

RESEARCH ARTICLE

Open Access



Insight into the adsorptive removal of Cr(VI) ions and 4-chlorophenol from aqueous media on cationic surfactant-modified cucumber peels

Sengul Tugba Ozeken¹, Duygu Ozdes² and Celal Duran^{1*} 

Abstract

A new and cost-effective adsorbent material was developed by chemical modification of cucumber peels (CP) with a cationic surfactant, cetyltrimethylammonium bromide (CTAB). The adsorptive behavior of CTAB-modified cucumber peels (CMCP) was investigated in the retention of an organic pollutant (4-chlorophenol) and an inorganic pollutant (Cr(VI)) through batch experiments. The adsorbents were characterized by Fourier transform infrared spectroscopy (FTIR) analysis and scanning electron microscopy (SEM) technique. Influences of initial concentrations of both pollutants, dosage of CMCP, initial solution pH, contact time, and foreign ions were parameters used to specify the optimized conditions. Results of the experiments were evaluated by three kinetic models, namely pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, to find out the dominant mechanisms in the retention of 4-chlorophenol and Cr(VI). Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models were applied to the adsorption data to estimate the adsorption capacity of CMCP and to describe the interactions between the species. Langmuir isotherm model fitted the data well, and the maximum Cr(VI) and 4-chlorophenol adsorption capacities of CMCP were 84.03 mg g^{-1} and 107.5 mg g^{-1} , respectively. Consequently, CMCP demonstrated outstanding performance in the adsorption of both inorganic and organic pollutants, offering a low-cost, easily prepared alternative to other adsorbents reported in the literature.

Highlights

- Cucumber peels were modified by CTAB for the first time to obtain an inexpensive and efficient adsorbent for the removal of organic and inorganic pollutants.
- CTAB modification significantly enhances the adsorption capacity of cucumber peels in Cr(VI) and 4-chlorophenol retention.
- CTAB-modified cucumber peels performed high capacity for the retention of inorganic and organic pollutants as compared with other adsorbents in the literature.

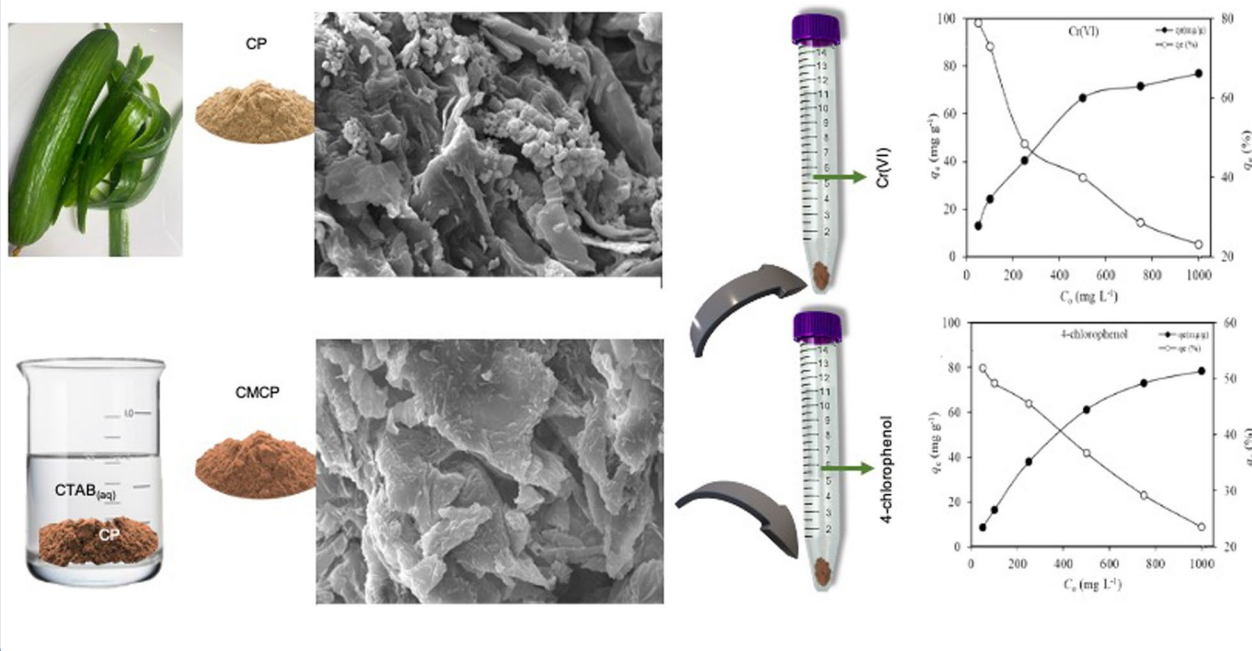
Keywords Adsorption, Cetyltrimethylammonium bromide, Chromium, Cucumber peel, 4-Chlorophenol

*Correspondence:

Celal Duran
cduran@ktu.edu.tr

Full list of author information is available at the end of the article

Graphical abstract



Introduction

The presence of organic and inorganic contaminants in industrial effluents attracts the attention of environmentalists and researchers because of their hazardous effects on the ecosystem and living things. Physical, chemical, and biological methods such as advanced oxidation, nanofiltration, precipitation, coagulation–floculation, and filtration are widely applied to overcome environmental problems by eliminating these pollutants. Most of these methods, in addition to having advantages over others, also have one or more disadvantages such as generating secondary sludge or highly toxic by-products, excessive chemical consumption, requiring high technological equipment, being impractical, and expensive (Zeghioud et al. 2022). However, the adsorption technique offers technologically simple solutions, effectively adapts to purification processes, and has better selectivity (Rambabu et al. 2021). Nevertheless, the high costs of commercial adsorbents activated by physical or chemical methods through high-energy-requiring technologies impede investments in these materials in the wastewater treatment sectors (Rambabu et al. 2020). This reason encouraged the researchers to develop eco-friendly materials that may substitute the high-cost commercial adsorbents with the advantages of being synthesized inexpensively

and responding to pollutants efficiently (Rambabu et al. 2021).

Chlorinated phenols are widely used toxic compounds in sectors due to their industrial importance despite their being responsible for many environmental problems, including large amounts of recalcitrant wastes contaminated to wastewater after secondary treatments in paper and pulp industries (Rubilar et al. 2008). 4-chlorophenol (p-chlorophenol), a toxic and stable organic pollutant with a disturbing odor, shows toxicity caused by inhalation, ingestion, and adsorption through the skin and emits fumes that irritate the tissues when heated to the decomposition (Gomez et al. 2012). Ding et al. (2016) investigated 4-chlorophenol adsorption performance of carboxylated and hydroxylated single-walled carbon nanotubes (SWCNTs). Ding et al. (2021) researched 4-chlorophenol adsorption capacity of N-doped porous carbon material obtained by HCl treatment applied to a substance prepared in a process including carbonization–activation of the amine residue which was previously pulverized with NaOH. Li et al. (2009) used salicylaldehyde-, β -cyclodextrin-, and cross-linked β -cyclodextrin-modified chitosan to remove 4-chlorophenol from aqueous solution. On the other hand, natural materials and their modified forms, such as cetyltrimethylammonium bromide (CTAB)-modified zeolite and benzyl

tetradecyl ammonium chloride-modified zeolite (Kuleyin 2007), dodecyl trimethylammonium bromide and CTAB-modified organoclay (Zhang et al. 2015), activated carbon from jack fruit (Jain and Jayaram 2007), hulls of *Prosopis africana* seeds (Garba and Rahim 2016), and pomegranate husk (Hadi et al. 2021), were used to remove 4-chlorophenol from aqueous solutions.

Cr(VI), another emerging pollutant, contaminates groundwater as a result of industrial applications such as plating, dyeing, and chromate production (Ou et al. 2020). The International Agency for Research on Cancer has stated that exposure to Cr(VI) compounds through inhalation is categorized as carcinogenic. In nature, chromium can be found as oxides and hydroxides of Cr(III) or salts of Cr(VI). Chromium (VI) is toxic, while Cr(III) is essential for human life. Thus, the solubility of Cr(III) compounds is poor compared to very soluble and mobile Cr(VI) forms, including strongly oxidant species such as $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , and HCrO_4^- (Georgaki et al. 2023). Adsorption technique provides an effective and economic means for the retention of chromium species. Many adsorbent materials were used to treat Cr(VI) pollution in the water. Cr(VI) removal performances of carbon, silicon, iron, polymer and titanate-based materials, and microplastics, mono- and multimetallic layered double hydroxides, hydrogels, aerogels, three-dimensional nanocomposites, montmorillonite clay, and biological adsorbents were criticized by Liu et al. (2023). Additionally, many raw or modified natural materials were researched as adsorbents to remove Cr(VI) species from wastewater. Sulfuric acid-modified peat (Li et al. 2019), natural moss (*Racomitrium ericoides* (Brid.) Brid.) (Ozeken et al. 2023), biofilm of bacterial species (*Streptococcus equisimilis*, *Bacillus coagulans*, *Escherichia coli*) supported on granular AC (activated carbon) (Quintelas et al. 2008), magnetic Fe_3O_4 -loaded EDTA-modified brewed tea waste (Camoglu et al. 2023), date palm empty fruit bunch (Rambabu et al. 2020), and normal powder and nanopowder of watermelon peel (El-Tawabty et al. 2024) were researched for Cr(VI) retention.

