Removal of Heavy Metals via h-B_2S_3 with Kagome Architecture: A First Principles Approach to Sustainable Water Treatment

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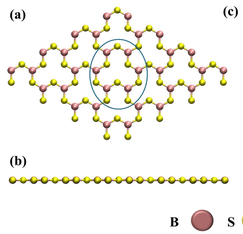
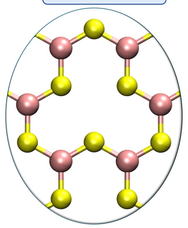
ABSTRACT

The pollution caused by toxic heavy metals poses growing environmental risks to ecosystems and human health. Heavy metal removal from wastewater and contaminated water systems involves a range of sophisticated treatment technologies, many of which are associated with high operational costs and significant energy demands. Among these approaches, adsorption-based metal separation using two-dimensional (2D) nanomaterials has emerged as one of the most efficient and promising techniques, owing to their exceptionally high surface area, abundant active sites, tunable surface chemistry, and superior adsorption capacity. Therefore, the development of reliable, cost-effective, and sustainable nanomaterials is essential. In this work, we present a first-principles approach to investigate the adsorption performance of h-B_2S_3 nanosheets toward different heavy metals (As, Hg, Ni, Cd, Cr, Pb, and Zn). The calculated adsorption energies for the monolayer and bilayer systems are: As (−0.261 eV and −0.284 eV), Hg (−0.262 eV and −0.280 eV), Ni (−5.882 eV and −6.333 eV), Cd (−0.280 eV and −0.301 eV), Cr (−5.145 eV and −7.016 eV), Pb (−1.990 eV and −2.140 eV), and Zn (−0.274 eV and −0.287 eV), respectively. These results indicate comparatively stronger adsorption for Ni, Cr, and Pb, whereas the remaining species exhibit relatively weak adsorption interactions with both systems. Atoms-in-molecules (AIM) analysis reveals that Ni, Cr, and Pb exhibit partially covalent interactions with the adsorbent surface, whereas Zn, Cd, and Hg predominantly display closed-shell, noncovalent interactions. In contrast, As demonstrates a mixed electrostatic-covalent interaction character. This interaction trend remains consistent within the bilayer system, suggesting enhanced binding strength and improved structural stability. The superior adsorption performance of the h-B_2S_3 sulfur-rich sites can be attributed to the soft-base nature of Sulfur, which promotes favourable interactions with soft-acid heavy metal species. Furthermore, the h-B_2S_3 nanosheet offers a high density of accessible active sites, thereby facilitating efficient adsorption. Overall, these findings provide a robust theoretical foundation for future experimental investigations aimed at validating the potential application of h-B_2S_3-based materials in heavy-metal filtration and water purification systems.

B2O3 Nanosheet



Site-view



METHODOLOGY

- DFT simulations were performed using the CP2K code with periodic boundary conditions (PBCs).
- DZVP basis sets and GTH pseudopotentials were applied for all atoms.
- Exchange–correlation was treated using the GGA-PBE functional with Grimme D3 dispersion correction.
- A 20 Å vacuum layer was added perpendicular to the h-B_2S_3 nanosheet.
- Bonding nature was analysed using AIM topology via the Multiwfn package.
- Charge transfer was evaluated by Bader charge analysis with Critic2.

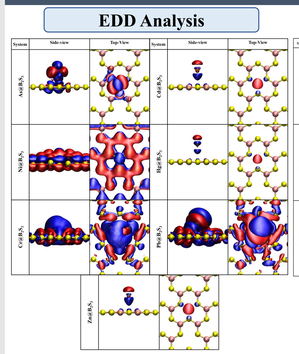
The optimized geometry of the 4x4 supercell of B_2S_3 exhibits a 2D Kagome lattice that belongs to P62m space group. The calculated lattice parameter of the unit cell, B–S bond length, and S–B–S bond angle are 5.46 Å, 1.83 Å, and 120°, respectively, which are in good agreement with previous studies. The above figure depicts the optimised configuration of the B_2S_3 nanosheet.

OBJECTIVES

- Investigate adsorption of heavy metals (As, Hg, Ni, Cd, Cr, Pb, Zn) on B_2S_3 nanosheets.
- Explore both neutral atoms and charged ions to mimic real aqueous conditions.
- Compare adsorption on monolayer vs. bilayer B_2S_3.
- Understand bonding, charge transfer, and interaction mechanisms through DFT-based analysis.
- Bring selectivity by vacancy engineering for specific targets.

RESULTS

EDD Analysis



NCI Analysis

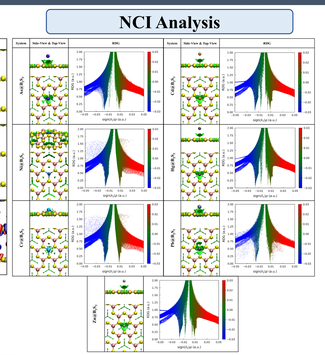
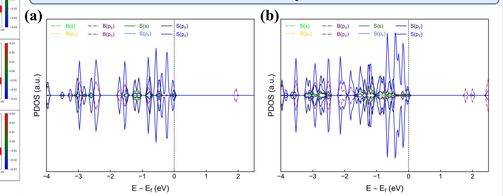


Illustration of the NCI and RDG graphs for heavy-metal-adsorbed mono/bilayer h-B_2S_3 nanosheets for As, Cd, Ni, Hg, Cr, Pb, and Zn. The NCI isosurfaces are colour-coded: blue for strong attractive interactions, green for weak van der Waals/electrostatic interactions, and red for steric repulsion. The bilayer shows more evenly spaced NCI isosurfaces around the metal centres than the monolayer, suggesting less surface distortion and steric hindrance and demonstrating that the bilayer B_2S_3 nanosheet provides a more favourable adsorption environment for heavy metal capture.

