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MODIFIED DIATOMACEOUS EARTH FOR EFFICIENT REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION

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Abstract

Heavy metal contamination in aquatic environments remains a considerable ecological threat, necessitating the development of cost-effective remediation technologies. Natural mineral sorbents, such as diatomaceous earth (DE), are valued for environmental remediation due to their affordability and inherent selectivity. This study investigates the synthesis and effectiveness of a sodium silicate-modified DE, specifically designed for the targeted adsorption of copper ions (Cu^{2+}) from wastewater. The modification process utilized a cost-effective sodium silicate solution to enhance the structural and surface properties of raw diatomaceous earth. To modify the substrate, raw DE was added to a diluted 0.5 M sodium silicate solution at a ratio of 5% sodium silicate by weight relative to the DE. The sodium-silicate-modified diatomaceous earth reduced the residual UV–Vis absorbance of the copper solution by approximately 50% compared with the unmodified material, indicating a substantially improved removal of dissolved copper species. The results demonstrate that sodium silicate modification significantly improves the material's structural stability and affinity for heavy metals, offering an efficient solution for industrial wastewater treatment.

Keywords**:** adsorption; diatomaceous earth; copper; sodium silicate, heat treatment.

Introduction

Heavy metal contamination in aquatic environments continues to pose a significant environmental challenge. Conventional treatment methods, such as precipitation, ion exchange, membrane filtration, and activated carbon adsorption, are commonly utilized. However, these methods frequently incur high operational costs and exhibit limited selectivity for specific pollutants [1, 2].

Consequently, there is significant interest in developing affordable, highly efficient, and selective alternatives that facilitate the effective transfer of pollutants from liquid to solid phases [3, 4, 5]. Bio-sorbents, including bacteria, algae, and fungi, provide a variety of functional groups [7, 8]. In contrast, mineral sorbents such as zeolites, perlite, and clay rocks are particularly esteemed for their abundance and mechanical stability. These properties are especially advantageous when these sorbents are in granular forms, making them suitable for use in demanding aquatic environments [6,7,8].

Among these mineral matrices, diatomaceous earth (DE) stands out as an environmentally friendly, siliceous sedimentary rock [9].

Characterized by a highly porous structure, large specific surface area, lightweight nature, and high thermal reactivity, DE consists primarily of amorphous silica (SiO_2) alongside minor metal oxides (Al_2O_3, Fe_2O_3, and MgO) [10, 11, 12].

Although raw diatomaceous earth (DE) serves as an effective sorbent for a range of organic and inorganic compounds [13, 14], attaining high selectivity for particular heavy metal cations, without interference from co-existing ions, continues to represent a significant research challenge [15]. Surface modification presents an effective approach to addressing selectivity limitations. The integration of sodium silicate into the diatomite matrix confers both structural and chemical advantages: it serves as a binder to enhance structural stability and provides a plentiful source of active silanol (Si-OH) groups upon activation [16,17,18]. This modification transforms the morphology and textural properties of the diatomite, thereby substantially enhancing its surface reactivity and compatibility for the adsorption of target heavy metals.

The impurities present in natural diatomite can unfavorably impact the uptake of heavy metal ions from aqueous solutions [19].

Therefore, modification of the diatomite surface was necessary to optimize heavy-metal removal. A variety of methodologies can be used to modify the diatomite surface. Ediz et al. showed that the characteristics of diatomite are improved for use in filtration [20] when calcinated at 1000 ◦C. It was demonstrated that, through this process, the density and permeability of the diatomite were enhanced from 2.29 to 2.34 g/cm3 and from 2.15×10−14 to 4.74×10-13 m2, respectively. In this way, calcinated diatomite could be used successfully for filtration purposes. Most of the modifications cited here concern the inorganic functionalization of diatomite. In the past, this has been in the past the most common way to improve the selectivity and extraction performance of the material. However, the fact that diatomite may be considered as amorphous silica opens the way for functionalization purposes [21,22].