Waste peels, thanks to their lignocellulosic content, serve new gateways as adsorbent materials in water treatment methods and contribute to the solution of health and environmental problems caused by the decrease in water quality as a result of anthropogenic activities such as unqualified use, industrialization, and urbanization (Bhatnagar et al. 2015). Cucumber peels (CP), which contain high amounts of cellulose, hemicellulose, and lignin, can provide a high adsorption capacity by interacting with heavy metals and organic pollutants through the hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups on their surface (Prasanna and Mitra 2020). From an environmental perspective, the use of CP, which are a significant

waste product in household consumption and the food industry, as an adsorbent and recycling them is of great importance (Basu et al. 2018). Compared to chemical-based adsorbents, CP are environmentally friendly and can be disposed of without harming the environment after use. Cucumber is a widely grown vegetable worldwide, making it a sustainable source of adsorbents (Stavrinou et al. 2018). Modification of organic wastes with a cationic surfactant increases hydrophobic interactions, allowing organic species such as 4-chlorophenol to be adsorbed more effectively. On the other hand, modification with a cationic surfactant can also make the adsorbent surface positively charged, which facilitates the adsorption of anionic ions, such as Cr(VI), or anionic dyes, through stronger electrostatic interactions (Tamjidi et al. 2021). Barboza et al. (2024) modified banana peels with CTAB, dodecyltrimethylammonium bromide (DTAB), and sodium dodecyl sulfate (SDS) and then used them for the removal of an anionic dye, Direct Blue 86. Foroughi-Dahr et al. (2015) researched the removal of Congo red dye from aqueous solutions using CTAB-modified tea waste. Abadian et al. (2023) utilized tetradecyltrimethylammonium bromide (TTAB)-modified *Cuminum cyminum* agri-waste to investigate the removal of diclofenac sodium from aqueous solutions.

In this study, CP were modified by CTAB, a cationic surfactant, to obtain a new, low-cost, and effective adsorbent for the retention of an organic pollutant (4-chlorophenol) and an inorganic pollutant (Cr(VI)). To the best of our knowledge, the modification of CP with CTAB for the removal of any toxic organic and inorganic pollutants has not been reported so far. CP and CTAB-modified CP (CMCP) were characterized by Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), and pH_{pzc} analysis, and the adsorptive performances of CMCP were researched through the influences of initial solution pH, contact time, CMCP dosage, and initial Cr(VI) and 4-chlorophenol concentration. Kinetic studies were used to define the mechanisms of adsorption. Isotherm models were evaluated to describe the interactions of CMCP surface sites with each interacting adsorbate species.

Experimental

Chemicals

Analytical-grade chemicals obtained from Fluka (Buch, Switzerland) and Merck (Darmstadt, Germany) were preferred in the experiments. CTAB was used as the chemical modifier. 4-chlorophenol and $\text{K}_2\text{Cr}_2\text{O}_7$ were used to prepare the stock solutions of pollutants. The initial pH values of the solutions were adjusted by diluted HNO_3 and NaOH. The effects of the foreign ions were

investigated in the presence of Na_2SO_4 and Na_3PO_4 salts in aqueous media. Distilled water was used in all stages of the experimental studies.

Apparatus

The adsorbent materials and the solid chemicals were weighed with Sartorius BP1106 model (Sartorius AG, Germany) analytical balance. IKA RCT Basic model (IKA-Werke GmbH & CO. KG, Germany) magnetic stirrer was used to stir the solutions, and Hanna pH-2221 model (Hanna Instruments, USA) digital pH meter was utilized to adjust the initial pH of the pollutant solutions. Surface structures of CP and CMCP were identified by PerkinElmer 1600 model (PerkinElmer, Inc., USA) FTIR, and the surface morphologies were examined by ZEISS Evo Ls 10 model (Carl Zeiss AG, Germany) SEM. The test samples, consisting of the pollutant solutions and adsorbent materials, were processed for adsorption on an Edmund Bühler GmbH KS-15 model (Germany) mechanical shaker (motion; horizontal, shaking platform; 400×300 mm, max. load; 15 kg, shaking speed; 30–420 rpm, stroke; 17 mm) in each batch experiment, and the liquid phase of each sample was separated by centrifugation on a BOECO S-8 model (Boeckel & Co. GmbH) centrifuge. The concentration of the Cr(VI) was determined by utilizing the PerkinElmer AAnalyst 400 model (PerkinElmer, Inc., USA) flame atomic absorption spectrometer (FAAS) at a wavelength of 357.87 nm. The concentration of 4-chlorophenol was determined by utilizing a PerkinElmer Lambda 25 model (Perkin Elmer, Inc., USA) UV-Vis spectrophotometer at a wavelength of 280 nm. The limit of detection (LOD) for Cr(VI) and 4-chlorophenol analysis has been determined to be $120 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$, respectively.

Surface modification of CP adsorbent

The cucumbers were obtained from a local seller. CP were washed with tap water to remove any dust or dirt, then washed with distilled water, and dried in the oven at 105°C for 24 h. The CMCP was prepared based on a revised version of the simple method used by Liu et al. (2019) to synthesize CTAB-modified activated carbon for the removal of sulfamethazine and sulfamethoxazole. Accordingly, 30 g of dried CP sieved with a blender was added into 15 g L^{-1} of CTAB solution (500 mL) and stirred for 24 h at room temperature. Then, the suspension was filtered through a $0.45\text{-}\mu\text{m}$ cellulose nitrate membrane filter. The solid substance was washed with distilled water several times. The final product (CMCP) was sifted to obtain the particles smaller than $100 \mu\text{m}$, dried in an oven at 105°C for 8 h, and placed in a glass container for experimental studies.

Batch experiments

All parameters were investigated by the experiments carried out by batch method. Cr(VI) or 4-chlorophenol solutions, with a definite concentration ($50\text{--}1000 \text{ mg L}^{-1}$) and a known pH ($1.5\text{--}10.0$), were added to planned amounts of adsorbent material ($1.0\text{--}20.0 \text{ g L}^{-1}$) which was previously weighed in a polypropylene centrifuge tubes with a 15 mL volume. The suspensions were processed for adsorption for the scheduled contact times ($1\text{--}480$ min) on a mechanical shaker at 350 rpm and then centrifuged at 4500 rpm for 5 min, and the residual concentration of Cr(VI) and 4-chlorophenol were determined by FAAS and UV-Vis spectrophotometer, respectively. The initial and equilibrium concentrations are evaluated through Eqs. 1 and 2 to calculate Cr(VI) and 4-chlorophenol adsorption capacities (q_e) of CMCP and the percentages of adsorption (%) in the present processes, respectively.

$$q_e = \frac{V(C_o - C_e)}{m_s} \quad (1)$$

$$\text{Adsorption}(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

q_e (mg g^{-1}) is the amount of Cr(VI) or 4-chlorophenol pollutant adsorbed by 1 g of CP or CMCP. C_o and C_e (mg L^{-1}) are the concentrations of the pollutant in initial and equilibrium stages, respectively. V is the volume (L) of the solution added onto weighed amounts (m_s (g)) of CP or CMCP.

Adsorption kinetics

Adsorption data were evaluated by pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion (IPD) models, to determine the reaction rates and to explain the dominant mechanisms in the adsorption of Cr(VI) and 4-chlorophenol onto CMCP. Equations 3, 4, and 5 represent the linear forms of PFO (Lagergren 1898), PSO (Ho and McKay 1998), and IPD (Weber Jr and Morris 1963) models, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_{id} t^{1/2} + c \quad (5)$$

q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amounts of Cr(VI) and 4-chlorophenol adsorbed onto 1 g of CMCP at any time t (min) and at equilibrium, respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the rate constants of the PFO and PSO kinetic models, respectively. k_{id} (mg

$\text{g}^{-1} \text{min}^{-1/2}$) represents the rate constant of IPD model. C value informs about the extent of boundary layer. k_1 and q_e values in the PFO model can be acquired by the slope and intercept of $\ln(q_e - q_t)$ versus t plot, and q_e and k_2 values in the PSO model can be obtained by the slope and intercept of the t/qt versus t plot, respectively. The slope and intercept of the figure drawn between q_t versus $t^{1/2}$ correspond to k_{id} and C parameters in the IPD model, respectively.

Adsorption isotherms

The adsorption isotherms were evaluated by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models. The Langmuir model describes the monolayer adsorption of the species onto a surface consisting of co-energized sites (Langmuir 1918), and the Freundlich model defines the multilayer adsorption of the adsorbate species onto a surface consisting of differently energized sites (Freundlich 1906). The D–R model donates information about the adsorption type (Dubinin and Radushkevich 1947).

