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REMOVAL OF CHROMIUM IONS FROM WATER USING ACID-ACTIVATED BENTONITES AND ADSORPTION MECHANISMS

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Abstract: The adsorption capacity of activated adsorbents for $Cr_2O_7^{2-}$ ions in water was analyzed, and their adsorption activity sequence was determined as **DB15 > DB25 > DB.** To enhance the efficiency of the adsorption process, the optimal stirring speed was established at **150 rpm.** The most effective adsorbent dose for efficient $Cr_2O_7^{2-}$ ion sorption was found to be **3.0 g/L**. The effect of pH on the adsorption process was investigated, revealing that the maximum adsorption efficiency for activated adsorbents was observed at **pH = 4.0**. The adsorption mechanism was explained by **electrostatic interactions, diffusion processes within meso- and macropores of the adsorbent, and complex formation with functional groups on the adsorbent surface.**

Key words: Bentonite, wastewater, chromium ions, pH influence, adsorption isotherm, adsorption mechanisms.

KISLOTALI MUHITDA FAOLLANGAN BENTONITLAR YORDAMIDA SUVDAN XROM IONLARINI TOZALASH VA ADSORBSIYA MEXANIZMLARI

Annotasiya: Faollashtirilgan adsorbentlarning suvdagi $Cr_2O_7^{2-}$ ionlarini adsorbsiyalash qobiliyati tahlil qilinganda, ularning adsorbsion faollik qatori **DB15 > DB25 > DB** tarzida joylashishi aniqlangan. Adsorbsiyalash jarayonining samaradorligini oshirish uchun optimal aralashtirish tezligi **150 ayl/min** deb belgilangan. $Cr_2O_7^{2-}$ ionlarini samarali sorbsiyalash uchun eng maqbul adsorbent dozasining **3,0 g/L** ekanligi ko‘rsatib o‘tilgan. Adsorbsiyalanish jarayoniga muhit pH ko‘rsatkichining ta’siri o‘rganilganida, faollashtirilgan adsorbentlar uchun maksimal adsorbsion samaradorlik **pH = 4,0** da kuzatilgan. Adsorbsiyalanish mexanizmi **elektrostatik o‘zaro ta’sirlar, adsorbentlarning mezo- va makrog‘ovaklaridagi diffuziya jarayonlari hamda adsorbent yuzasidagi funksional guruhlar bilan kompleks hosil qilish** mexanizmlari orqali amalga oshishi izohlangan.

Kalit so‘zlar: Bentonit, oqova suv, xrom ionlari, pH ta’siri, adsorbsiya izotermasi, adsorbsiyalanish mexanizmlari.

ОЧИЩЕНИЕ ВОДЫ ОТ ИОНОВ ХРОМА С ПОМОЩЬЮ КИСЛОТНО-АКТИВИРОВАННЫХ БЕНТОНИТОВ И МЕХАНИЗМЫ АДСОРБЦИИ

Аннотация: Была проведена оценка адсорбционной способности активированных адсорбентов к ионам $Cr_2O_7^{2-}$ в воде, и установлена их адсорбционная активность в следующем порядке: **DB15 > DB25 > DB.** Для повышения эффективности процесса адсорбции оптимальная скорость перемешивания была определена как **150 об/мин**. Оптимальная доза адсорбента для эффективной сорбции ионов $Cr_2O_7^{2-}$ составила **3,0 г/л**. Исследовано влияние pH на процесс адсорбции, и установлено, что максимальная эффективность адсорбции активированными адсорбентами наблюдается при **pH = 4,0**. Механизм адсорбции объясняется **электростатическими взаимодействиями, диффузионными процессами в мезо- и макропорах адсорбента, а также образованием комплексов с функциональными группами на его поверхности.**

Ключевые слова: Бентонит, сточные воды, ионы хрома, влияние pH, изотерма адсорбции, механизмы адсорбции.

