



Jurnal Pena Sains

Jurnal Pendidikan Sains dan Sains Murni

Journal homepage: <https://journal.trunojoyo.ac.id/penasains>



THE INFLUENCE OF HEAVY METALS ON THE ABSORPTION OF CATIONIC DYES

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ABSTRACT

Cationic dyes are dyes containing amine derivatives that can be used on cellulose, protein, nylon, acrylic and synthetic fibers but these dyes are less fast in coloring. This study investigates the impact of Pb²⁺ heavy metal ions on cationic dye absorption utilizing molecularly imprinted polymers as adsorbents. Concentrations of Pb²⁺ ranging from 0 to 50 mg/L were examined. In a one-hour interaction, 50 mg of adsorbent was introduced into a solution containing 100 ppm methylene blue dye and Pb²⁺ with varying concentrations. Following centrifugation, the filtrate was collected, and dye concentration was measured using a visible light spectrophotometer. The sorption capacity of the dye with Pb²⁺ reached 41.22 mg/g at the highest concentration and 35.83 mg/g at the lowest. Notably, an inverse relationship was observed between Pb²⁺ concentration and absorption capacity, indicating a decrease as metal ion concentration increased, though stability was maintained. These findings contribute valuable insights into the nuanced dynamics of heavy metal ions and cationic dye absorption, shedding light on potential applications of molecularly imprinted polymers as effective adsorbents.

Article Info

Article history:

Received: February 24, 2024

Accepted: April 15, 2024

Published: April 28, 2024

Keywords:

Adsorption capacity;

Imprinted polymers;

Cationic dyes;

Heavy metals;

Molecular

Introduction

Cationic dyes are dyes containing amine derivatives that can be used on cellulose, protein, nylon, acrylic and synthetic fibers but these dyes are less fast in coloring. One example of this dye is methylene blue, which is a cationic dye with an affinity that tends to be strong. Generally, this dye is used in wool dyeing, textile production, paint, paper, cosmetics and office equipment, in the field of microbiology. Dyes, at low concentration levels, have the potential to affect the quality and aesthetics of the water in question (El Kerdoudi et al., 2023; Loutfi et al., 2023). Therefore, the need for a process to treat liquid wastes containing dyes before they are discharged into the environment is essential and requires serious attention.

Contemporary waste management strategies frequently employ adsorption methods for the removal of dyes from effluents (Jagadeesh & Sundaram, 2023; Rajakaruna et al., 2023). While various adsorbents, such as natural zeolite, activated carbon, and biomass, have found widespread application in this context, their utility is encumbered by limitations, particularly concerning material regeneration and sustainable reuse. The inherent challenges associated with the recyclability of these adsorbents underscore the need for alternative materials that exhibit enhanced functionality and environmental sustainability.

A promising avenue for exploration in this domain is the application of molecularly imprinted polymers (MIP) as adsorbents (Kaya et al., 2023; Wu et al., 2022). MIPs, characterized by their tailored molecular recognition sites, offer a unique and efficient approach to selectively adsorb target molecules. Their distinct advantages, including tunable selectivity and reusability, make them an intriguing focus of study in the quest for advanced and sustainable adsorption materials. As research in this area advances, the potential of MIPs to address the shortcomings of traditional adsorbents becomes increasingly evident, paving the way for innovative and environmentally conscious solutions in the realm of waste management.

Molecularly Imprinted Polymers (MIPs) represent a class of polymers characterized by their ability to undergo specific recognition interactions with a target analyte molecule. The distinctive feature of MIPs lies in the selection of functional monomers during their synthesis, possessing shapes and structures conducive to interactions with the target analyte molecules through either covalent or non-covalent bonds. The

polymerization process, facilitated by a specific method utilizing these chosen monomers, is initiated with the analyte molecule serving as the template. Subsequently, the imprinted molecule is extracted from the template, resulting in the formation of a polymer endowed with an active site that exhibits specific binding affinity to the structural configuration of the target analyte molecule. The tailored molecular recognition sites of MIPs contribute to their heightened selectivity, facilitating precise binding interactions (Mabrouk et al., 2023).

The distinctive attributes of MIPs, including their enhanced selectivity, durability, and the capacity for repetitive use, render them noteworthy materials for diverse applications (Mabrouk et al., 2023; Murdaya et al., 2022). These characteristics make MIPs particularly valuable in the context of adsorption processes, offering an efficient and sustainable alternative to traditional adsorbents. The utilization of MIPs in waste management and environmental remediation showcases their potential to contribute significantly to the development of advanced and eco-friendly technologies in the field (Mabrouk et al., 2023).

