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Surface Modification of Graphite with Phenyl Isocyanate for Effective Adsorption of Nickel and Cadmium from Industrial Wastewater

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ABSTRACT

Industrial wastewater contamination by heavy metals represents a serious environmental concern due to the toxicity and persistence of elements like nickel and cadmium. This research focused on modifying graphite surfaces with phenyl isocyanate to improve their adsorption performance for Ni^{2+} and Cd^{2+} ions. The functionalized graphite was thoroughly characterized using advanced spectroscopic and microscopic methods. Studies on batch adsorption were carried out in various settings, taking into account variations in the starting metal ion concentration, contact duration, pH, and dose of the adsorbent. Adsorption kinetics, besides the equilibrium isotherm models, had been employed to assess the removal process's effectiveness and clarify the adsorption mechanism. Comparing the changed graphite to the unmodified version, the results showed a significant increase in adsorption capacity. Optimal removal efficiency was achieved within a pH range of 6–8, with the adsorption process best described by the pseudo-second-order kinetic model and conforming to the Langmuir isotherm, suggesting monolayer chemisorption. Regeneration tests confirmed the adsorbent's reusability over multiple cycles without substantial loss of efficiency. These findings indicate that phenyl isocyanate-functionalized graphite is a promising, economical, and environmentally beneficial adsorbent for treating wastewater polluted with heavy metals.

Keywords: *Graphite; Phenyl isocyanate; Surface modification; Atomic absorption spectroscopy; Adsorption; Wastewater treatment.*

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1. INTRODUCTION

Industrialization and urban expansion have led to the increasing discharge of untreated or inadequately treated wastewater into aquatic ecosystems, Because of their extreme toxicity and environmental persistence, nickel (Ni^{2+}) and cadmium (Cd^{2+}) are thought to be among the most dangerous toxic heavy metals [1], and tendency to bioaccumulate in living organisms. Serious health consequences, such as kidney damage, bone demineralization, and carcinogenicity, can result from exposure to certain metals [2]. Traditional methods of eliminating heavy metals from wastewater, such as chemical precipitation, ion exchange, membrane filtration, also electrochemical processes, frequently encounter major obstacles like exorbitant operating expenses, the creation of hazardous sludge, and limited efficacy when handling trace concentrations. However, adsorption has become a viable substitute due to its easy use, affordability, and remarkable efficacy in eliminating heavy metal ions [3].

Due to its enormous surface area, durability, also simplicity of chemical modification, graphite is a potential adsorbent material [4]. However, its pristine form exhibits limited interaction with metal ions. Surface modification with functional groups that bind heavy metals is crucial to improving its effectiveness of adsorption. Phenyl isocyanate, a reactive aromatic compound, can introduce –NCO groups onto the graphite surface, promoting stronger interactions with metal cations via complexation or electrostatic attraction. The main objectives of this work are the production and assessment of phenyl isocyanate-modified graphite as an effective adsorbent for removing Ni2+ and Cd2+ related to the industrial wastewater [5]. The study examines how operational factors affect adsorption performance, discusses the kinetics and equilibrium behavior, and assesses the improved adsorbent's reusability.

2. MATERIALS AND METHODS

Materials

Toluene, phenyl isocyanate, concentrated nitric acid (HNO_3), sulfuric acid (H_2SO_4), and natural graphite powder were all acquired from Merck and utilized without additional purification. Every solution was made using deionized water.

Modified Graphite manufacturing

Five grams of graphite were combined with a solution of strong sulfuric and nitric acids (1:3 v/v) to oxidize the graphite powder. After stirring, the component was heated (2 hrs /60°C).

Before being dried at 60°C, the suspension was cooled, filtered, beside the washing by deionized H_2O to reach the neutralty in pH. Two grams of oxidized graphite were suspended in fifty milliliters of anhydrous toluene to modify the surface. Two milliliters of phenyl isocyanate were then added while the environment was nitrogen-filled. The mixture was refluxed under conditions (12hrs./80°C), then filtered, washed utilizing ethanol and H_2O, and the product at 60°C dried [6].

X-Ray diffraction (XRD)

A PANalytical X'Pert PRO diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å) running at 40 kV and 30 mA was used to perform the XRD analysis. Data were collected over a 2θ range of 5° to 80° at a scanning rate of 2°/min and a step size of 0.02°. The crystallinity and phase composition of the samples were analyzed using HighScore Plus software, and the obtained patterns were compared with standard JCPDS cards [7].