The study aimed to synthesize a sodium-silicate-modified diatomite, thoroughly characterize its modified physicochemical properties, and systematically assess its efficacy in selectively removing heavy metal ions from aqueous solutions. The use of sodium silicate offers several advantages, including low cost, non-toxic processing, a straightforward one-step modification route, thermal stabilization at a relatively low calcination temperature (400 °C), and the production of mechanically robust adsorbents suitable for continuous filtration systems.

Materials and Methods

The diatomaceous earth (DE) used in this study consisted of granulates with a grain size of 0.5–1 mm and was purchased from the "DIATOMITE" Research and Production Closed Joint-Stock Company (CJSC). Copper sulfate pentahydrate CuSO4 • 5H2O was utilized to prepare the experimental solutions at a fixed concentration of 0.5 g/L. Sodium silicate solution (liquid glass), characterized by the generalized formula Na2O(SiO2)x · xH2O was used as an inorganic binder and surface modifier.

Modification and Calcination of Diatomaceous Earth

To modify the substrate, raw DE was added to a diluted 0.5 M sodium silicate solution at a ratio of 5% sodium silicate by weight relative to the DE. The resulting slurry was thoroughly mixed for 60 minutes to ensure complete penetration of the sodium silicate into the microscopic pores of the DE. To synthesize a rigid, water-insoluble structure suitable for long-term filtration, the modified DE was calcined in a muffle furnace at 400°C for 2 hours.

Results and discussion

By using sodium silicate, the DE becomes a highly active silica surface that has superior mechanical stability in water filtration columns and an enhanced capacity to adsorb dissolved heavy metal contaminants compared to raw DE.

It increases the density of silanol groups (-Si-OH) on the surface. These groups act as chemical anchors that can either directly bind to certain heavy metal cations (Cu^{+2}) or serve as a bridge to attach other organic molecules. Sodium silicate acts as an excellent, chemically compatible inorganic binder. This enables the fabrication of stable pellets, beads, or granules that won't disintegrate when submerged in water.

Water glass deposits additional silica species on the diatomite surface:

$$Si{-}O^{-} + Cu^{2+} \rightarrow Si{-}O{-}Cu^{+} \quad (1)$$

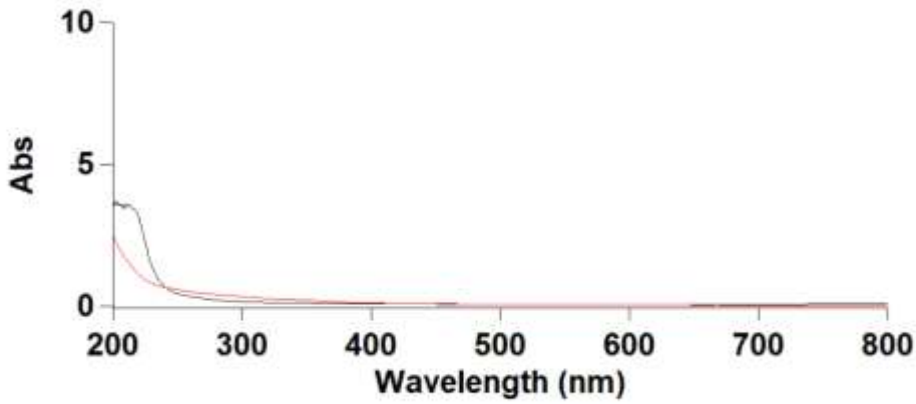

Fig.1 UV-Vis analysis of unmodified and modified DE

This increases the number of active silanol groups (Si–OH), which become negatively charged at neutral pH and attract Cu^{2+} ions. The calcination at 400 °C removes physically adsorbed water, improves pore accessibility, and strengthens the silica network. At 400 °C, the silica surface still retains hydroxyl groups necessary for metal binding.

The UV–Vis spectra revealed a pronounced absorption in the ultraviolet region below 230 nm, while negligible absorbance was observed at wavelengths above 300 nm. After treatment with the adsorbent, the absorbance intensity decreased markedly, indicating a reduction in the concentration of dissolved copper-containing species. The absence of significant absorption bands in the visible region suggests either a low residual Cu^{2+} concentration or efficient removal of copper ions from the aqueous phase.