INTRODUCTION. Currently, the global demand for leather products is increasing daily, leading to a rise in the number of leather processing facilities. In these facilities, chromium salts are widely used as essential raw materials for leather processing, playing a critical role in enhancing leather quality. However, the discharge of untreated wastewater from leather processing plants into water bodies has resulted in significant environmental degradation. The rapid acceleration of industrialization in recent years has led to an increase in the concentration and accumulation of $Cr_2O_7^{2-}$ ions, one of the most prevalent heavy metals found in water and the environment. High concentrations of chromium pose serious health risks to humans [1]. In nature, chromium ions occur in compound forms. These ions are toxic to plants and animals, do not biodegrade, and tend to accumulate in living cells. Chromium exists in several oxidation states, forming Cr^{2+}, Cr^{3+}, and Cr^{6+} ions. Among these, Cr^{6+} (hexavalent chromium) ions present in wastewater are particularly toxic. In the leather industry, chromium compounds account for 25-30% of the total pollutants found in industrial effluents [2].

LITERATURE REVIEW AND METHODS. Chromium and its compounds, classified as heavy metal ions, are commonly found in wastewater generated from industries such as leather tanning, metallurgy, cadmium and nickel battery production, fungicides, insecticides, and other manufacturing processes [3]. The permissible maximum concentration limit for chromium in wastewater is 0.05 mg/L. However, its concentration in industrial effluents is often significantly higher. Therefore, to comply with environmental protection regulations, chromium ion concentrations must be reduced to 0.05 mg/L [4].

Considering these factors, this study explores the use of acid-activated samples of locally sourced Dehqonobod bentonite as a cost-effective adsorbent for chromium removal from water resources. Model chromium solutions were prepared by dissolving 2.83 g of $K_2Cr_2O_7$ (Titrisol, Merck KGaA, Germany) in 1000 mL of distilled water, followed by appropriate dilution to achieve the desired $Cr_2O_7^{2-}$ ion concentrations. All adsorption experiments were conducted using conical flasks (100 mL) containing varying adsorbent doses of 0.05, 0.1, 0.2, 0.25, and 0.3 g/L. The mixtures were agitated at rotational speeds ranging from 100 to 250 rpm using a GFL 3033 model shaker [5].

Chromium ion concentrations in water samples were analyzed using a Shimadzu UV-1800 spectrophotometer. In this method, a diphenylcarbazide reagent (prepared by dissolving 0.1 g of diphenylcarbazide in 10 mL of acetone) was employed. Additionally, 0.2 mL of concentrated phosphoric acid was added to the solution and thoroughly mixed. This method is based on the principle that chromium ions form a colored complex (purple) with 1,5-diphenylcarbazide. The absorbance spectra were recorded at a wavelength of 540 nm using a UV spectrophotometer. A calibration curve was first established using standard chromium solutions [6].

RESULTS AND DISCUSSION. To determine the effect of temperature on the adsorption process, adsorption isotherms of chromium ions were studied at different temperatures: 288 K, 293 K, 298 K, 308 K, and 318 K. The experiments were conducted across a range of initial chromium concentrations from 0.05 to 0.5 mg/L. The influence of temperature on the adsorption of chromium ions onto acid-activated bentonites (DB, DB15, and DB25) is illustrated in Figure 1.

