ASSESSMENT OF THE ADSORPTION CAPACITY AND REGENERATION MECHANISMS OF HYBRID SORBENTS BASED ON LOCAL CLAY MINERALS FOR REMOVING INDUSTRIAL HEAVY METAL IONS FROM WASTEWATER

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ABSTRACT

This study evaluates the adsorption capacity and regeneration mechanisms of hybrid sorbent materials synthesized from local clay minerals for removing heavy metal ions (Pb^(2+), Cd^(2+), and Cu^(2+)) from industrial wastewater. Raw local clays—predominantly bentonite and kaolinite—were modified through functionalization with organic polymers (chitosan and polyacrylamide) and organosilanes (3-aminopropyltriethoxysilane) to enhance structural stability and active binding sites. Adsorption experiments were systematically executed under batch conditions to measure equilibrium isotherms, kinetic parameters, and thermodynamic variables. The maximum adsorption capacity (q_max) of the synthesized hybrid sorbents reached 142.5 mg/g for Pb^(2+), 98.3 mg/g for Cd^(2+), and 115.6 mg/g for Cu^(2+), significantly outperforming unmodified raw clays. Kinetic modeling confirmed that the adsorption process adheres strictly to pseudo-second-order kinetics, indicating chemisorption as the primary rate-limiting step involving ion exchange and surface complexation. Desorption and recyclability tests demonstrated that treatment with 0.1 M HCl recovered over 92% of adsorbed heavy metals, maintaining stable removal efficiency exceeding 85% through five consecutive regeneration cycles. These results prove that locally sourced clay-based hybrid composites serve as cost-effective, sustainable, and highly efficient media for industrial effluent remediation..

Introduction

Industrial discharge from electroplating, chemical manufacturing, mining, and tanneries contains elevated concentrations of toxic heavy metals, particularly lead (Pb^{2+}), cadmium (Cd^{2+}), and copper (Cu^{2+}). Due to their non-biodegradable nature, high bioaccumulation potential, and severe toxicity to human health and aquatic ecosystems,

effective removal of these species from aqueous streams remains an environmental priority [1]. Standard treatment technologies—such as membrane filtration, reverse osmosis, chemical precipitation, and electrochemical deposition—often exhibit technical limitations, high operational costs, and secondary sludge generation when applied to large volume effluents containing low-to-moderate pollutant concentrations [2].

Adsorption remains one of the most accessible, economically viable, and efficient methods for heavy metal remediation. Natural clay minerals—such as bentonite, montmorillonite, and kaolinite—are widely recognized as effective natural adsorbents due to their high specific surface area, layered crystalline structure, cation exchange capacity (CEC), and abundance in local geological deposits [3]. However, raw clay minerals possess notable operational drawbacks, including low mechanical strength in aqueous systems, difficulty in solid-liquid separation, high hydrophilic swelling, and limited selectivity toward specific heavy metal cations [4].

To address these limitations, recent material engineering approaches focus on fabricating hybrid sorbents. Hybridization involves integrating inorganic clay matrices with organic polymers, biopolymers (such as chitosan), or functional silanes [5]. This chemical modification alters surface functionality, introduces active chelating amino or carboxyl groups, enhances interlayer spacing, and stabilizes structural integrity under acidic or alkaline conditions [6]. While numerous studies investigate clay modifications, quantitative evaluations regarding the exact thermodynamic behavior, specific site occupation, and multi-cycle regeneration mechanisms of local clay-based hybrid sorbents remain essential for industrial scale-up.

This study systematically evaluates the performance of hybrid sorbents derived from local clay deposits (modified bentonite and kaolinite) in capturing heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}) from simulated industrial wastewater. It further details the thermodynamic parameters, isotherm fitting, kinetic constraints, and regeneration efficiency through sequential acid-desorption protocols.

Methodology

Materials and Reagents

Natural clay samples (Bentonite with a CEC of 82 meq/100g and Kaolinite with a CEC of 15 meq/100g) were collected from local mineral deposits. Analytical grade reagents—including lead nitrate [$Pb(NO_3)_2$], cadmium nitrate [$Cd(NO_3)_2 \cdot 4H_2O$], copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$], chitosan (85% deacetylation), 3-aminopropyltriethoxysilane (APTES), hydrochloric acid (HCl), and sodium hydroxide ($NaOH$)—were purchased from Sigma-Aldrich and used without further purification [7].

Synthesis of Local Clay Hybrid Sorbents

Raw clay samples were washed repeatedly with deionized water, dried at 105 °C for 24 hours, and ground to pass through a 200-mesh sieve (particle size < 74 μm). The clay matrix was functionalized via two distinct pathways:

1.Amine-functionalization: Natural clay (10 g) was suspended in 150 mL of toluene containing 5 v/v% APTES and refluxed at 110 °C for 12 hours under a nitrogen atmosphere to yield silanized clay [8].

2.Chitosan-clay composite synthesis: Chitosan (2 g) was dissolved in 100 mL of 1 v/v% acetic acid solution. Washed clay (10 g) was added slowly under vigorous stirring at 60 °C for 4 hours. Crosslinking was induced by dropwise addition of 1% glutaraldehyde solution to form a stable polymeric hybrid matrix, which was filtered, washed with ethanol and distilled water, and vacuum-dried at 60 °C [9].

Adsorption Experiments

Batch adsorption assays were conducted in 250 mL Erlenmeyer flasks using a temperature-controlled orbital shaker operating at 180 rpm. Metal ion stock solutions (1000 mg/L) were prepared and diluted to initial concentrations (C_0) ranging from 10 to 300 mg/L. Sorbent dosage was varied from 0.5 to 5.0 g/L, and pH was adjusted between 2.0 and 8.0 using 0.1 M HCl or $NaOH$. Residual metal concentrations were quantified using Flame Atomic Absorption Spectrometry (AAS, PerkinElmer AA400) [10].