UV–Vis spectra of the $CuSO_4$ solutions before and after adsorption revealed a pronounced decrease in absorbance intensity in the 200–250 nm region after treatment. Before modification, the residual absorbance was approximately 3.6. After modification, the residual absorbance changed to 1.8. The sodium-silicate-modified diatomaceous earth reduced the residual copper concentration by approximately 50% compared with the unmodified diatomaceous earth, demonstrating a significant enhancement in adsorption performance.

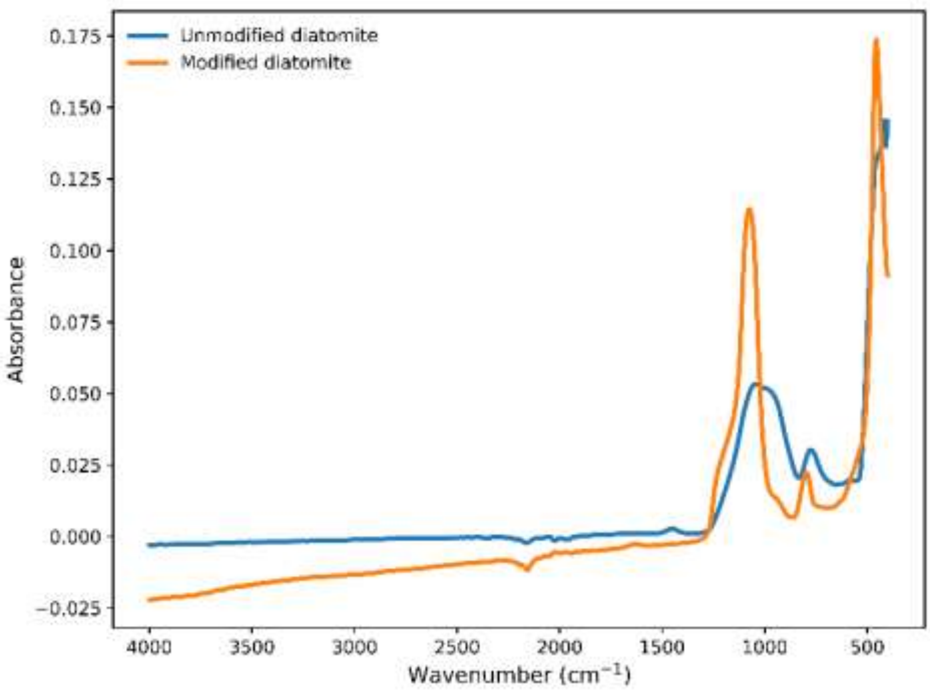

Fig. 2 FTIR analysis of unmodified and modified DE

The FTIR (Shimadzu IRTracer-100), spectra of both unmodified and modified diatomite display the characteristic absorption bands associated with silica-rich diatomite.

The predominant absorption band in the 1000–1100 cm^{-1} range is linked to the asymmetric stretching vibration of Si–O–Si bonds. Additionally, the bands near 790–800 cm^{-1} and approximately 460 cm^{-1} are attributed to the symmetric stretching and bending vibrations of the siloxane network, respectively. Post-modification, these characteristic silica bands persist, indicating that the treatment does not compromise the fundamental structure of diatomite. Nonetheless, slight variations in band intensity and broadening of the Si–O–Si absorption, along with a modest increase in the hydroxyl absorption region, imply alterations in the surface silanol groups and an increase in surface-bound hydroxyl species. These spectral modifications confirm successful surface modification while maintaining the original porous silica framework of the diatomite.

Conclusions

In this study, a high-performance functional material was successfully developed through the chemical modification of natural diatomite using sodium silicate. The systematic characterization and subsequent performance evaluations yielded the following key conclusions:

- The sodium silicate modification successfully altered the surface characteristics of the raw diatomite. Analytical results from FTIR confirmed that the sodium silicate was uniformly distributed across the diatom frustules, introducing a high density of reactive silanol (Si-OH) groups and establishing strong Si-O-Si chemical bonds without destroying the underlying porous framework of the diatomite.
- The sodium-silicate modified diatomite exhibited outstanding efficiency when applied to adsorb heavy metals from wastewater. Specifically, before modification, the residual absorbance was approximately 3.6. After modification, the residual absorbance changed to 1.8. The modified material left 50% less copper in the solution compared to the unmodified material (a 50% reduction in residual copper).
- The research demonstrates a facile, cost-effective, and environmentally friendly strategy to upgrade low-cost natural diatomite into a high-value functional material. The excellent performance and straightforward synthesis route suggest that sodium-silicate modified diatomite holds immense potential for large-scale industrial applications in wastewater treatment.