Experimental data can be used to obtain b and q_{max} from the intercept and the slope of C_e/q_e versus C_e graph, respectively, according to the linear equation of Langmuir model (Eq. 6). Then, b is used to calculate the non-dimensional R_L values by using Eq. 7 to evaluate the feasibility of present process to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). q_e (mg g^{-1}) represent the amount of the inorganic or organic pollutant species adsorbed per g of CMCP at the equilibrium, and q_{max} (mg g^{-1}) represents the monolayer adsorption capacity. C_0 (mg L^{-1}) is the initial, and C_e (mg L^{-1}) is the equilibrium concentration of species in aqueous media. Langmuir constant, b (L mg^{-1}), represents the free energy.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (6)$$

$$R_L = \frac{1}{1 + b \cdot C_0} \quad (7)$$

The constants of the Freundlich model, n (unitless), and K_f (mg g^{-1}) can be obtained by the slope and the intercept of $\ln q_e$ versus $\ln C_e$ plot, respectively, according to the linear form of this model (Eq. 8). The process developed is commented to be favorable if the value of n ranges between 1 and 10.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

The constants q_m (mol g^{-1}) and β ($\text{mol}^2 \text{kJ}^{-2}$) of the D–R isotherm model can be determined using Eqs. 9, 10,

and 11. The Polanyi potential (ϵ) calculated by using Eq. 9 is evaluated in Eq. 10 to determine the adsorption capacity (q_m) and the activity coefficient (β) corresponding to the intercept and slope of $\ln q_e$ versus ϵ^2 plot, respectively. Moreover, the mean adsorption energy (E) calculated by Eq. 11 provides extra information about the mechanisms. Chemical adsorption ($E > 16 \text{ kJ mol}^{-1}$) based on chemical interactions, physical adsorption ($E < 16 \text{ kJ mol}^{-1}$) based on the van Der Waals, or dipole–dipole interactions or ion-exchange ($16 > E > 8 \text{ kJ mol}^{-1}$)-based mechanisms can dominate the process according to the calculations (Helfferich 1962).

$$\epsilon = RT \ln(1 + 1/C_e) \quad (9)$$

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (10)$$

$$E = 1/(-2\beta)^{1/2} \quad (11)$$

Results and discussion

Characterization of the CP and CMCP

According to the images of CP (Fig. 1a, b) and CMCP (Fig. 1c, d) obtained by SEM technique, CTAB modification expanded the surface of the CP. The surfaces of both samples had non-uniform structures, yet the aggregation in unmodified CP seemed to be more than in the CMCP, and the flake-like structures in CP (Fig. 1b) decreased in CMCP (Fig. 1d). Moreover, the aggregated species seemed to spread and the bulk material seemed more regular in CMCP than in CP (Shirzad-Siboni et al. 2015).

Each FTIR spectrum was obtained within the 500–4000 cm^{-1} range and plotted in this wavenumber scale versus transmittance ordinate (Fig. 2) to identify the functional groups present in unmodified and CTAB-modified adsorbents by their vibrational frequencies. The broad band between 3000 and 3500 cm^{-1} corresponds to the stretching vibrations of –OH groups. The two peaks that appeared at 2919 cm^{-1} and 2851 cm^{-1} correspond to –CH stretching in –CH₃ and –CH₂ groups, respectively, and seemed to sharpen in the FTIR spectrum of CMCP adsorbent caused by modification process. Modification with CTAB alters the surface properties of the adsorbent, leading to observable differences in the FTIR spectrum. Due to the long alkyl chain of CTAB, the bands at 2850 cm^{-1} (–CH₂ stretching) and 2920 cm^{-1} (–CH₃ stretching) become more prominent. Consequently, the appearance of distinct –CH₂ and –CH₃ stretching vibration bands in the FTIR spectrum is expected after CTAB modification. This phenomenon is also observed in other CTAB-modified adsorbents (Hua et al. 2023; Luo et al. 2024). The peaks at 1729 cm^{-1} and 1627 cm^{-1} are commented to indicate the C=O stretching of aliphatic acids

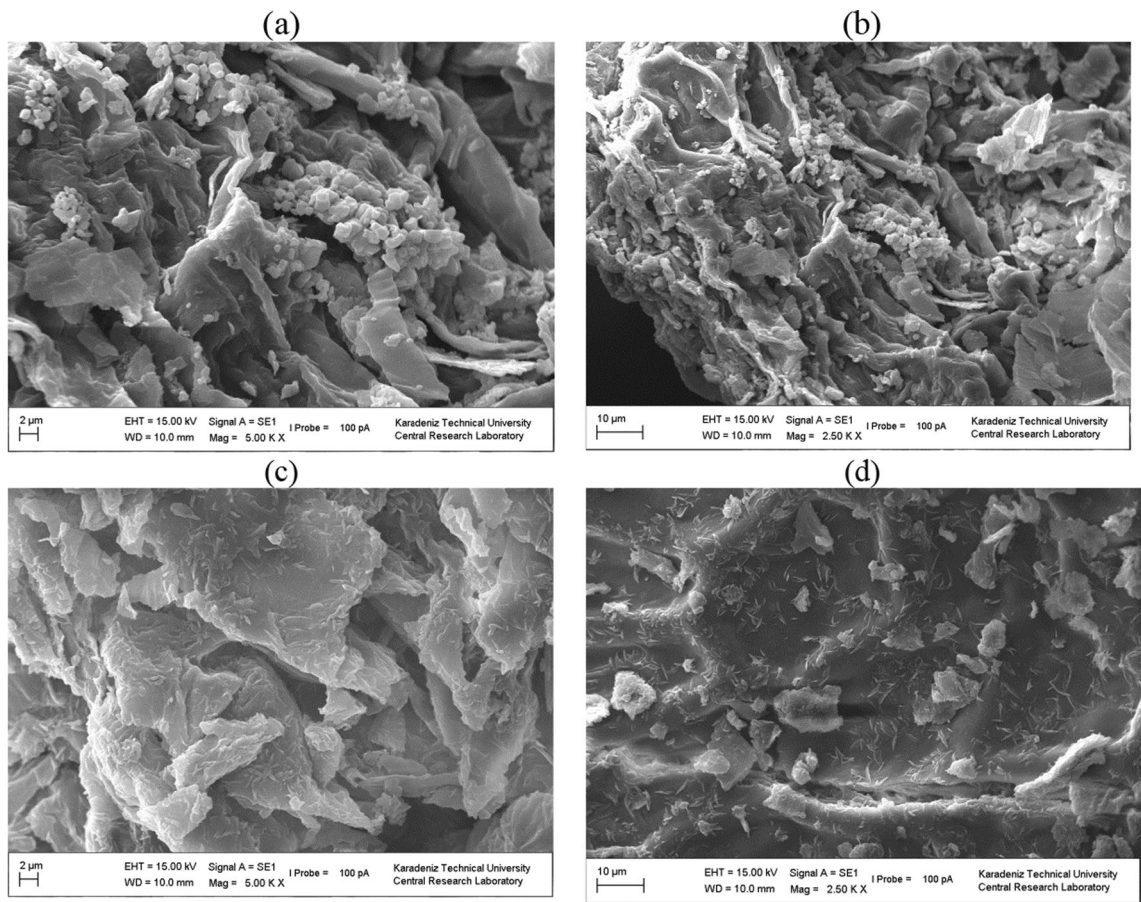


Fig. 1 SEM images of **a, b** CP and **c, d** CMCP

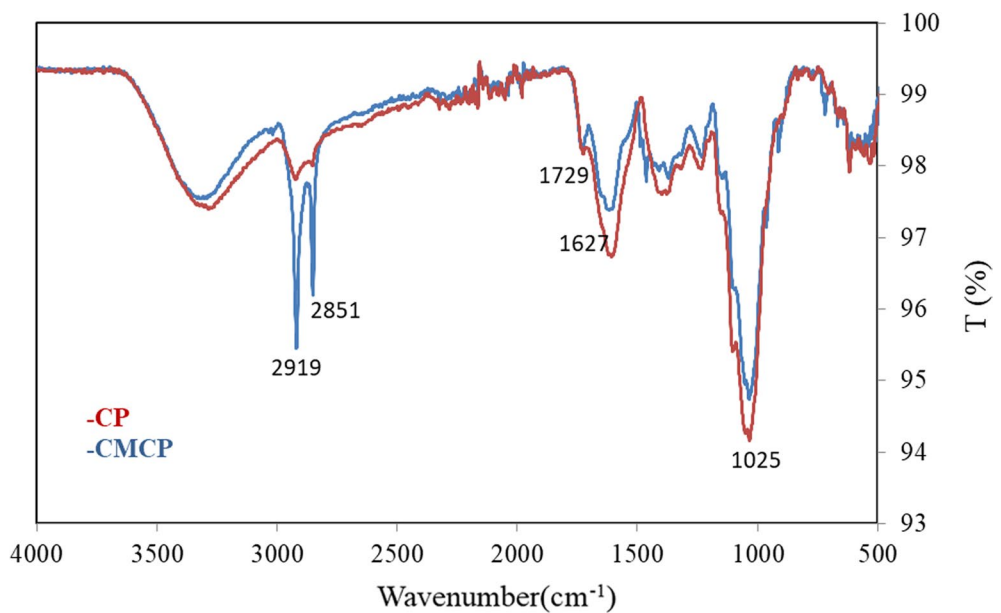


Fig. 2 FTIR spectra of CP and CMCP

and C=O vibration of ionic carboxylate groups, respectively (Akkaya and Guzel 2013). Several peaks appearing between 1300 and 1500 cm^{-1} are commented to belong to phenolic groups in the adsorbents (Khosravi et al. 2014). The peak at 1025 cm^{-1} reveals the presence of amine groups in the structure (Akkaya and Guzel 2013). These results indicated that CP and CMCP adsorbents consist of various functional groups responsible for the adsorption of Cr(VI) and 4-chlorophenol.

One key property of an adsorbent material used to assess its interactions through the electrical behaviors in aqueous media is the value of pH_{pzc} (point of zero charge). Surface functional groups of the adsorbent charged negatively if the pH of the solution is higher than pH_{pzc} or charged positively if the pH of the aqueous media is less than pH_{pzc} . The pH_{pzc} of CP and CMCP were determined to be 6.2 and 5.0, respectively. A close pH_{pzc} value (6.42) was determined by Akkaya and Guzel (2013) for cucumber peel.