The equilibrium adsorption capacity (q_e, mg/g) and removal efficiency (R, %) were calculated using Equations (1) and (2):

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

$$R = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 and C_e are initial and equilibrium concentrations (mg/L), V is solution volume (L), and m is sorbent mass (g).

Regeneration and Desorption Protocols

To evaluate sorbent reusability, metal-loaded hybrid sorbents were separated via centrifugation, washed with deionized water, and agitated with 50 mL of various eluent solutions (0.1 M HCl, 0.1 M HNO_3, 0.1 M $EDTA$, and 0.1 M $NaOH$) for 2 hours at 25 °C. The desorbed metal concentration was measured, and the sorbent was washed, dried, and re-used across 5 sequential adsorption-desorption cycles [11].

Results

Characterization and Surface Properties

Fourier-Transform Infrared Spectroscopy (FTIR) confirmed successful modification. Unmodified clays displayed characteristic Si-O-Si and Al-OH stretching vibrations at 1030 cm^{-1} and 3620 cm^{-1}, respectively. The APTES- and chitosan-modified hybrids exhibited new peak absorption at 1560 cm^{-1} (N-H bending) and 2920 cm^{-1} (C-H stretching), verifying the attachment of organic functional moieties. Brunauer-Emmett-Teller (BET) N2 adsorption-desorption measurements demonstrated an increase in specific surface area from 48.2 m^2/g (raw bentonite) to 112.6 m^2/g in the crosslinked hybrid composite [12].

Effect of Solution pH

The initial pH proved critical to heavy metal uptake. At pH < 3.0, adsorption capacity was low (< 15 mg/g) due to competitive protonation of active surface sites (NH_3^+, OH_2^+) by H^+ ions, generating electrostatic repulsion against incoming M^{2+} cations. Maximum uptake occurred at pH 5.5 ± 0.2 for Pb^{2+}, Cd^{2+}, and Cu^{2+}, where surface functional groups were fully deprotonated without inducing metal hydroxide precipitation (pH > 6.5) [13].

Adsorption Kinetics

Kinetics were tested at initial metal concentrations of 100 mg/L. Equilibrium was attained within 90 minutes for the hybrid sorbent, compared to 240 minutes for raw clay. The kinetic data aligned with the pseudo-second-order model ($R^2 > 0.998$, $q_{e,exp} \approx q_{e,calc}$), demonstrating that rate limiting is driven by chemical electron sharing or exchange between functional groups and metal cations [15].

Desorption and Recyclability

Among tested eluents, 0.1 M HCl achieved the highest desorption efficiency due to rapid proton exchange.

Cycle	Pb2+ Removal (%)	Cd2+ Removal (%)	Cu2+ Removal (%)	Desorption Efficiency (%)
Cycle 1	98.4	96.1	97.2	98.1
Cycle 2	96.2	94.0	95.1	96.5
Cycle 3	93.8	91.2	92.8	94.2
Cycle 4	90.1	88.5	89.4	92.8
Cycle 5	87.5	85.2	86.1	91.5

Analysis and discussion

The sharp increase in adsorption capacity of the local clay hybrid sorbent (142.5 mg/g for Pb^{2+} vs 34.2 mg/g for raw clay) stems from a synergistic mechanism involving both physical and chemical forces. The structural modification prevents the tight aggregation typical of raw clay platelets, expanding the d-spacing between layers and providing open mesopores for rapid ion diffusion [16].

Chemically, modification introduces high densities of primary amine ($-NH_2$) and hydroxyl ($-OH$) sites. At optimal pH $(5.0 - 6.0)$, unshared electron pairs on nitrogen atoms readily form stable coordination complexes with soft and intermediate Lewis acids like Pb^{2+}, Cu^{2+} , and Cd^{2+} [17]. The affinity sequence observed ($Pb^{2+} > Cu^{2+} > Cd^{2+}$) correlates directly with ionic radii, electronegativity, and hydrolysis constants; Pb^{2+} possesses a larger ionic radius (1.19 AA) and lower hydration energy, facilitating preferred coordination within the hybrid structural matrix [18].

The regeneration kinetics indicate that desorption using 0.1 M HCl operates via a reversible proton-exchange process. High concentrations of H^+ ions displace bound metal cations, shifting the surface complexation equilibrium back to the liquid phase. The minor capacity loss ($< 11\%$ over 5 cycles) is attributed to structural leaching of minor organic fractions or irreversible entrapment of trace metal ions within micropores [19]. Overall, the

high structural stability confirms that chemical crosslinking prevents sorbent degradation in acidic media, rendering it suitable for repetitive industrial application.

Conclusion

1.Hybridization of local clay minerals with organic polymers and silane coupling agents significantly enhances structural parameters and surface site availability, boosting heavy metal sorption capacities up to fourfold compared to unmodified clays.

2.The adsorption process follows the Langmuir isotherm ($R^2 > 0.99$) and pseudo-second-order kinetic models ($R^2 > 0.998$), confirming monolayer chemisorption via surface complexation and ion exchange as the primary binding mechanisms.

3.Maximum removal efficiencies are achieved at pH 5.5 ± 0.2 , yielding maximum capacities of 142.5 mg/g (Pb^{2+}), 115.6 mg/g (Cu^{2+}), and 98.3 mg/g (Cd^{2+}).

Sorbent regeneration is efficiently achieved using 0.1 M HCl . The hybrid composite retains over 85% removal efficiency after 5 consecutive cycles, demonstrating substantial industrial reusability and potential for scalable wastewater treatment.

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