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ՄՈԴԻՖԻԿԱՑՎԱԾ ԴԻԱՏՈՄԻՏ՝ ՋՐԱՅԻՆ ԼՈՒԾՈՒՅԹԻՑ ՊՂՆՁԻ ԻՈՆՆԵՐԻ ԱՐԴՅՈՒՆԱՎԵՏ ՀԵՌԱՑՄԱՆ ՀԱՄԱՐ

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Ջրային միջավայրերում ծանր մետաղներով աղտոտումը հանդիսանում է զգալի էկոլոգիական սպառնալիք, ինչը անհրաժեշտ է դարձնում մշակել ծախսարդյունավետ վերականգնման տեխնոլոգիաներ: Բնական հանքային սորբենտները, ինչպիսիք են դիատոմիտը, գնահատվում են շրջակա միջավայրի վերականգնման համար՝ իրենց մատչելիության և բնածին ընտրողականության շնորհիվ: Այս աշխատանքում ուսումնասիրվել է նատրիումի սիլիկատով ձևափոխված դիատոմիտի գործընթացը և արդյունավետությունը, որը նախատեսված է կեղտաջրերից պղնձի իոնների (Cu^{2+}) ադսորբցիայի համար: Ձևափոխման գործընթացում օգտագործվել է ծախսարդյունավետ նատրիումի սիլիկատի լուծույթ: Մոդիֆիկացված նյութի կառուցվածքային ամբողջականությունը և ֆիզիկական բնութագրերը գնահատվել են ջրի կլանման արդյունքների միջոցով: Հետագայում անցկացվել են խմբաքանակային ադսորբցիայի փորձեր՝ ձևափոխված դիատոմիտի արդյունավետությունը պղնձի իոնները հեռացնելու գործում գնահատելու համար: Արդյունքները ցույց են տվել, որ նատրիումի սիլիկատով մակերևույթի ձևափոխումը զգալիորեն բարելավում է նյութի կառուցվածքային կայունությունը և ծանր մետաղների նկատմամբ հակվածությունը՝ ստեղծելով արդյունավետ լուծում, արդյունաբերական կեղտաջրերի մաքրման համար:

Բանալի բառեր. ադսորբցիա; դիատոմիտ; պղինձ; նատրիումի սիլիկատ, ջերմային մշակում:

МОДИФИЦИРОВАННЫЙ ДИАТОМИТ ДЛЯ ЭФФЕКТИВНОГО УДАЛЕНИЯ ИОНОВ МЕДИ ИЗ ВОДНОГО РАСТВОРА

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Загрязнение водных сред тяжелыми металлами представляет собой серьезную экологическую угрозу, что обусловливает необходимость разработки экономически эффективных технологий очистки. Природные минеральные сорбенты, такие как диатомит, ценятся для очистки окружающей среды благодаря своей доступности и присущей им селективности. В данной работе исследовались синтез и эффективность модифицированного силикатом натрия диатомита для адсорбции ионов меди (Cu^{2+}) из сточных вод. В процессе модификации использовался экономически эффективный раствор силиката натрия. Структурная целостность и физические характеристики модифицированного материала оценивались по результатам водопоглощения. Затем были проведены эксперименты по адсорбции в периодическом режиме для оценки эффективности модифицированного диатомита в удалении меди из загрязненных вод. Результаты показали, что модификация силикатом натрия значительно улучшает структурную стабильность материала и его восприимчивость к тяжелым металлам, предлагая эффективное и масштабируемое решение для очистки промышленных сточных вод.

Ключевые слова: адсорбция; диатомитовая земля; медь; силикат натрия; термическая обработка

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