Imprinted Polymers have gained wide usage in various fields, including in solid-phase separation processes, various chromatography applications, and sensor development. Their usefulness extends to various sectors due to their potential ability to capture specific analyte compounds. Generally, these functional materials are synthesized or prepared using various monomers such as methyl methacrylate, methacrylic acid, vinylpyridine, acrylamide, and crosslinking agents such as ethylene glycol dimethacrylate (Roland et al., 2023; Zhang et al., 2023).

In this study, molecularly imprinted polymers (MIPs) will be synthesized using methacrylic acid monomer, divinyl benzene crosslinking agent, and 2,2-azo bis isobutyronitrile (AIBN) initiator, with template molecules in the form of methylene blue cationic dye. Adsorption evaluation of the MIP adsorbent will be carried out on methylene blue solution with respect to the impact of heavy metal interfering ions in the test solution matrix.

Research Methods

Synthesis and Characterization of MIPs

The synthesis of the Molecularly Imprinted Polymer (MIP) involved dissolving 0.5 mmol of

methylene blue, 10 mmol of divinyl benzene (DVB), 2 mmol of methacrylic acid (MAA), and 20 mg of the initiator 2,2-azo bis isobutyronitrile (AIBN) in 20 mL of acetonitrile solvent. The resulting mixture underwent polymerization on an ice bath under a flow of nitrogen gas (N₂) and was subsequently subjected to the polymerization stage for 10 minutes in a MAOST Microwave. The resultant polymer solid was then finely crushed and subjected to washing with a mixture of acetic acid and methanol in a volumetric ratio of 1:9.

The ensuing characterization of functional groups within the synthesized MIP polymer was conducted utilizing an Agilent FTIR spectrophotometer instrument operating in the wave number range of 400-4500 cm⁻¹. The FTIR spectra were recorded to discern and analyze the distinctive functional groups present in the polymers. This instrumental analysis provides critical insights into the chemical composition and structural attributes of the MIP, establishing a foundation for understanding its potential efficacy in targeted adsorption applications.

Adsorption and MIP Evaluation

The assessment of the adsorption properties of the refined Molecularly Imprinted Polymer (MIP) was conducted through its interaction with a methylene blue solution. In the experimental setup, 50 mg of MIP adsorbent was introduced into 25 mL of a mixed methylene blue solution with a concentration of 100 ppm, maintained at pH 10, and subjected to continuous stirring for a duration of 60 minutes. The investigation further encompassed an examination of the impact of interfering ions on the adsorption capacity of methylene blue. To elucidate this, ion solutions containing Pb²⁺ ions at varying concentrations ranging from 10 to 50 ppm were introduced into the methylene blue solution concurrently with the adsorbent.

Throughout the interaction period, the mixture of adsorbent and methylene blue solution underwent continuous stirring to facilitate optimal contact between the MIP and the dye molecules. Upon completion of the absorption process, the resultant mixture underwent centrifugation, and the filtrate was analyzed to ascertain the remaining concentration of methylene blue. The assessment of the remaining concentration was conducted using a visible light spectrophotometer operating at a wavelength of 664 nm. The calculated percent adsorption of methylene blue utilizing the MIP

adsorbent was determined employing a specified equation.

This meticulous experimental design allows for a comprehensive exploration of the adsorption capabilities of the MIP adsorbent, taking into account both the inherent characteristics of methylene blue solution and the potential influence of interfering ions, particularly Pb²⁺. The incorporation of varying concentrations of Pb²⁺ ions offers valuable insights into the versatility and selectivity of the MIP adsorbent under diverse conditions, contributing to a nuanced understanding of its potential applications in adsorption processes:

$$\text{Adsorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i represents the initial concentration of the solute in the solution, measured in milligrams per liter (mg/L), and C_e signifies the concentration of the solute in the final solution after the adsorption process, also expressed in mg/L. This equation allows for a precise determination of the percentage of the solute adsorbed by the adsorbent material, providing a quantitative measure of the adsorption efficiency. The utilization of this equation is integral to the rigorous assessment of the adsorption capacity of materials such as Molecularly Imprinted Polymers (MIPs) under specific experimental conditions, contributing to the elucidation of their efficacy in targeted applications.