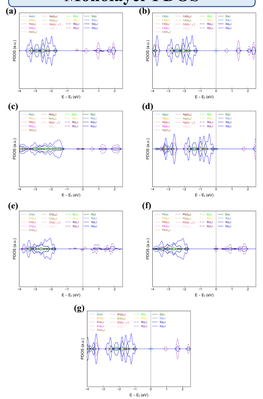
Illustrating EDD plots between adsorbed heavy metals and h-B_2S_3 mono/bilayer nanosheet: top view and side view clearly showing the electron density difference between Heavy metals and the h-B_2S_3. The electron density depletion is represented by blue and accumulation by red isosurfaces, with an isovalue of 0.0004 e/Å^3.

PDOS Analysis

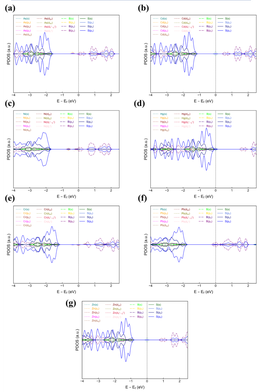


Illustrating the PDOS of pristine monolayer **(a)** and bilayer **(b)** h-B_2S_3 nanosheets.

Monolayer PDOS



Bilayer PDOS



QTAIM Analysis

System	ρ (a.u.)	∇²ρ (a.u.)	V/G	H/ρ
Pb@B_2S_3	0.0341	0.0692	−1.342	−0.109
Zn@B_2S_3	0.0072	0.0151	−0.807	+0.085
As@B_2S_3	0.0154	0.0294	−0.984	+0.009
Cd@B_2S_3	0.0279	0.0150	−0.804	+0.087
Cr@B_2S_3	0.0845	0.2845	−1.245	−0.274
Hg@B_2S_3	0.0072	0.0186	−0.768	+0.122
Ni@B_2S_3	0.1202	0.2910	−1.444	−0.483

Adsorption Energy

System	Monolayer Eads	Bilayer Eads
As	−0.261	−0.284
Hg	−0.262	−0.280
Ni	−5.882	−6.333
Cd	−0.280	−0.301
Cr	−5.145	−7.016
Pb	−1.990	−2.140
Zn	−0.274	−0.287

Bader Charge Analysis

System	Monolayer	Bilayer
As	0.0034	0.0044
Hg	-0.006	-0.006
Ni	0.220	0.262
Cd	0.0174	0.0188
Cr	0.862	0.804
Pb	0.713	0.654
Zn	0.0137	0.0145

DISCUSSION

- B_2S_3 nanosheets show favourable physisorption to moderate chemisorption.
- Analyses included adsorption site identification, electronic structure, charge density, and Bader charge evaluation.
- QTAIM confirms diverse bonding, with sulfur-rich sites driving strong reactivity.
- The soft base nature of Sulfur favors interactions with soft acid-type heavy metals.
- B_2S_3 combines high adsorption affinity, chemical stability, and abundant active sites.
- Outperforms materials like doped graphene, MOFs, and sulfur-decorated surfaces.
- Demonstrates strong potential for water purification and future real-world remediation.

CONCLUSION

In conclusion, this study investigates the adsorption behaviour of heavy metals (As, Hg, Ni, Cd, Cr, Pb, and Zn) on h-B_2S_3 nanosheets. Both monolayer and bilayer systems were systematically examined through a comprehensive first-principles investigation to elucidate how structural configuration influences adsorption performance. The h-B_2S_3 nanosheet exhibited a wide range of interaction strengths, from physisorption to strong chemisorption, and broad-spectrum adsorption capability. Among these heavy metals, Zn, Cd, Hg, and As exhibit weaker physisorption interactions, whereas Ni, Cr, and Pb show stronger adsorption, with highly negative E_{ads}, enhanced orbital overlap with Sulfur p-orbitals, and greater Bader charge transfer. This trend is consistent across the bilayer system, where E_{ads} become more negative, Bader charge transfer increases slightly, and layer distortions decrease, indicating stronger interaction, greater stability, and an optimised electronic environment, highlighting its practical relevance for real-world applications. In addition to E_{ads} and charge transfer analyses, AIM, NCI, PDOS, and EDD analyses were combined to provide a detailed understanding of the adsorption mechanism. The trigonal centre among three Sulfur atoms provides a sulfur-rich surface on the h-B_2S_3 nanosheet, playing a critical role in facilitating interactions with heavy metals and acting as an active site for charge transfer and adsorption. The enhanced adsorption performance and suitable electronic environment of h-B_2S_3 demonstrate broad-spectrum applications for various heavy metals, highlighting its potential for sustainable water treatment. This study highlights the superior potential of h-B_2S_3 nanosheets for wastewater treatment and offers a strong theoretical basis for experimental groups to develop cutting-edge nanoscale filtration systems for heavy metal removal.

FUTURE PERSPECTIVE

This study demonstrates that B_2S_3 nanosheets exhibit strong potential for heavy metal remediation due to their high affinity, chemical stability, and abundant active sites. Adsorption energy calculations, Bader charge analysis, and QTAIM confirm a range of interactions from physisorption to moderate chemisorption, with sulfur-rich sites playing a dominant role. The enhanced reactivity is attributed to the soft base nature of Sulfur, which favours interactions with soft acid-type heavy metals. Overall, h-B_2S_3 outperforms several reported materials such as doped graphene, MOFs, and sulfur-decorated surfaces, making it a promising platform for water purification applications.

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