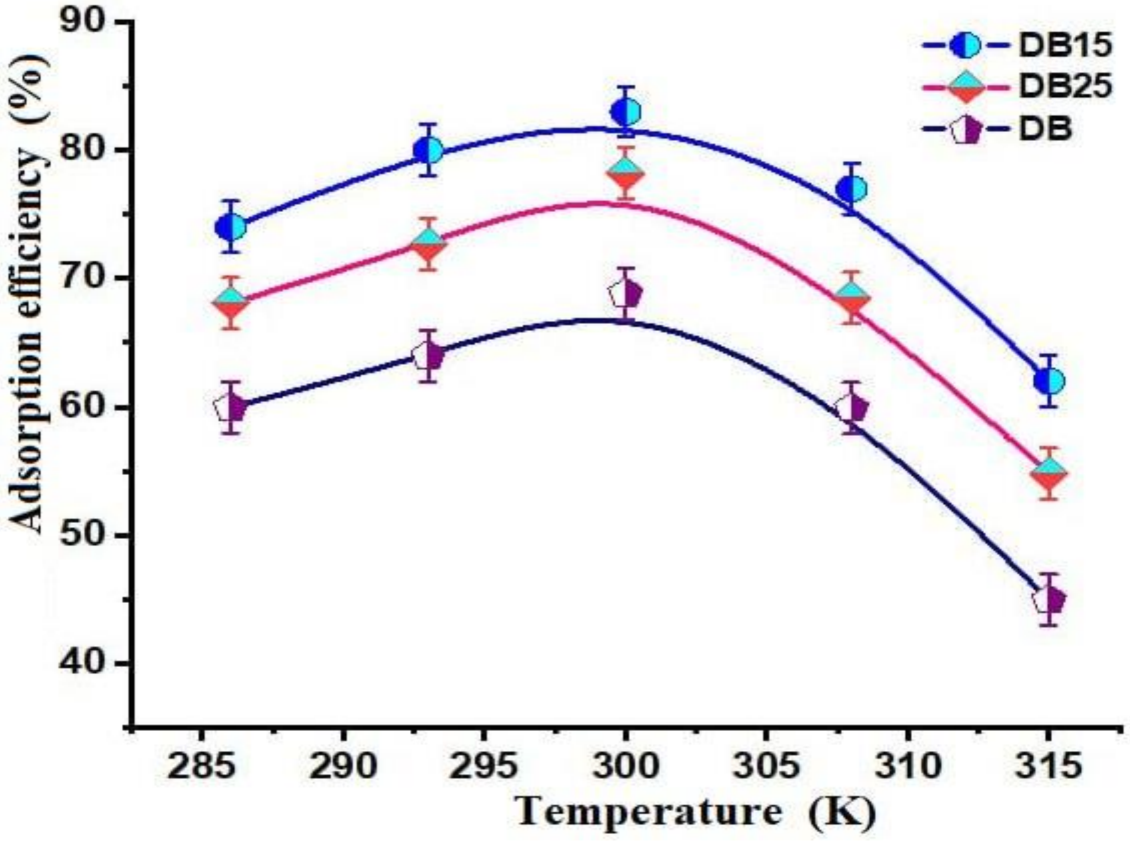

Figure 1. Effect of temperature on the adsorption of chromium ions onto DB, DB15, and DB25 bentonites.

Adsorption isotherms and temperature effect. As observed from the adsorption isotherms, an increase in temperature within the range of 288–308 K led to a higher adsorption capacity of chromium ions onto the adsorbents. The enhancement in adsorption efficiency with increasing temperature can be attributed to the rise in molecular kinetic energy, which accelerates the mobility of chromium ions. This, in turn, facilitates the diffusion of chromium ions into the active sites and pores of the adsorbents. It was determined that carrying out the adsorption process at 298 K resulted in an increased adsorption efficiency of up to **82.5%.** The adsorption capacity of chromium ions onto bentonites followed the order **DB15 > DB25 > DB,** indicating the highest adsorption activity for DB15 [7].

Effect of pH on the adsorption process. The solution pH plays a crucial role in determining the adsorption efficiency of chromium ions onto acid-activated bentonites. Depending on the pH, chromium ions may exist in different forms, such as **hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}), or dichromate ($Cr_2O_7^{2-}$)** [8]. According to the adsorption-pH dependency diagram for chromium ion adsorption onto acid-activated bentonites, an increase in adsorption efficiency was observed within the pH range of **2.0–4.0.** The highest adsorption efficiency was achieved at **pH 4.0**. However, when the pH was increased from **5.0 to 7.0,** a noticeable decline in Cr^{6+} adsorption onto acid-activated bentonites was observed. The adsorption of Cr^{6+} is influenced by electrostatic interactions between the positively charged bentonite surface and the negatively charged chromium species. A positively charged bentonite surface effectively retains anionic species. The effect of pH on the adsorption of **PO_4^{3-} ions** onto **DB, DB15, and DB25 bentonites** is illustrated in **Figure 2.**