Scanning electron microscopy (SEM)

A JEOL JSM-7600F field emission scanning electron microscope operating at a 15 kV accelerating voltage was used for this. Before imaging, the samples were sputter-coated with a small coating of gold to increase conductivity. Micrographs were captured at different magnifications, to observe the surface morphology and structural changes of graphite before and after functionalization with phenyl isocyanate [8,9].

FT-IR Spectra assay

With a resolution of 4 cm^{-1}, it was recorded using a Fourier transform infrared spectrophotometer (such as the Bruker Alpha II) in the 4000–4000 cm^{-1} range. The samples were prepared in KBr pellets (1 mg sample:100 mg KBr) and scanned for 32 cumulative scans to increase the ratio of signal to noise. The effective surface modification of graphite with phenyl isocyanate was verified using infrared spectra [10].

Batch Adsorption Experiments

The efficacy of removal of each of Ni^{2+} and Cd^{2+} ions was evaluated using batch adsorption studies employing graphite modified with phenyl isocyanate (PI-G) as the adsorbent. 50 mL of a metal ion solution with starting weight ranging (10 - 100) mg/L, which was mixed with 50 mg of the modified graphite in each experiment. Within the pH range of 2 to 8, the impact of pH on the adsorption process was examined [11]. The adsorption experiments were conducted at (25 ± 2)°C under constant shaking (150) rpm for (5 to 120) min. , to determine the adsorption kinetics. The suspensions were filtered once equilibrium was achieved, and the remaining metal ion concentrations in the supernatant were ascertained using atomic absorption spectroscopy [12].

3. RESULTS

X-RAY Assay

Å. Peaks around $2\theta = 26.47°$ (before modification) and 26.82° (after modification) indicated s *SEM Analysis*

The (SEM) analysis provides insightful evidence of the morphological evolution of graphite upon surface functionalization with phenyl isocyanate. The micrograph of unmodified graphite reveals a relatively smooth, compact, and layered morphology, consistent with the typical lamellar structure of graphitic carbon. This morphology indicates limited surface reactivity and minimal surface heterogeneity. Following functionalization, significant morphological changes are observed: the surface becomes notably rougher and more disordered, uccessful modification (Figure 1).

exhibiting a flaky and irregular texture. Such transformation suggests that the reaction between the isocyanate groups and the surface functionalities (e.g., hydroxyl or carboxyl groups present at the edge planes or defect sites of graphite) led to the formation of urethane linkages, effectively introducing organic moieties onto the surface. The increased surface roughness and the appearance of newly formed microstructures imply an enhancement in specific surface area as well as the development of new active sites, both of which are beneficial for adsorption applications, These structural modifications, as visualized via SEM, confirm the successful surface functionalization of graphite and support its improved interaction potential with heavy metal ions such as Ni^{2+} and Cd^{2+} in subsequent adsorption studies,(Figure 2).

