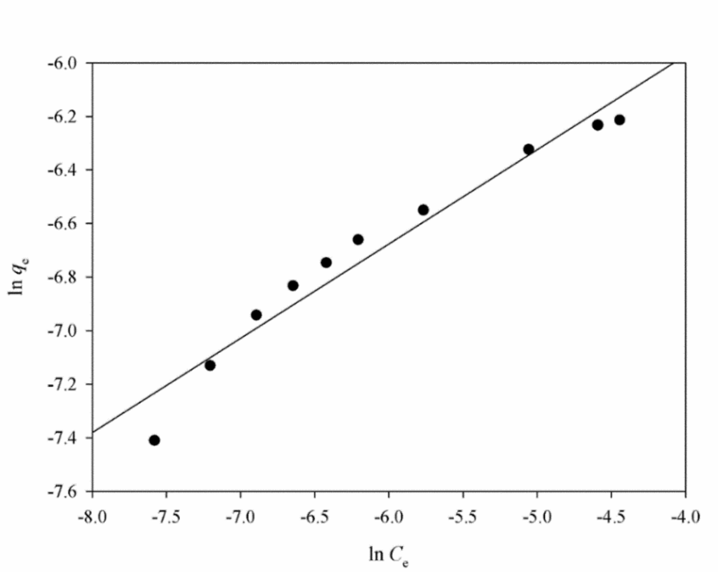

Figure 9. Linearized Freundlich isotherm plots for the Ni (II) adsorption onto CCAC.

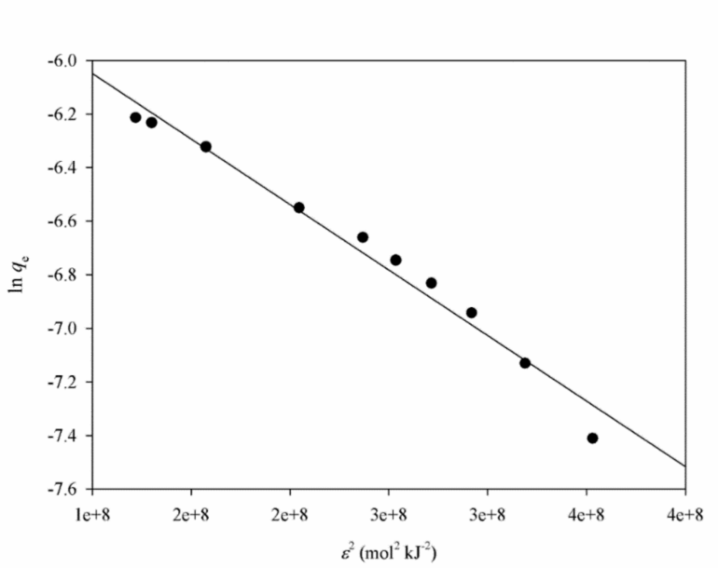

Figure 10. Linearized D-R isotherm plot for the Ni (II) adsorption onto CCAC.

Table 1. Isotherm parameters for the adsorption of Ni (II) by CCAC

Langmuir			**Freundlich**			**Dubinin-Radushkevich (D-R)**			
$q_{\max}$	K_L	r^2	n	K_F	r^2	q_m	β	r^2	ε
(mol g^{-1})	(L mol^{-1})					(mol g^{-1})	(mol^2 kJ^{-2})		(kJ mol^{-1})
2.1×10^{-3}	7.8×10^{2}	0.997	2.8	0.010	0.952	3.9×10^{-3}	4.9×10^{-9}	0.977	10.1

F. Comparison with Recent Works

The Ni (II) adsorption performance of CCAC in terms of equilibrium time, adsorption efficiency, and adsorption capacity was compared to those of other clay minerals and biomaterials (Table 2). The present study proved that CCAC could be employed as an effective alternative composite adsorbent in the industrial operations for Ni (II) elimination due to its greater adsorption efficiency and capacity, as well as its faster equilibrium time.

Table 2. Comparison of the Ni (II) adsorption parameters with recent clay- and biomass-based adsorbents

Adsorbent	*t* (min)	*E* (%)	*q* (mg g^{-1})	References
Surfactant-modified bentonite	5	–	65.8	[43]
Activated bentonite clay	120	75.5	2.0	[44]
Montmorillonitic clay	15	96	3.8	[45]
Bentonite clay composite	270	95.6	37.9	[46]
Serratia marcescens	60	–	13.5	[47]
Parmotrema tinctorum	120	58.9	33.9	[48]
Narcissus tazetta L. leaf powder	15	43.5	36.0	[49]
Brewed green tea bag waste	15	76	7.6	[50]
Red tea bag waste	30	62	6.2	[50]
CCAC	20	97.5	126	Present study

IV. CONCLUSION

The present study proved that clay-biomass based composite adsorbent (CCAC) was effective for Ni (II) removal from polluted water medium. Ni (II) adsorption by CCAC was a fast, spontaneous, and pH-dependent process. The role of hydroxyl and silicate groups in the adsorption processes was discovered using the FTIR method. SEM morphological analysis revealed a heterogeneous, relatively porous and rough surface structure. CCAC successfully removed Ni (II) ions with a maximum adsorption yield of 97.5% and adsorption capacity of 126 mg g^{-1}. Adsorption equilibrium was attained in a short period (20 min). Various kinetic and equilibrium models were used to analyze the experimental data. Langmuir isotherm and PSO kinetic models described better Ni (II) adsorption process by CCAC. As a result, CCAC may be considered a promising adsorbent for the removal of Ni (II) ion pollution in wastewater.

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