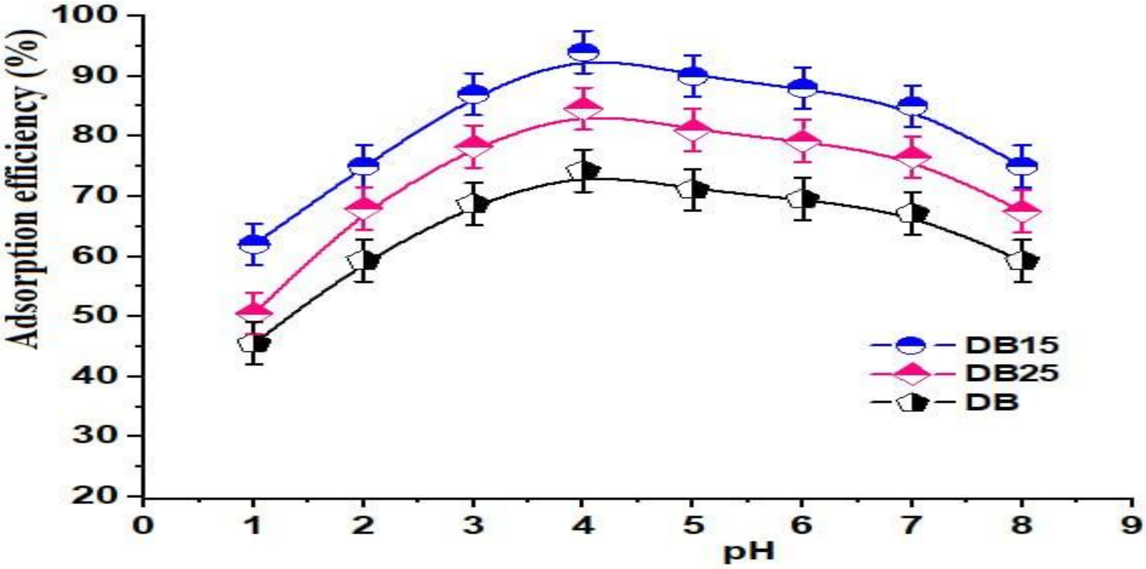

Figure 2. Effect of pH on the adsorption of PO_4^{3-} ions onto DB, DB15, and DB25 bentonites

Moderate pH (pH ≈ 5-6): Adsorption efficiency decreases due to a reduction in electrostatic attraction forces. Alkaline pH (pH > 7): Adsorption efficiency significantly declines. The bentonite surface becomes negatively charged, leading to the repulsion of chromate ions. In contrast, acid-activated bentonite acquires a positive (+) charge, which enhances the electrostatic attraction between the bentonite surface and chromate anions ($HCrO_4^-$, $Cr_2O_7^{2-}$). As a result, adsorption efficiency increases under acidic conditions. The adsorption process is influenced by the protonation and deprotonation of the bentonite surface at different pH levels, as described below: Under acidic conditions, the bentonite surface undergoes protonation (becoming enriched with H^+ ions), following the reactions: $\equiv SiOH + H^+ \rightarrow \equiv SiOH_2^+$, $=AlOH + H^+ \rightarrow =AlOH_2^+$ The positively charged $=AlOH_2^+$ sites facilitate the electrostatic attraction of chromate anions. At higher pH levels, deprotonation occurs, leading to:$\equiv SiOH_2^+ \rightarrow \equiv SiOH + H^+$, $=AlOH_2^+ \rightarrow =AlOH + H^+$, This process reduces the adsorption capacity of the bentonite surface for chromium ions. In conclusion, the highest Cr^{6+} adsorption was observed within the pH range of 3.0 to 4.0, achieving an adsorption efficiency of 84.95% [9].

Effect of stirring speed on adsorption efficiency. Stirring speed significantly influences the efficiency of Cr ion adsorption from water by acid-activated bentonites. This effect is closely related to the kinetics of the process and the mass transfer mechanisms. Stirring speed is a crucial parameter in adsorption, as it directly affects the transport of Cr ions from the solution to the external surface of the adsorbent. Figure 3 illustrates the effect of stirring speed on the adsorption efficiency of Cr ions onto acid-activated bentonites. Experiments were conducted at stirring speeds of 100, 150, 200, 250, and 300 rpm. Increasing the stirring speed enhances turbulence and reduces the boundary layer near the adsorbent surface, facilitating the penetration of chromate ions into the porous structure of the adsorbents. However, it is important to note that excessively high stirring speeds may lead to particle aggregation or desorption of Cr ions from the adsorbent surface. Conversely, at very low stirring speeds, insufficient time for adsorption may result in lower efficiency, while excessively high speeds may also decrease adsorption performance.