Influences of the initial pH

Given that the ionization degrees of pollutants and the surface charge of the adsorbent are greatly influenced by the pH of the aqueous environment, optimizing pH is the primary focus in adsorption studies. Cr(VI) solution in 100 mg L^{-1} concentration or 4-chlorophenol solution in 50 mg L^{-1} concentration was used in pH investigations. The pH was adjusted to various values in the range of 1.5–7.0 for Cr(VI) retention and in the range of 2.0–10.0 for 4-chlorophenol retention. 10 mL of pollutant solution was added to each adsorbent material (CP and CMCP) in a 3.0 g L^{-1} dosage. Batch experiments were utilized for 120 min. As demonstrated in Fig. 3, Cr(VI) adsorption is higher at lower pH levels, reaching its maximum

at pH 2.5, before rapidly decreasing as the pH increases. When the pH of Cr(VI) solutions increases from 2.5 to 7.0, the adsorbed amount of Cr(VI) ions onto CMCP and CP decreases from 22.2 to 10.3 mg g^{-1} and from 4.40 to 2.87 mg g^{-1} , respectively. This phenomenon can be explained by the predominance of HCrO_4^{-2} and $\text{Cr}_2\text{O}_7^{-2}$ at pH range of 2.0–6.0, while CrO_4^{-2} dominated when $\text{pH} > 6.0$ (Chen et al. 2023). Figure 3 demonstrates that with decreasing pH, the surface of CMCP and CP becomes increasingly positively charged. This enhances the electrostatic attraction between the anionic Cr(VI) species and the CMCP and CP surface, making Cr(VI) adsorption more favorable at lower pH values. Conversely, at higher pH levels, the surface of CMCP and CP becomes more negatively charged, leading to increased competition between OH^- ions and anionic Cr(VI) species, as well as stronger electrostatic repulsion between the adsorbate and the adsorbent surface (Nguyen et al. 2025). These results are compatible with the pH_{pzc} values determined for the CP and CMCP (6.2 and 5.0, respectively). When the pH of the aqueous solution is lower than the pH_{pzc} of the adsorbent ($\text{pH} < \text{pH}_{\text{pzc}}$), the surface of the adsorbent becomes positively charged. As a result, the adsorption efficiency of anionic species, such as Cr(VI), which are present in the solution in their anionic form, increases. This result is consistent with previous studies on chromium removal using various other adsorbents (Khalfaoui et al. 2024; Masuku et al. 2024). In addition to these, it is observed that the modification of CP with CTAB significantly increases the Cr(VI) adsorption efficiency. Cationic surfactants like CTAB can bind to the CP surface, making the surface positively charged. The positively charged surface can then adsorb anionic

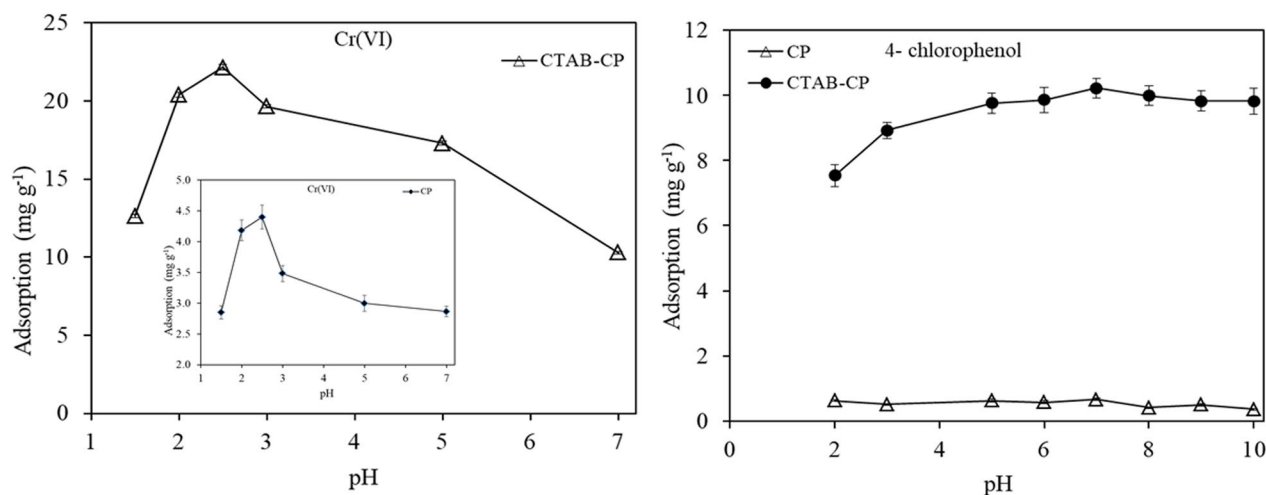


Fig. 3 Influences of initial pH on the uptake of Cr(VI) and 4-chlorophenol

Cr(VI) species more effectively through electrostatic attraction (Karnjanakom and Maneechakr 2019).

On the other hand, when comparing the 4-chlorophenol adsorption capacities of CP and CMCP across different pH levels, it is observed that CP adsorbs a negligible amount of 4-chlorophenol in the pH range of 2.0–10.0, whereas CMCP exhibits significant adsorption over a wide pH range. The maximum 4-chlorophenol adsorption capacities of CP and CMCP at pH 7.0 are recorded as 0.67 mg g⁻¹ and 10.2 mg g⁻¹, respectively (Fig. 3). 4-chlorophenol behaves as a weak acid with a pK_a value of 9.38. Below this pH, 4-chlorophenol predominantly exists in molecular form, and a neutral molecule has greater hydrophobicity than its ionic form. The modification of CP with CTAB introduces a long alkyl chain into the structure, indicating that hydrophobic interactions play a dominant role in the adsorption of 4-chlorophenol onto the CMCP surface in the pH range of 2.0–9.0. Similar results have been reported by Zhang et al. (2015) in the evaluation of the adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solutions. At pH 10.0, the significant retention of 4-chlorophenol suggests that the 4-chlorophenolate ions formed at this pH interact electrostatically with the positive charge induced on the CMCP surface due to CTAB modification. As a result, subsequent removal experiments were conducted with a fixed initial pH value of 2.5 for Cr(VI) and a natural initial pH value of 7.3 for 4-chlorophenol.

Influences of the contact time and the kinetic studies

To investigate how contact time affects the adsorption capacity, a solution of 100 mg L⁻¹ Cr(VI) was adjusted to an initial pH of 2.5, while 50 mg L⁻¹ of 4-chlorophenol was processed at its natural initial pH of 7.3. Both pollutants were treated with 3.0 g L⁻¹ of CMCP for durations ranging from 1 to 480 min. At the end of each duration, the liquid phases of the centrifuged samples were analyzed to determine the final concentrations of Cr(VI) and 4-chlorophenol remaining in the solution, to compute the adsorbed amounts (q_e) by using Eq. 1. The processes occurred rapidly at the beginning of the adsorption because many adsorption sites were readily available for uptake (Fig. 4). The adsorption capacity of CMCP increased in the range of 1–120 min of contact time for both adsorbates and then became almost constant since the attainable surface sites of CMCP reached saturation in the state of equilibrium (El-Tawabty et al. 2024). The contact time for the CMCP with both pollutants was optimized to be 120 min from this stage.

The kinetic parameters obtained by PFO, PSO, and IPD models and the correlation coefficients (R^2) are represented in Table 1.

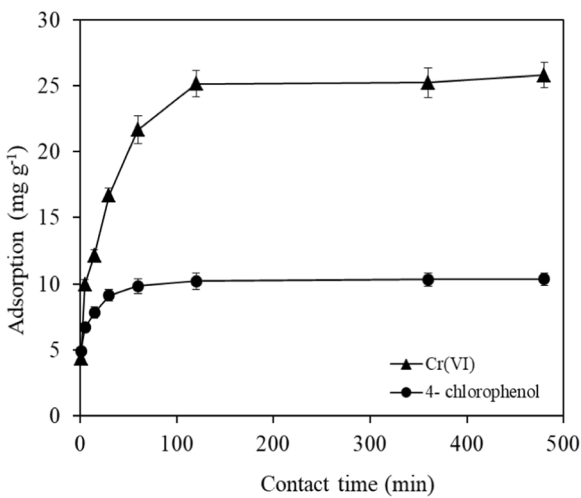


Fig. 4 Impact of contact time on the adsorption of Cr(VI) and 4-chlorophenol

Table 1 Kinetic model parameters for the adsorption of Cr(VI) and 4-chlorophenol onto CMCP

	Adsorbate	
	Cr(VI)	4-chlorophenol
$q_{e\text{ exp}}$	25.80	10.35
PFO		
k_1	- 0.0099	- 0.0152
$q_{e\text{ cal}}$	11.28	2.53
R^2	0.7105	0.8992
PSO		
k_2	0.003	0.029
$q_{e\text{ cal}}$	26.31	10.42
R^2	0.9992	0.9999
IPD		
$k_{id,1}$	2.45	0.71
R^2	0.9780	0.9399
$k_{id,2}$	0.05	0.01
R^2	0.6140	0.9745
C	9.44	2.84