Result and Discussion

Characterization of MIP Adsorbent

The comprehensive characterization of the molecularly imprinted polymer (MIP) adsorbent was undertaken through the application of Fourier-Transform Infrared (FTIR) spectroscopy, a powerful analytical technique. Figure 1 prominently displays the resulting FTIR spectrum, offering a visual representation of the vibrational modes associated with the functional groups present in the MIP adsorbent. This spectrum serves as a fundamental tool for the identification and confirmation of distinctive functional groups within the polymer matrix, laying the groundwork for a meticulous evaluation of its molecular structure.

FTIR spectroscopy allows for a detailed examination of the chemical composition and structure of the MIP adsorbent by providing

information on the vibrational frequencies associated with specific functional groups. Through this analytical approach, valuable insights are garnered into the nature of chemical interactions and bonding mechanisms operating within the polymer matrix. The elucidation of such interactions is pivotal in understanding the adsorption capabilities of the MIP, as it offers a nuanced understanding of how the material engages with target molecules.

The acquired FTIR spectrum not only aids in the identification of characteristic functional groups but also facilitates a comprehensive assessment of the molecular structure of the MIP adsorbent. This structural understanding is indispensable for evaluating the suitability of the MIP in targeted adsorption applications. The detailed information obtained through FTIR spectroscopy contributes to advancing our knowledge of the MIP's chemical makeup, allowing for informed decisions regarding its potential effectiveness in diverse adsorption scenarios.

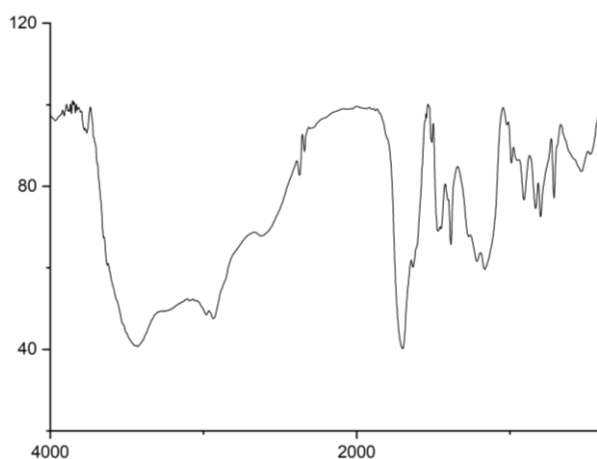


Figure 1. FTIR Spectrum

In the MIP spectrum, a prominent peak discerned at 1699.29 cm^{-1} signifies the presence of characteristic C=O vibrations, attributed to methacrylic acid. This distinctive spectral feature is instrumental in confirming the incorporation of methacrylic acid into the molecularly imprinted polymer (MIP) matrix. Furthermore, the observation of a peak at 1215.15 cm^{-1} in the MIP spectrum is indicative of C-OH vibrations, suggesting the involvement of hydroxyl groups in the MIP composition.

The manifestation of the C=O and C-OH vibrations in the FTIR spectrum provides critical molecular-level information regarding the functional groups within the MIP adsorbent. These findings contribute to the comprehensive

characterization of the polymer, elucidating its chemical structure and aiding in the understanding of potential interactions during adsorption processes. The identification of specific vibrational modes associated with methacrylic acid and hydroxyl groups enhances our understanding of the MIP's chemical composition, underscoring the relevance of FTIR spectroscopy as a powerful tool for detailed structural analysis in the realm of molecularly imprinted polymers.

The analysis of the MIP spectrum reveals distinct peaks corresponding to C=O and C-OH vibrations, indicative of the presence of methacrylic acid and hydroxyl groups, respectively. These insights enrich the understanding of the MIP's chemical structure and hold implications for its functionality in selective adsorption applications.

Evaluation of the Effect Pb^{2+} on the Adsorption of MIP adsorbent

Effluent, as a complex matrix, encompasses not only dyes but also potentially hazardous heavy metals such as lead (Pb). Given this multifaceted composition, it becomes imperative to conduct systematic testing to unravel the intricate dynamics and assess the consequential impact of the matrix on the adsorption process. The integration of heavy metals into the effluent demands a comprehensive understanding of their role in influencing the efficacy of adsorption mechanisms. This study, therefore, embarks on a nuanced examination to elucidate the interplay between the adsorption process and the coexistence of dyes and Pb^{2+} ions within the matrix.