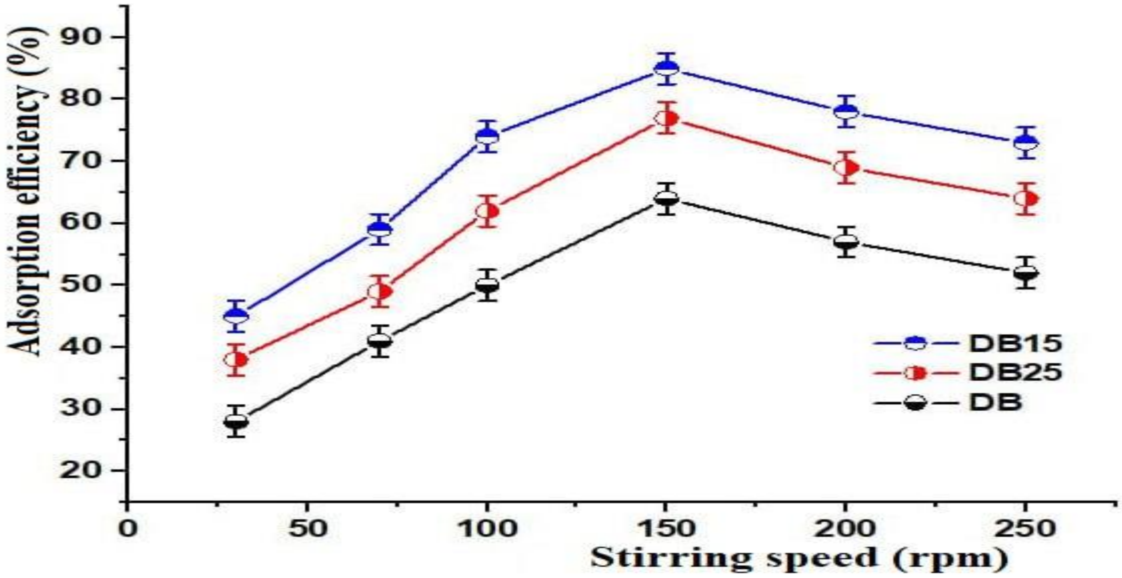

Figure 3. Effect of stirring speed on the adsorption of chromium ions onto acid-activated bentonites

In the experiment, the adsorption efficiency initially increased with stirring speed for all three adsorbents, reaching a maximum at 150 rpm. Beyond this point, the efficiency decreased, likely due to desorption occurring at higher stirring speeds. Among the tested adsorbents, DB15 exhibited the highest adsorption efficiency at 150 rpm (~85%), while DB showed the lowest, with a maximum efficiency of approximately 55%. The decline in adsorption efficiency in the 200–250 rpm range may be attributed to desorption of the adsorbate from the adsorbent surface or the formation of turbulent flow, which disrupts the adsorption process.

Effect of adsorbent dosage on Cr^{6+} adsorption onto acid-activated bentonites. Figure 4 illustrates the influence of adsorbent dosage on the adsorption of Cr^{6+} ions onto acid-activated bentonites. The adsorbent dosage varied from 1.0 to 5.0 g. A rapid increase in chromium ion adsorption was observed as the adsorbent dosage increased from 1.0 to 3.0 g. However, beyond this point, the increase in adsorption per unit of adsorbent mass was less significant, which has implications for economic efficiency. These findings suggest that the enhanced adsorption is primarily due to the increased surface area and the availability of more active adsorption sites. However, it is important to note that despite the increase in active adsorption sites, some of them may remain unutilized during the adsorption of chromate ions.