According to Table 1, the calculated capacities ($q_{e\text{ cal}}$) for the adsorption of Cr(VI) and 4-chlorophenol (26.31 mg g⁻¹ and 10.42 mg g⁻¹, respectively) in the PSO model are compatible with the experimental capacities ($q_{e\text{ exp}}$, 25.80 mg g⁻¹ and 10.35 mg g⁻¹, respectively). However, $q_{e\text{ cal}}$ values calculated by using PFO model (11.28 mg g⁻¹ for Cr(VI) and 2.53 mg g⁻¹ for 4-chlorophenol) are not compatible with $q_{e\text{ exp}}$. Moreover, another result is that the R^2 values of the PSO model found to be 0.9992 for Cr(VI) and 0.9999 for 4-chlorophenol

retention are higher than obtained for PFO model (0.7105 and 0.8992, respectively) and closer to linear. According to these results, PSO model is favorable for the adsorption processes as the correlation coefficients (R^2) of PFO and PSO kinetic models are compared to each other, and the experimental adsorption capacities ($q_{e\text{ exp}}$) are compared to calculated ones ($q_{e\text{ cal}}$) predicted from both models revealing that chemical adsorption is the dominant mechanism in the adsorption processes of Cr(VI) and 4-chlorophenol onto CMCP (Ho and McKay 1998; Gao et al. 2023). Similarly, PSO kinetic model is demonstrated to be favorable for the adsorption of Cr(VI) onto calcined CoFe-LDH/T g- C_3N_4 (Ou et al. 2020) and H_3PO_4 -activated carbon prepared by from apple peels (Enniya et al. 2018), and for the adsorption of 4-chlorophenol onto surfactant-modified zeolite (Kuleyin 2007), chemically modified chitosan (Zhou et al. 2014) and activated carbon obtained from the hulls of *Prosopis africana* seed (Garba and Rahim 2016).

In addition, the adsorption process is controlled by intraparticle diffusion if a straight line is obtained from q_t vs. $t^{1/2}$ plot, yet the multilinearity of the same plot is the clue of adsorption occurring in several stages where more steps may have control on the process (Huang et al. 2009). Thus, situated, film diffusion is the first stage in which the pollutant species in bulk solution are transported to the external surface of the solid material. Here, pore diffusion (or intraparticle diffusion) occurs as the second stage, where the pollutant species at the external surface are gradually adsorbed into the pores of the solid adsorbent. In the third stage (the equilibrium), the pollutant species rapidly attack to the internal surfaces of the pores and get adsorbed

onto the available active sites. The second stage usually controls the adsorption rate, yet the third stage usually occurs so rapidly. The rate constant of the rapid stage (3rd stage) is neglected, and the rate constants of the 1st and 2nd ones ($k_{id,1}$ and $k_{id,2}$, respectively) were calculated to state the dominant one for a better definition of the mechanisms since the slowest stage determines the rate of adsorption. As noticed in Table 1, intraparticle diffusion seems to control the reaction rates in the adsorption mechanisms of Cr(VI) and 4-chlorophenol effectively since $k_{id,2}$ values are smaller than the $k_{id,1}$ values, whereas C values, found to be unequal to zero, revealed that the film diffusion, besides the intraparticle diffusion, contributed the adsorption of Cr(VI) and 4-chlorophenol onto CMCP (Chieng et al. 2015).

Impact of CMCP dosage

Solutions of Cr(VI) at an initial pH of 2.5 and 4-chlorophenol at a natural pH of 7.3 were prepared at a concentration of 250 mg L^{-1} . A 10 mL of each pollutant solution was treated with varying amounts of CMCP (ranging from 1.0 to 10.0 g L^{-1}) over a period of 120 min to study the effects of dosage, and the results are depicted in Fig. 5. As the adsorbent dosage increased, the adsorption capacities of Cr(VI) and 4-chlorophenol on CMCP at equilibrium decreased. This decrease could be attributed to an excess of active sites, many of which remain unsaturated after only a portion of the CMCP participates in pollutant adsorption at a constant concentration. Additionally, possible agglomeration may occur, leading to a reduced overall surface area (Huang et al. 2014). However, the

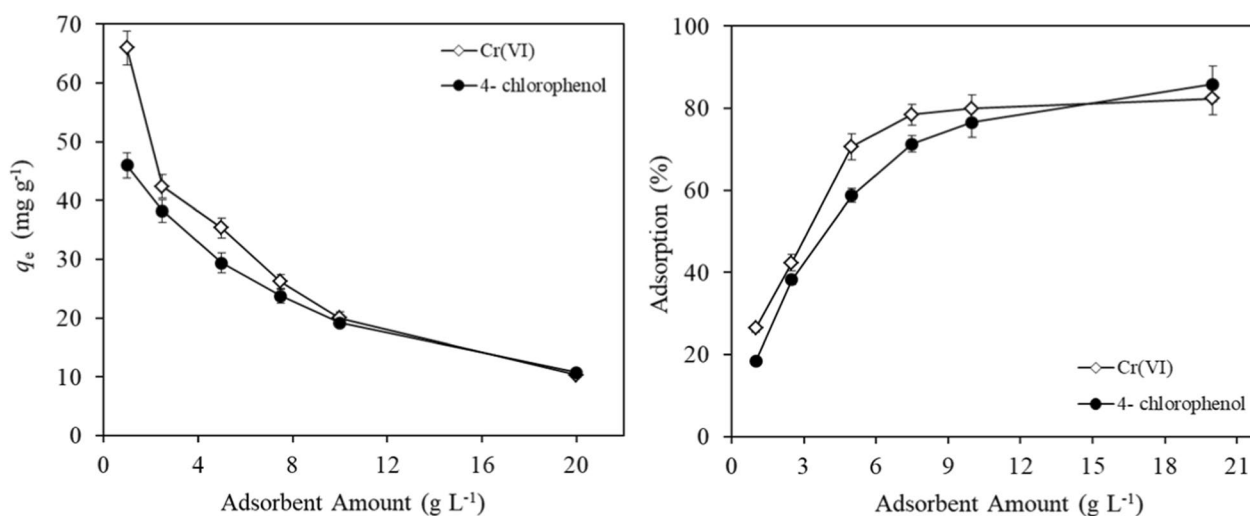


Fig. 5 Effect of adsorbent amount on adsorption of Cr(VI) and 4-chlorophenol

percentage of adsorption increase in accordance to increasing amounts of the adsorbent, which means exchangeable numbers of candidate active sites were available for adsorption (Semerjian 2010).

Influences of Cr(VI) and 4-chlorophenol concentrations and isotherm studies

A dosage of 3.0 g L^{-1} of CMCP was treated with 10 mL of pollutant solutions at varying concentrations ($50\text{--}1000 \text{ mg L}^{-1}$) over a period of 120 min. The initial pH of the solutions was adjusted to 2.5 for Cr(VI) and remained at a natural pH of 7.3 for 4-chlorophenol. As the pollutant concentration increased from 50 to 1000 mg L^{-1} , the capacity of CMCP also increased from 13.15 to 77.00 mg g^{-1} for Cr(VI) adsorption and from 8.65 to 78.33 mg g^{-1} for 4-chlorophenol adsorption, while the percentage of adsorption decreased from 78.9 to 23.1% for Cr(VI) and from 51.9 to 23.1%

for 4-chlorophenol (Fig. 6). In brief, the amounts of adsorbed organic and inorganic pollutants increased with the increase in initial concentrations in the liquid phase suggesting that adsorption is driven by the concentration gradient (Nasanjargal et al. 2021), as higher concentrations of pollutant species more effectively occupied the active sites of the CMCP. Moreover, the chlorine in the chemical structure of 4-chlorophenol may cause low energy for interactions with water, low water-solubility, and highly hydrophobic interactions with CMCP, which enhances the adsorption capacity (Rawajfih and Nsour 2006). However, the adsorption percentages decreased due to surface saturation, as the constant number of available active sites became clogged and fully occupied by the highly concentrated pollutant species (Senturk et al. 2009).

Equilibrium data were evaluated by Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm