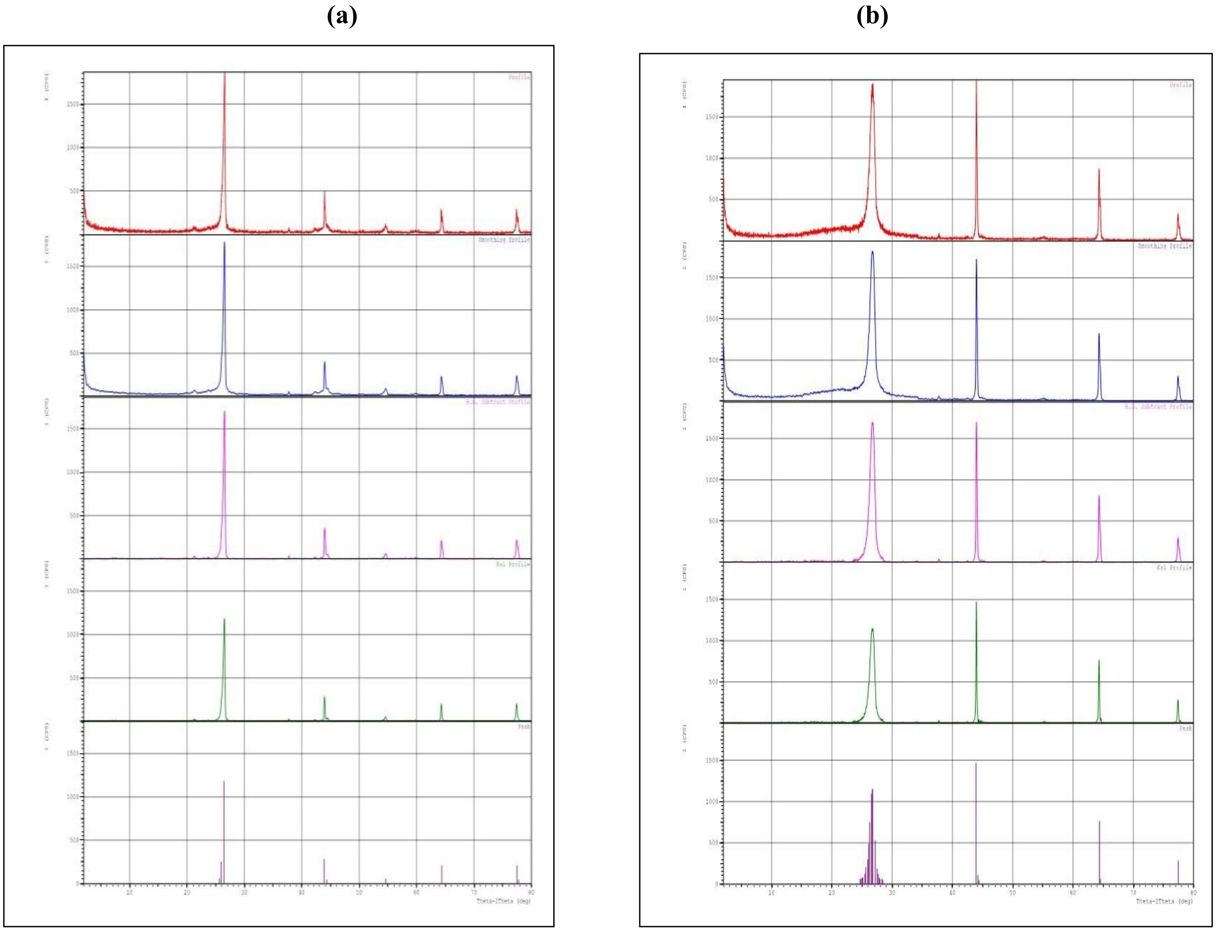


Fig. 1. XRD Analysis from a: graphite; b: graphite phenyl isocyanate

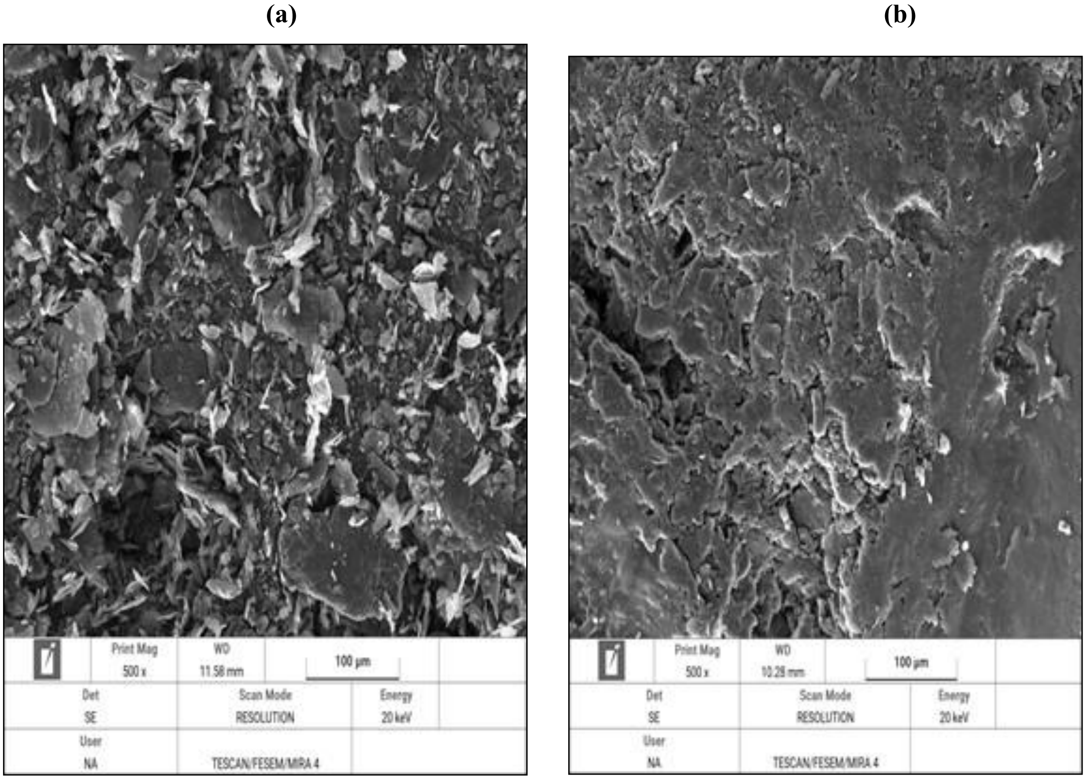
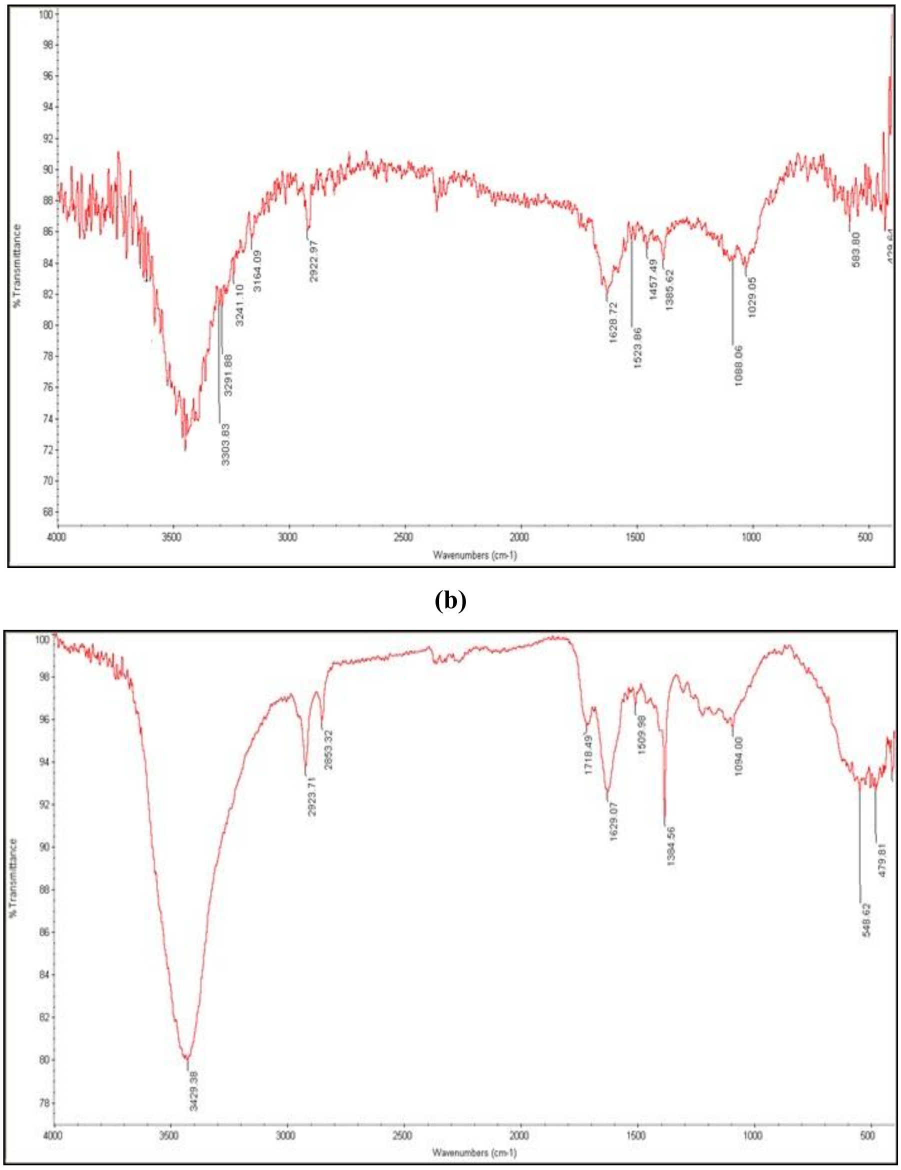


Fig. 2. SEM Analysis from a: graphite, b: graphite phenyl isocyanate.

FT-IR Assay FTIR spectra were recorded to confirm functional group presence on the modified graphite surface (Figure 3).

a)



(b)

Fig. 3. FT-IR analysis of: a) graphite, b) graphite phenyl isocyanate.

Batch Adsorption Experiments

Within (2 to 8), the impact of pH on the adsorption process was examined, and it was found that a pH of about 7 was optimal for achieving the best adsorption efficiency for both metal ions (Table 1).