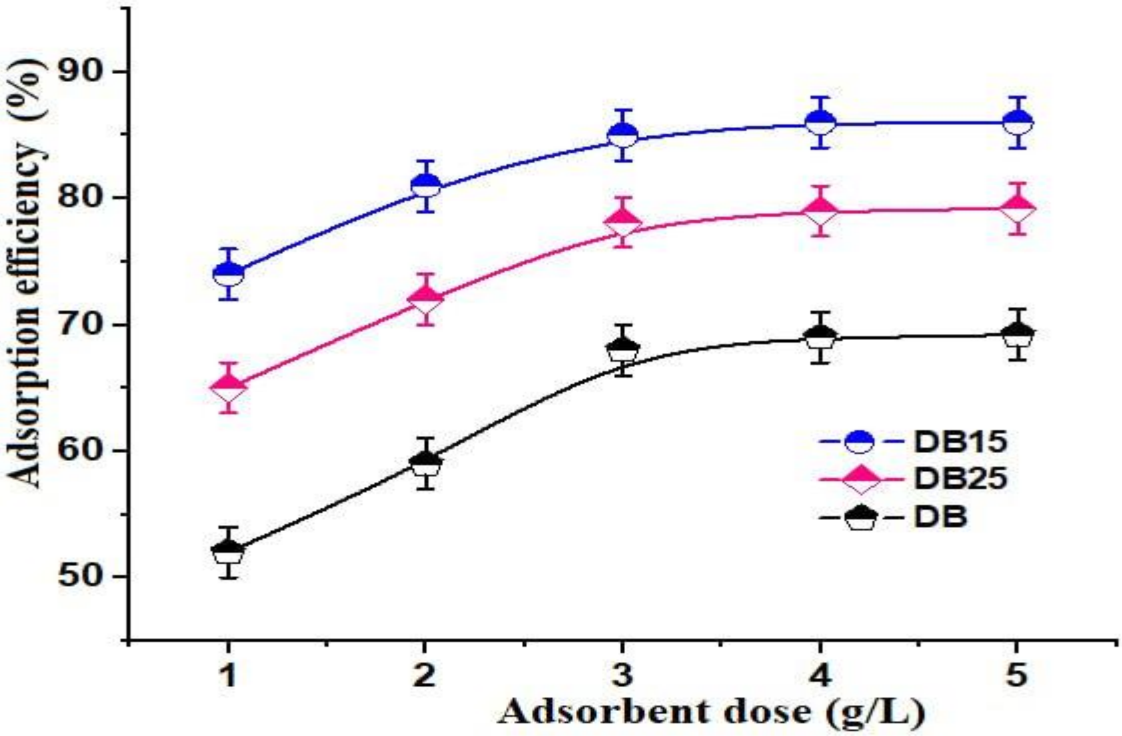

Figure 4. Dependence of chromium ion adsorption efficiency on the amount of DB, DB15, and DB25 adsorbents

The correlation between adsorbent dosage and adsorption efficiency generally depends on their proportional relationship and the saturation point of the process. In most cases, increasing the amount of adsorbent leads to an increase in adsorption efficiency. However, beyond a certain point, no significant changes in efficiency are observed. At this stage, an excessive amount of adsorbent does not contribute to improved performance but rather results in resource wastage.

Adsorption mechanisms. The adsorption of chromium ions onto DB, DB25, and DB15 bentonites is a complex process involving multiple mechanisms. These mechanisms are influenced by the surface properties and structure of the bentonites, as well as the interactions between chromium ions and the adsorbent. The main mechanisms of Cr ion adsorption onto DB, DB15, and DB25 bentonites can be explained as follows:

Complexation: This process involves chemical interactions between functional groups on the adsorbent surface and metal ions. For example, aluminum (Al) and silicon (Si) atoms in the adsorbent can form stable complexes with chromium ions due to their electron-donating properties. This occurs through coordination bonding between the electron cloud of metal ions and the electron pairs of functional groups on the adsorbent surface. As a result, chromium ions strongly adhere to the adsorbent surface, leading to their effective removal from solution. This mechanism is not only governed by physico-chemical interactions but is also influenced by factors such as the adsorbent structure, active surface sites, and solution pH. **Electrostatic interactions:** Electrostatic attraction occurs between chromium ions and positively charged sites on the adsorbent surface. Hydroxyl groups ($H\delta^+$) enhance this process, facilitating stronger adsorption of chromium species. **Pore adsorption:** chromium ions are adsorbed into the mesopores and macropores of the adsorbent surface, allowing for enhanced retention within the porous structure. **Ion exchange process:** Partial reduction of Cr(VI) to Cr(III) is observed, facilitated by hydrogen donor sites (H) on the adsorbent surface. This transformation enhances chromium removal by promoting its retention in a less mobile form.