The outcomes of this investigation are encapsulated in Figure 2, which delineates the adsorption results concerning methylene blue in the presence of Pb^{2+} ions at varying concentrations. The graphical representation serves as a visual narrative of the intricate relationship between the adsorbent material and the coexisting heavy metal ions within the effluent matrix. The variations in adsorption efficiency across diverse concentrations of Pb^{2+} ions provide invaluable insights into the dynamic nature of the adsorption process in the complex effluent milieu.

The exploration of effluent as a matrix reveals the potential coexistence of dyes and heavy metals, prompting a meticulous investigation into their collective impact on the adsorption process. Figure 2 encapsulates the empirical results, shedding light on the nuanced interplay between

the adsorbent and Pb^{2+} ions at varying concentrations, thereby advancing our comprehension of the intricate adsorption mechanisms within the multifaceted effluent matrix.

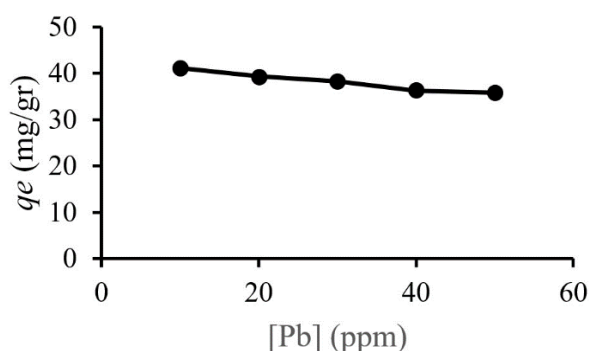


Figure 2. Effect of Pb^{2+} on Adsorption Capacity by MIPs

The insights gleaned from the findings depicted in Figure 2 shed light on the adsorption dynamics of methylene blue by the Molecularly Imprinted Polymer (MIP) adsorbent in the presence of increasing concentrations of Pb^{2+} ions. Surprisingly, the observed trend suggests a tendency for the adsorption capacity to remain relatively stable despite the escalating concentration of Pb^{2+} . This unexpected phenomenon prompts a closer examination to elucidate the underlying mechanisms governing the interaction between the metal ions and the MIP adsorbent surface.

One plausible explanation for the observed trend may lie in the environmental conditions created during the experimental setup. The alkaline pH of the environment employed in the study may play a pivotal role in diminishing the significance of interactions between the metal ions and the adsorbent surface. The alkaline nature of the environment potentially mitigates the reactivity of the metal ions with the functional groups present on the adsorbent. Consequently, the weakened interaction may impede the formation of hydroxide precipitates, reducing the overall impact of metal ions on the adsorption process.

An intriguing possibility arises concerning the formation of hydroxide precipitates in the solution containing metal ions. It is plausible that, under the prevailing conditions, the significance of this precipitation phenomenon is notably low. The diminished reactivity and subsequent limited formation of hydroxide precipitates may contribute to the observed stability in the adsorption capacity of methylene blue by the MIP adsorbent, even in the face of increasing concentrations of Pb^{2+} ions.

The unexpected constancy in the adsorption capacity of methylene blue by the MIP adsorbent amid rising concentrations of Pb^{2+} ions beckons a comprehensive investigation into the underlying factors at play. The alkaline pH of the experimental environment emerges as a critical determinant, influencing the interactions between metal ions and the adsorbent surface. This elucidation opens avenues for further exploration into the potential role of hydroxide precipitates, offering a nuanced understanding of the complex interplay in the adsorption process within this unique environmental context.

Conclusion

The synthesis of Molecularly Imprinted Polymer (MIP) from methacrylic acid and divinyl benzene has been successfully carried out and investigated through analysis using FT-IR spectrophotometer. The adsorption capacity towards methylene blue in the presence of Pb^{2+} interfering ions with concentrations ranging from 0 to 50 mg/L was about 41.22 to 35.83 mg/g. The findings of the study showed that, as the concentration of the disrupting ions increased, the adsorption capacity of methylene blue by the polymer prepared via molecular molding showed a tendency to remain constant.

Further investigations are needed on a wide variety of interfering ions that may be present in a given effluent, in order to obtain a variety of findings that may explain how these metals affect the adsorption capacity of MIP adsorbents.

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