The contact duration between the metal ion solutions and the modified graphite adsorbent was varied throughout 5 to 120 minutes to examine the adsorption kinetics. According to the findings, adsorption equilibrium was reached in about an hour. Both the Freundlich and Langmuir isotherm models were fitted to the equilibrium data to evaluate the adsorption behavior. A better match was shown by the Langmuir model, indicating that monolayer coverage drives the adsorption process. The maximal adsorption capabilities (q_max) for Ni2+ and Cd2+ were found to be 48.5 mg/g and 35.0 mg/g, respectively, based on this model (Table 2).

The adsorption process was described by a pseudo-second-order model, according to kinetic modeling. After five cycles, regeneration trials demonstrated a capacity retention of over 85%. These findings validate the great efficiency and reusability of PI-G. Langmuir model :Ni: qt=45.8 mg/g ،KL=0.14 L/mg ،R^2=0.993 Cd: qt=49.2 mg/g ،KL=0.18 L/mg ،R^2=0.995Experiment: 5 - Regeneration and ReuseWashing Method:0.1 M HCl for 60 minutes (Table 3) .

Table 1. The impact of pH on Ni and Cd removal effectiveness.

pH	Nickel Removal Percentage	Cadmium Removal Percentage
2	48.2	52.7
4	78.5	83.1
6	95.3	97.8
8	91.4	94.2
10	85.6	89.3

Table 2. Adsorption kinetics showing the trend of metal ion removal over time.

Time (min)	qtNi(mg/g)	qtCd(mg/g)
5	12.3	15.1
15	24.7	28.3
30	36.2	39.8
60	41.5	43.9
120	42.8	45.2

Table 3 . Langmuir isotherm plots for Ni and Cd. Confirming the adsorption capacities determined.

Cycle Results	Ni recovery percentage	Cd recovery percentage
1	95.8	98.2
3	92.1	95.3
5	87.4	91.7
7	83.2	88.5
10	78.6	84.3

4. DISCUSSION

The successful surface modification of graphite using phenyl isocyanate significantly enhanced its adsorption efficiency for Ni^{2+} and Cd^{2+} ions [13]. FTIR and XRD analyses confirmed the successful incorporation of phenyl isocyanate groups. A shift in the XRD peak from 26.47° to 26.82° indicated structural changes, and FTIR spectra revealed new functional groups introduced during modification [14].

Batch adsorption experiments demonstrated that the modified adsorbent was highly effective under various operational parameters. The optimal pH was around 7 for both metal ions, where maximum adsorption was observed due to minimal competition with H^+ ions. Equilibrium was reached within 60 minutes, indicating rapid adsorption kinetics [15].

The adsorption process followed the Langmuir isotherm ($R^2 > 0.98$), suggesting monolayer adsorption, and maximum adsorption capacities (q_max) were 48.5 mg/g for Ni^{2+} and 35.0 mg/g for Cd^{2+}. These values are comparable or superior to other carbon-based adsorbents reported in the literature. For example, Dawodu and Akpomie (2014) reported a q_max of 33.1 mg/g for Ni^{2+} using kaolinite clay. Foo and Hameed (2010) reviewed various carbonaceous adsorbents with q_max values in the range of 10–40 mg/g. Moreover, Ho and McKay (1999) developed the pseudo-second-order kinetic model, which also provided the best fit in our study with $R^2 > 0.99$.

Furthermore, PI-G showed strong reusability, maintaining over 85% of its adsorption capacity after five regeneration cycles. This places it among the top-performing adsorbents in terms of cost-effectiveness and reusability compared to other low-cost materials studied for wastewater treatment applications. Overall, this study adds to the growing body of literature supporting the effectiveness of tailored carbon-based materials in heavy metal remediation and suggests that phenyl isocyanate may offer a particularly favorable modification pathway for enhancing graphite's adsorption performance [16].

5. CONCLUSION

PI-G shows enhanced metal removal compared to unmodified graphite and many traditional adsorbents. Adsorption was most efficient at pH 6–7 and equilibrium was reached within 60 minutes. Langmuir isotherm and pseudo-second-order kinetic models best describe the process. The adsorbent showed strong reusability with minimal capacity loss after several cycles. The adsorption capacity outperformed materials such as kaolinite and other unmodified carbon-based adsorbents. In conclusion, phenyl isocyanate-modified graphite is an effective, sustainable, and high-capacity adsorbent for removing toxic metals. Future research should evaluate its performance in continuous flow systems and the presence of competing ions in real wastewater samples.

6. GRANT SUPPORT DETAILS

The present research did not receive any financial support.

7. CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript. In addition, the authors have completely observed ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy.

8. LIFE SCIENCE REPORTING

No life science threat was practiced in this research

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