These mechanisms play a crucial role in the effective removal of chromium ions from aqueous solutions or other environments, making acid-activated bentonites a promising material for water purification

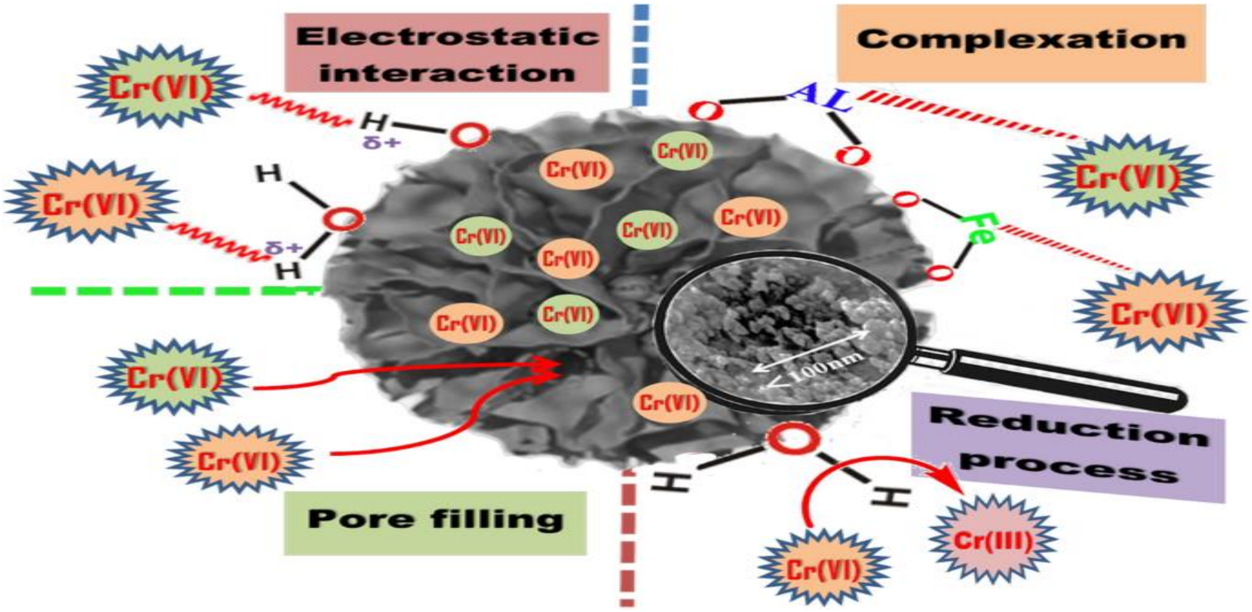

Figure 5. Adsorption mechanism of chromium ions onto activated bentonites

CONCLUSION. The maximum allowable concentration of Cr^{6+} in wastewater should not exceed 0.05 mg/L. The spectra of Cr^{6+} were obtained using a UV spectrometer at a wavelength of 540 nm. The adsorption capacity of chromium ions onto bentonites follows the order: **DB15 > DB25 > DB,** indicating that DB15 exhibits the highest adsorption activity. The effect of solution pH on the adsorption efficiency of chromium ions onto acid-activated bentonites was investigated. The maximum adsorption efficiency was observed at **pH 4.0,** which is attributed to strong electrostatic interactions between the positively charged bentonite surface and chromate ions at this pH level. The optimal bentonite dosage for chromium ion adsorption was determined to be **3.0 g**, while the most effective stirring speed for maximum adsorption efficiency was found to be **150 rpm.** At this stirring speed, **DB15 exhibited the highest adsorption efficiency (~85%),** making it the most effective adsorbent among the tested samples.

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