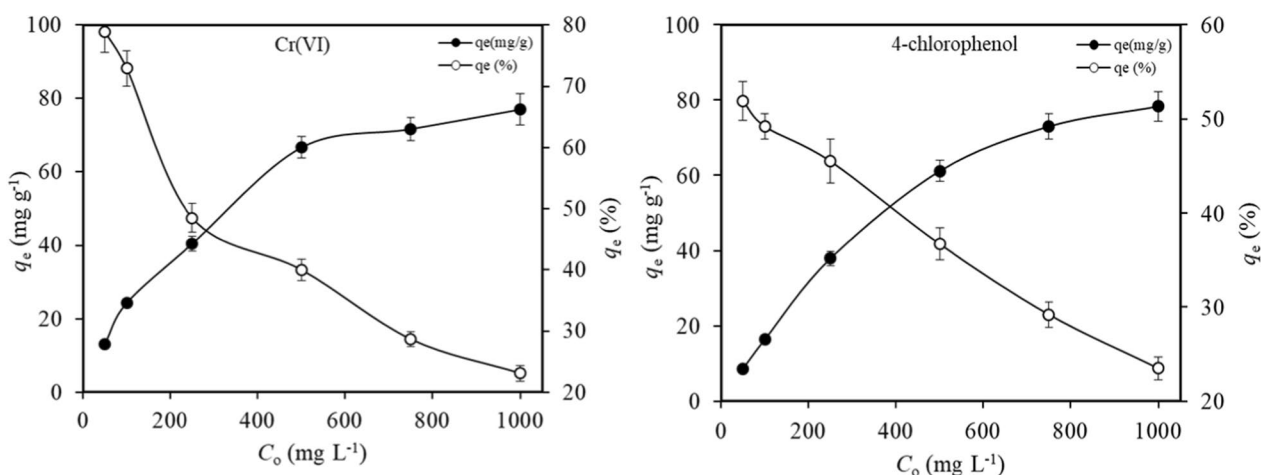


Fig. 6 Effect of initial adsorbate concentration on their uptake

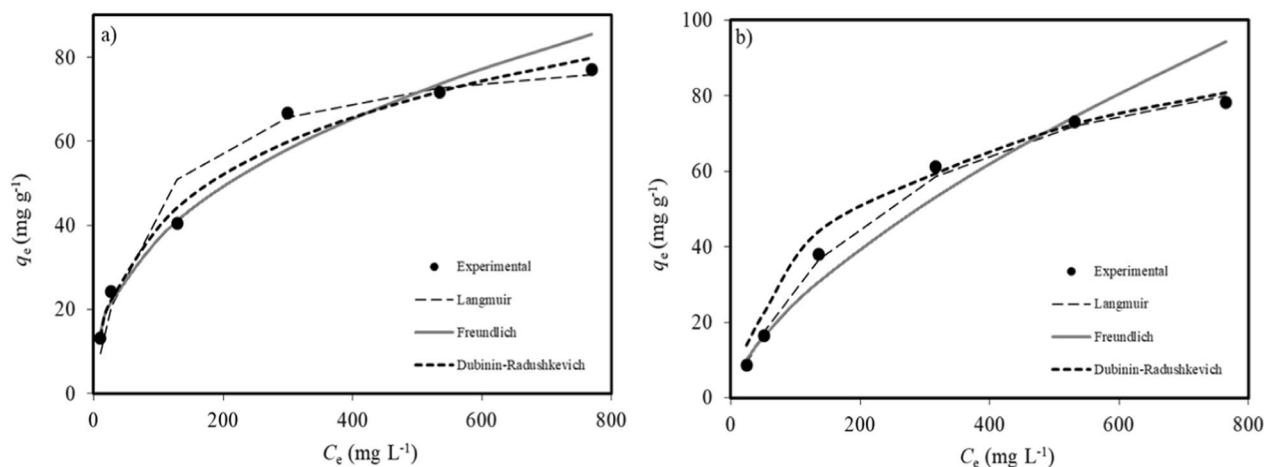


Fig. 7 Adsorption isotherm models for **a** Cr(VI) uptake by CMCP **b** 4-chlorophenol uptake by CMCP

Table 2 Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm parameters for the adsorption of organic and inorganic pollutants onto CMCP

	Cr(VI)	4-chlorophenol
Langmuir isotherm model		
$q_{\max}$	84.03	107.5
b	0.0120	0.0038
R^2	0.9907	0.9958
Freundlich isotherm model		
K_f	5.60	1.26
n	2.44	1.54
R^2	0.9775	0.9706
D–R isotherm model		
q_m	11.94	13.03
β	−0.0053	−0.0046
E	9.71	10.4
R^2	0.9885	0.9879

models to commentate the characteristics of the process by interpreting the information on the interactions between CMCP and the inorganic and organic adsorbate species (Fig. 7a, b). The results of the isotherm studies are presented in Table 2.

Langmuir monolayer adsorption capacity ($q_{\max}$) of CMCP was 84.03 mg g^{−1} for Cr(VI) and 107.5 mg g^{−1} for 4-chlorophenol adsorption. The monolayer adsorption capacity of CMCP in the retention of inorganic and organic pollutants is higher than many other adsorbent materials (Kuleyin 2007; Ding et al. 2016; Gao et al. 2023; Kurniawan et al. 2010; Gupta and Babu 2009; Quintelas et al. 2008; Rambabu et al. 2020) reported in the literature

(Table 3). On the other hand, R_L values were in the range of 0–1, and n values were in the range of 1–10, showing that both pollutants' adsorption processes were favorable in optimized experimental conditions. As the correlation coefficients were compared, R^2 values obtained by the Langmuir model were higher than Freundlich model (Table 2), revealing that the adsorption processes in the retention of Cr(VI) and 4-chlorophenol onto CMCP can be interpreted better by Langmuir equation (Park et al. 2021). This result demonstrates that the CMCP surface comprises uniform binding regions with areas of identical energy. Mean adsorption energies were 9.71 kJ mol^{−1} and 10.4 kJ mol^{−1} for Cr(VI) and 4-chlorophenol, respectively, indicating that ion-exchange-based mechanism is dominant in the adsorption processes of both pollutants.

Influences of ionic strength

Separate solutions of Cr(VI) at a concentration of 125 mg L^{−1} (pH 2.5) and 4-chlorophenol at 100 mg L^{−1} (natural pH 7.3) were treated with 3.0 g L^{−1} of CMCP for 120 min in the presence of 0.01–0.1 M Na₂SO₄ and Na₃PO₄ to investigate the influence of foreign ions on the process (Fig. 8). The Cr(VI) adsorption capacity of CMCP decreased in the presence of Na₂SO₄ and Na₃PO₄. The presence of sulfate and phosphate was commented to decrease the adsorption of Cr(VI) because of the competing behavior of multivalent anions with the targeted pollutant (chromate anions) to adsorb to the available sites on CMCP (Korus et al. 2020). The decreasing trend in the adsorption capacity was stronger in the presence of phosphate anions as compared to that of sulfate anions. Heidari et al. (2011) observed this trend in the adsorptive removal of the As(V), which behaves chromium-like

Table 3 Comparison of 4-chlorophenol and Cr(VI) adsorption capacities of various adsorbents

Adsorbent	Adsorbate	$q_{\max}$ (mg g ^{−1})	Reference
HDTMA-zeolite	4-chlorophenol	12.7065	Kuleyin (2007)
BDTDA-zeolite		6.4102	
Hydroxylated and carboxylated SWCNTs	4-chlorophenol	29	Ding et al. (2016)
Hydroxylated CNT composites (HCNTs/Fe ₃ O ₄)	4-chlorophenol	41.6	
NaOH-treated coconut shell charcoal		54.65	Kurniawan et al. (2010)
HNO ₃ -treated coconut shell charcoal		23.13	
TiO ₂ -coated coconut shell charcoal	4-chlorophenol	48.42	This study
CMCP (CTAB-modified cucumber peels)	4-chlorophenol	107.5	
Sawdust	Cr(VI)	41.9	Gupta and Babu (2009)
<i>Streptococcus Equisimilis</i> , <i>Bacillus coagulans</i> , <i>Escherichia coli</i> supported on granular AC	Cr(VI)	16.077	
		19.455	Quintelas et al. (2008)
		9.533	
Date palm empty fruit bunch	Cr(VI)	70.49	Rambabu et al. (2020)
CMCP (CTAB-modified cucumber peels)	Cr(VI)	84.03	

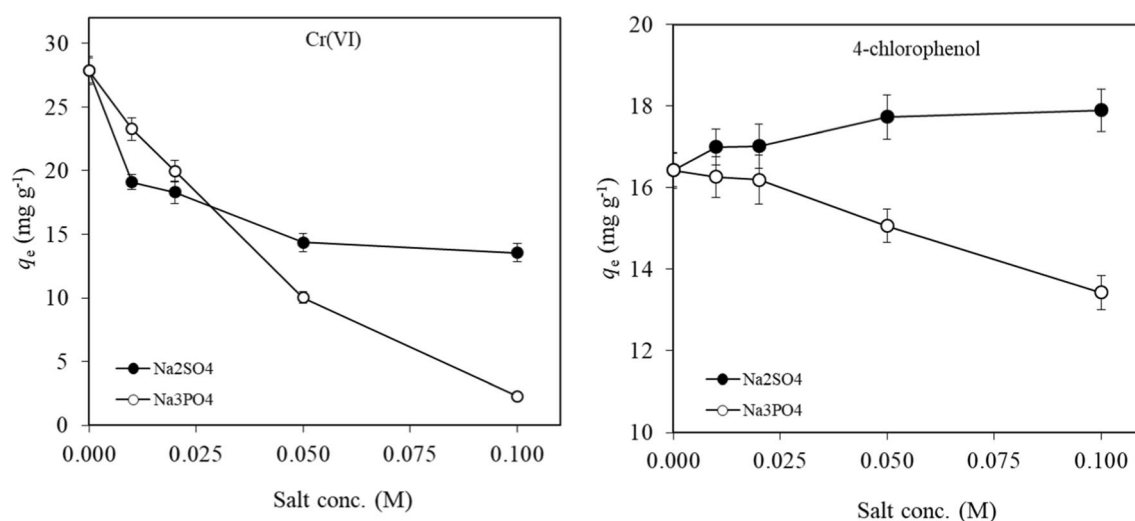


Fig. 8 Effect of salt concentration on the adsorption of Cr(VI) and 4-chlorophenol

in the aqueous solution by being predominantly present in anionic species (H_2AsO_4^- and HAsO_4^{2-}), and reported a stronger competition between the phosphate anions and arsenate species than that of the sulfate anions. Phosphate anions strongly interfered with the Cr(VI) species and reduced the capacity of the CMCP adsorbent in adsorbing the targeted Cr(VI) species in this study.

Moreover, the presence of Na_3PO_4 reduced the 4-chlorophenol adsorption capacity, yet the presence of Na_2SO_4 improved the 4-chlorophenol adsorption capacity of CMCP. Phosphate anions compete with 4-chlorophenol to adsorb to the active sites of CMCP, and this competition becomes stronger with the increasing concentrations of salt. Conversely, the presence of sulfate up to 0.05 M concentration improved the adsorption capacity of CMCP, and beyond that concentration, the effect of the ionic strength became almost constant. Navarro et al. (2017) also investigated a similar effect for the presence of sulfate ions with various concentrations in 0–0.2 M range for the adsorption of phenol onto *Chaetomorpha*, which tended to increase the adsorption in 0–0.05 M range and then became nearly stable, and reported that sulfate anions didn't compete to adsorb to the active sites because of their being very poor nucleophiles.

Conclusion

A novel and cost-effective adsorbent was developed by chemically modifying cucumber peels (CP) with the cationic surfactant cetyltrimethylammonium bromide (CTAB). The adsorptive properties of the CTAB-modified cucumber peels (CMCP) were examined for the first time in the present study for the removal of

an organic pollutant, 4-chlorophenol, and an inorganic pollutant, Cr(VI). At pH 2.5, the adsorption amount of Cr(VI) was obtained as 4.40 mg g^{-1} and 22.15 mg g^{-1} for natural CP and CMCP, respectively, while at pH 7.0, the adsorption amount of 4-chlorophenol was determined as 0.67 mg g^{-1} and 10.22 mg g^{-1} , respectively. The results indicate that CTAB modification significantly enhances the adsorption capacity of cucumber peels in Cr(VI) and 4-chlorophenol retention. With the advantages of being low-cost, easily prepared, and efficient adsorbent material, CTAB-modified cucumber peels performed high capacity for the retention of inorganic and organic pollutants as compared with other adsorbents in the literature. In our future research, we plan to investigate the removal of other toxic organic and inorganic pollutant species from water and wastewaters through adsorption, using CMCP as the adsorbent.

Acknowledgements

We would like to thank Karadeniz Technical University and Gümüşhane University for the use of their laboratory facilities.

Author contributions

CD contributed to conceptualization and methodology; STO, DO, CD contributed to investigation and writing—original draft; CD contributed to supervision; STO, DO, CD contributed to writing—review & editing.

Funding

Not applicable.

Availability of data and materials

The data that support the findings of this study are available on request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors have no competing interests to declare.

Author details

¹Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey. ²Gumushane Vocational School, Gumushane University, 29100 Gumushane, Turkey.

Received: 12 November 2024 Accepted: 6 March 2025

Published online: 23 June 2025

References

- Abadian S, Shayesteh H, Rahbar-Kelishami A. Effective adsorption of diclofenac sodium from aqueous solution using cationic surfactant modified *Cuminum cyminum* agri-waste: kinetic, equilibrium, and thermodynamic studies. *Int J Phytoremed*. 2023;25(7):840–50.
- Akkaya G, Güzel F. Optimization of copper and lead removal by a novel biosorbent: cucumber (*Cucumis Sativus*) peels—kinetic, equilibrium, and desorption studies. *J Dispers Sci Technol*. 2013;34(10):1295–307. <https://doi.org/10.1080/01932691.2012.743863>.
- Barboza JAT, Penido ES, Ferreira GMD. Production of surfactant-modified banana peel biosorbents applied to treatment and decolorization of effluents. *Colloids Surf a: Physicochem Eng*. 2024;680: 132650.
- Basu M, Guha AK, Ray L. Adsorption of cadmium on cucumber peel: kinetics, isotherm and co-ion effect. *Indian Chem Eng*. 2018;60(2):179–95.
- Bhatnagar A, Sillanpää M, Witek-Krowiak A. Agricultural waste peels as versatile biomass for water purification—A review. *Chem Eng J*. 2015;270:244–71.
- Camoglu AY, Ozdes D, Duran C. Adsorption behaviour of EDTA modified magnetic Fe₃O₄ coated brewed tea waste on Cr(VI) removal. *Chem Afr*. 2023;6:921–31. <https://doi.org/10.1007/s42250-022-00545-8>.
- Chen Y, Yang J, Abbas A. Enhanced chromium (VI) adsorption onto waste pomegranate-peel-derived biochar for wastewater treatment: performance and mechanism. *Toxics*. 2023;11:440.
- Chieng HI, Priyantha N, Lim LB. Effective adsorption of toxic brilliant green from aqueous solution using peat of *Brunei Darussalam*: isotherms, thermodynamics, kinetics and regeneration studies. *RSC Adv*. 2015;5:34603–15. <https://doi.org/10.1039/C5RA01572C>.
- Ding H, Li X, Wang J, Zhang X, Chen C. Adsorption of chlorophenols from aqueous solutions by pristine and surface functionalized single-walled carbon nanotubes. *J Environ Sci*. 2016;43:187–98. <https://doi.org/10.1016/j.jes.2015.09.004>.
- Ding J, Li X, Shan Y, Yu S, Yu W, Liu Y, Zhao W, Li X, Liu M, Ding Y. Super facile one-step synthesis of aromatic amine waste residue derived N-rich porous carbon for hyper efficient p-nitrophenol adsorption. *J Environ Chem Eng*. 2021;9(2): 105106. <https://doi.org/10.1016/j.jece.2021.105106>.
- Dubinin MM, Radushkevich LV. Equation of the characteristic curve of activated charcoal. *Proc Acad Sci USSR Phys Chem Sect*. 1947;55:331–3.
- El-Tawabty DS, Abd El-Aleem IM, Ahmed S, El-Hadary AE, Ali RM. Hexavalent chromium adsorption by watermelon peels from tannery wastewater. *Egypt J Chem*. 2024;67(13):241–50. <https://doi.org/10.21608/ejchem.2024.257332.9027>.
- Enniya I, Rghioui L, Jourani A. Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels. *Sustain Chem Pharm*. 2018;7:9–16. <https://doi.org/10.1016/j.scp.2017.11.003>.
- Foroughi-dahr M, Abolghasemi H, Esmaili M, Nazari G, Rasem B. Experimental study on the adsorptive behavior of Congo red in cationic surfactant-modified tea waste. *Process Saf Environ Prot*. 2015;95:226–36.
- Freundlich HMF. Über die adsorption in lösungen. *Z Phys Chem*. 1906;57:385–470.
- Gao H, Han X, Wang R, Zhu K, Han R. Adsorption and catalytic degradation of bisphenol A and p-chlorophenol by magnetic carbon nanotubes. *Environ Res*. 2023;231(3): 116314. <https://doi.org/10.1016/j.envres.2023.116314>.
- Garba ZN, Rahim AA. Evaluation of optimal activated carbon from an agricultural waste for the removal of para-chlorophenol and 2,4-dichlorophenol. *Process Saf Environ Prot*. 2016;102:54–63. <https://doi.org/10.1016/j.psep.2016.02.006>.
- Georgaki MN, Charalambous M, Kazakis N, Talias MA, Georgakis C, Papamitsou T, Mytigiaki C. Chromium in water and carcinogenic human health risk. *Environments*. 2023;10(2):33. <https://doi.org/10.3390/environments10020033>.
- Gómez M, Murcia MD, Dams R, Christofi N, Gómez E, Gómez JL. Removal efficiency and toxicity reduction of 4-chlorophenol with physical, chemical and biochemical methods. *Environ Technol*. 2012;33(9):1055–64. <https://doi.org/10.1080/09593330.2011.606847>.
- Gupta S, Babu BV. Modeling, simulation, and experimental validation for continuous Cr(VI) removal from aqueous solutions using sawdust as an adsorbent. *Bioresour Technol*. 2009;100(23):5633–40. <https://doi.org/10.1016/j.biortech.2009.06.025>.
- Hadi S, Taheri E, Amin MM, Fatehizadeh A, Lima EC. Fabrication of activated carbon from pomegranate husk by dual consecutive chemical activation for 4-chlorophenol adsorption. *Environ Sci Pollut Res*. 2021;28:13919–30. <https://doi.org/10.1007/s11356-020-11624-z>.
- Heidari M, Moattar F, Naseri S, Samadi M, Khorasani N. Evaluation of aluminum-coated pumice as a potential arsenic(V) adsorbent from water resources. *Int J Environ Res*. 2011;5(2):447–56. <https://doi.org/10.22059/ijer.2011.329>.
- Helferich F. Ion exchange. New York: McGraw-Hill; 1962.
- Ho YS, McKay G. Kinetic models for the sorption of dye from aqueous solution by wood. *Process Saf Environ Prot*. 1998;76(2):183–91.
- Hua Z, Pan Y, Hong Q. Adsorption of Congo red dye in water by orange peel biochar modified with CTAB. *RSC Adv*. 2023;13:12502.
- Huang J, Wang X, Deng X. Synthesis, characterization, and adsorption properties of phenolic hydroxyl group modified hyper-cross-linked polymeric adsorbent. *J Colloid Interface Sci*. 2009;337(1):19–23. <https://doi.org/10.1016/j.jcis.2009.04.070>.
- Huang Y, Li S, Chen J, Zhang X, Chen Y. Adsorption of Pb(II) on mesoporous activated carbons fabricated from water hyacinth using H₃PO₄ activation: adsorption capacity, kinetic and isotherm studies. *Appl Surf Sci*. 2014;293:160–8. <https://doi.org/10.1016/j.apsusc.2013.12.123>.
- Jain S, Jayaram RV. Adsorption of phenol and substituted chlorophenols from aqueous solution by activated carbon prepared from jackfruit (*artocarpus heterophyllus*) peel-kinetics and equilibrium studies. *Sep Sci Technol*. 2007;42(9):2019–32.
- Karnjanakom S, Maneechakr P. Adsorption behaviors and capacities of Cr(VI) onto environmentally activated carbon modified by cationic (HDTMA and DDAB) surfactants. *J Mol Struct*. 2019;1186:80–90.
- Khalfaoui A, Benalia A, Selama Z, Hammoud A, Derbal K, Panico A, Pizzi A. Removal of chromium (VI) from water using orange peel as the biosorbent: experimental, modeling, and kinetic studies on adsorption isotherms and chemical structure. *Water*. 2024;16:742.
- Khosravi R, Fazlzadehdavil M, Barikbin B, Taghizadeh AA. Removal of hexavalent chromium from aqueous solution by granular and powdered *Peganum Harmala*. *Appl Surf Sci*. 2014;292:670–7. <https://doi.org/10.1016/j.apsusc.2013.12.031>.
- Korus I, Bobik M, Bąk K. (2020) Influence of ionic environment on the process of adsorption of heavy metal ions on magnetic iron oxides. *Desalin Water Treat*. 2020;186:224–33. <https://doi.org/10.5004/dwt.2020.25330>.
- Kuleyin A. Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite. *J Hazard Mater*. 2007;144(1–2):307–15. <https://doi.org/10.1016/j.jhazmat.2006.10.036>.
- Kurniawan TA, Waihung L, Repo E, Sillanpää ME. Removal of 4-chlorophenol from contaminated water using coconut shell waste pretreated with chemical agents. *Int J Chem Technol*. 2010;85:1616–27. <https://doi.org/10.1002/jctb.2473>.
- Lagergren S. About the theory of so-called adsorption of soluble substance. *Kungl Svenska Vetenskapsakad Handl*. 1898;24:1–39.
- Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J Am Chem Soc*. 1918;40(9):1361–403.
- Li H, Hou R, Chen Y, Chen H. Removal of hexavalent chromium from aqueous solutions using sulfonated peat. *Water*. 2019;11(10):1980. <https://doi.org/10.3390/w11101980>.
- Li JM, Meng XG, Hu CW, Du J. Adsorption of phenol, p-chlorophenol and p-nitrophenol onto functional chitosan. *Biores Technol*. 2009;100(3):1168–73. <https://doi.org/10.1016/j.biortech.2008.09.015>.
- Liu B, Xin YN, Zou J, Khoso FM, Liu YP, Jiang XY, Peng S, Yu JG. Removal of chromium species by adsorption: fundamental principles, newly developed

- adsorbents and future perspectives. *Molecules*. 2023;28:639. <https://doi.org/10.3390/molecules28020639>.
- Liu Y, Liu X, Zhang G, Ma T, Du T, Yang Y, Lu S, Wang W. Adsorptive removal of sulfamethazine and sulfamethoxazole from aqueous solution by hexadecyl trimethyl ammonium bromide modified activated carbon. *Colloid Surf A Physicochem Eng Asp*. 2019;564:131–41. <https://doi.org/10.1016/j.colsurfa.2018.12.041>.
- Luo M, Duan W, Li S-W, Yang Y, Yang G, Li H, Yu X. Remediation of hexavalent chromium in water and soil by pristine and chemically modified pine barks: effects and mechanisms. *Environ Technol Inno*. 2024;36: 103876.
- Masuku M, Nure JF, Atagana HI, Hlongwa N, Nkambule TTI. Pinecone biochar for the Adsorption of chromium (VI) from wastewater: Kinetics, thermodynamics, and adsorbent regeneration. *Environ Res*. 2024;258: 119423.
- Nasanjargal S, Munkhpurev B, Kano N, Kim H, Ganchimeg Y. The removal of Chromium(VI) from aqueous solution by amine-functionalized zeolite: kinetics, thermodynamics, and equilibrium study. *J Environ Prot*. 2021;12:654–75. <https://doi.org/10.4236/jep.2021.129040>.
- Navarro AE, Hernandez-Vega A, Masud ME, Roberson LM, Diaz-Vázquez LM. Bioremoval of phenol from aqueous solutions using native caribbean seaweed. *Environments*. 2017;4(1):1. <https://doi.org/10.3390/environments4010001>.
- Nguyen ML, Nguyen TT, Nguyen TTT, Chau NTT, Ngo HL, Tran ATK, Juang R-S. Composite adsorbent of Terminalia catappa fruit shell-derived activated carbon and chitosan for enhanced removal of chromium(VI): kinetics, thermodynamics, equilibrium and adsorption mechanism. *J Chem Technol Biotechnol*. 2025;100:231–42.
- Ou B, Wang J, Wu Y, Zhao S, Wang Z. Efficient removal of Cr(VI) by magnetic and recyclable calcined CoFe-LDH/g-C₃N₄ via the synergy of adsorption and photocatalysis under visible light. *Chem Eng J*. 2020;380: 122600.
- Ozeken ST, Ozdes D, Duran C. Adsorptive removal of Cr(VI) and Cu(II) ions from aqueous solutions by a natural moss. *Aqua Water Infrastruct Ecosyst Soc*. 2023;72(11):2170–85.
- Park JM, Kim CM, Jhung SH. Melamine/polyaniline-derived carbons with record-high adsorption capacities for effective removal of phenolic compounds from water. *Chem Eng J*. 2021;420(2): 127627. <https://doi.org/10.1016/j.cej.2020.127627>.
- Prasanna NS, Mitra J. Isolation and characterization of cellulose nanocrystals from *Cucumis sativus* peels. *Carbohydr Polym*. 2020;247: 116706. <https://doi.org/10.1016/j.carbpol.2020.116706>.
- Quintelas C, Fernandes B, Castro J, Figueiredo H, Tavares T. Biosorption of Cr(VI) by three different bacterial species supported on granular activated carbon—a comparative study. *J Hazard Mater*. 2008;153(1–2):799–809. <https://doi.org/10.1016/j.jhazmat.2007.09.027>.
- Rambabu K, Bharath G, Banat F, Show PL. Biosorption performance of date palm empty fruit bunch wastes for toxic hexavalent chromium removal. *Environ Res*. 2020;187: 109694. <https://doi.org/10.1016/j.envres.2020.109694>.
- Rambabu K, Thanigaivelan A, Bharath G, Sivarajasekar N, Banat F, Show PL. Biosorption potential of Phoenix dactylifera coir wastes for toxic hexavalent chromium sequestration. *Chemosphere*. 2021;268: 128809. <https://doi.org/10.1016/j.chemosphere.2020.128809>.
- Rawajfih Z, Nsour N. Characteristics of phenol and chlorinated phenols sorption onto surfactant-modified bentonite. *J Colloid Interface Sci*. 2006;298(1):39–49. <https://doi.org/10.1016/j.jcis.2005.11.063>.
- Rubilar O, Diez MC, Gianfreda L. Transformation of chlorinated phenolic compounds by white rot fungi. *Crit Rev Environ Sci Technol*. 2008;38(4):227–68.
- Semerjian L. Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust. *J Hazard Mater*. 2010;173(1–3):236–42. <https://doi.org/10.1016/j.jhazmat.2009.08.074>.
- Senturk HB, Ozdes D, Gundogdu A, Duran C, Soyak M. Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: equilibrium, kinetic and thermodynamic study. *J Hazard Mater*. 2009;172(1):353–62.
- Shirzad-Siboni M, Khataee A, Hassani A, Karaca S. Preparation, characterization and application of a CTAB-modified nanoclay for the adsorption of an herbicide from aqueous solutions: Kinetic and equilibrium studies. *CR Chim*. 2015;18(2):204–14. <https://doi.org/10.1016/j.crci.2014.06.004>.
- Stavrinou A, Aggelopoulos CA, Tsakiroglou CD. Exploring the adsorption mechanisms of cationic and anionic dyes onto agricultural waste peels of banana, cucumber and potato: adsorption kinetics and equilibrium isotherms as a tool. *J Environ Chem Eng*. 2018;6:6958–70.
- Tamjidi S, Moghadasa BK, Esmaeili H, Khoo FS, Gholami G, Ghasemi M. Improving the surface properties of adsorbents by surfactants and their role in the removal of toxic metals from wastewater: a review study. *Process Saf Environ Prot*. 2021;148:775–95.
- Weber WJ Jr, Morris JC. Kinetics of adsorption on carbon from solution. *J Sanit Eng Div*. 1963;89:31–60.
- Zeghioud H, Fryda L, Mahieu A, Visser R, Kane A. Potential of flax shives and beech wood-derived biochar in methylene blue and carbamazepine removal from aqueous solutions. *Materials*. 2022;15(8):2824. <https://doi.org/10.3390/ma15082824>.
- Zhang L, Zhang B, Wu T, Sun D, Li Y. Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution. *Colloid Surf A Physicochem Eng Asp*. 2015;484:118–29. <https://doi.org/10.1016/j.colsurfa.2015.07.055>.
- Zhou LC, Meng XG, Fu JW, Yang YC, Yang P, Mi C. Highly efficient adsorption of chlorophenols onto chemically modified chitosan. *Appl Surf Sci*. 2014;292:735–41. <https://doi.org/10.1016/j.apsusc.2013.12.041>.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.