

PERFORMANCE OF BORON NITRIDE NANOSHEETS IN DYE ADSORPTION: A MINI-REVIEW

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Abstract

Cleaning water before draining is necessary because of its harmful effects on aquatic ecosystems. Adsorption is an economically feasible and easy process that provides a good solution to remove toxic dyes from water. An adsorbent which can be used in dye adsorption have some features such as high adsorption, binding energy, and negative interaction energy. Carbon materials, metal-organic frameworks (MOFs), silica, and titania are among the most used adsorbent for dye adsorption in the literature. Nowadays, 2D materials have a popularity. The study aims to point out the importance of boron nitride nanosheets (BNNSs) in dye adsorption.

Key Words: Boron nitride nanosheets, dye adsorption, environmental remediation

1. Introduction

It is clear that water pollution originates from excess urbanization and industrialization. So, it has formed a crucial problem throughout the world. Sources of this contamination caused chemicals and synthetic dyes among the other pollutants due to their high solubility in water. Synthetic dyes mix as textile wastes to the water. It is obvious that these dyes are carcinogenic, hazardous for human beings and aquatic ecosystem. Besides that, these dyes are responsible for decrease in water quality. It can be preferred several methods for dye removal from water. They are photocatalysis, adsorption, chemical oxidation, ion exchange, membrane separation, and biological degradation. However, these methods require complex, long-time processes and high energy usage. However, adsorption covers easy and conventional steps. Besides that, to recover adsorbents and use them several times render adsorption economically feasible (Liu et al., 2022).

Textile dyes are organic substances. There are two types of textile dyes concerning their water solubility. They are soluble and insoluble dyes. Soluble dyes can be acid (anionic), basic(cationic), reactive, or direct. While insoluble dyes are examined in four topics which are sulfur, disperse, vat, and pigments (Sharma et al., 2021).

In this research, it aimed to review water-soluble dyes. Because the adsorption studies majorly carried out in a water environment. Anionic dyes are applied to hydrophilic materials like wool, cotton, and nylon at a 2-6 pH range. Most of the synthetic dyes utilized in the textile industry are anionic. These dyes are classified in several ways concerning their functional groups. For example, Acid Red 27 belongs to the azo dye class. On the other hand, Cationic dyes are synthesized from organic bases. They can ionize in a water environment and form cations. Auramine O, Malachite Green, Nile Blue, and Rhodamine B are among the cationic dyes class. Reactive dyes accepted as anionic dyes formed covalent bonds to the materials like wool, and cotton. Reactive Red 3 and Reactive Blue 19 are among to reactive dyes class. Direct dyes are applied to the fabric like rayon, linen, and silk at nearly 80-90°C temperature ranges. They are the cheapest ones compared to the other types of textile dyes. Direct Blue 1 is one of them as an azo dye (Sharma et al., 2021).

Adsorbents used in dye adsorption are expected to have several properties such as high surface area, uptake capacity, recyclability, selectivity and, easy obtainable. Besides that, the surface features of an adsorbent are crucial to achieving good adsorption performance for dyes. Adsorbents can be natural or synthetic based. The most studied synthetic materials in literature are Carbon Nanotubes (CNTs), graphene oxide, metal-organic frameworks (MOFs), and covalent-organic frameworks (COFs). Natural materials are mesoporous silica, clays, chitosan, and porous carbon (Lan et al., 2021). Adsorption of dyes using natural-based low-cost adsorbents has been an important research area. However, they are in microparticle form. So, they have a small surface area. To achieve good adsorption conditions, it needs to carry out the adsorption process for a long time. For industrial processes, natural-based adsorbents are regarded as not feasible (Tan et al., 2015).

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Nanomaterials are composed of particles whose 1-100 nm. They have excellent properties like low-weight, highly active sites. And, in dye adsorption, a small amount of nanomaterial can be adequate (Tan et al., 2015). Nowadays, several studies have been carried out for dye adsorption in water by using nanomaterials. For example, Wang et al. (2021) synthesized a novel spherical montmorillonite-supported nanocomposite which was composed of COF with sulfhydryl groups and gold nanoparticles. The researchers recorded that the catalytic activity of this catalyst did not alter after the 20th cycle for methylene blue adsorption (Wang et al., 2021). Yang et al. (2018) investigated the effect of a nanocomposite that included ZIF-67 on methyl orange degradation. They caught a 738 mg/g adsorption capacity after a 7 h adsorption experiment with only 5 mg adsorbent (Yang et al., 2018). Fard et al. (2018) researched direct blue 71 adsorptions from an aqueous solution by using Multi-Walled Carbon Nanotube. They obtained 96% removal efficiency under the conditions which were 0.6 g/L adsorbent concentration, and 90 min adsorption time in an acidic dye solution (Fard et al., 2018). Fraga et al. (2020) studied the effect of a nano-scale adsorbent which included graphene oxide on reactive drimaren red adsorption. At room temperature, they reached 220 mg/g as the maximum adsorption value. They also carried out phytotoxicity measurements for the adsorbent (Fraga et al., 2020).

Today, 2D materials have gained attention because of their several properties like high anisotropy, flexible mechanically, and transparent optically. Most Studied 2D materials for dye adsorption were WS₂ (Khataee et al., 2018), MoS₂ (Massey et al., 2016), and Nb₂CT_x Mxene (Yan et al., 2021). As 2D material, Boron Nitride Nanosheets (BNNSs) possess a skeletal composition of nitrogen and boron (Yadav & Dindorkar, 2022). BNNSs has regarded as crucial materials as adsorbents due to their properties which are high oxidation resistance, thermal conductivity, polarity, and specific area. Besides that, they can stay inert against the majority of chemicals. However, in literature, the adsorption studies against dyes within the water with BNNSs are scarce (Bangari et al., 2022). This study aimed to enlighten the adsorption potential of BNNSs on the water-soluble cationic and anionic textile dyes.

2. Definition, Synthesis, Properties and Applications of BNNSs

Boron nitride (BN) is a crystalline material that formed in several morphologies such as rhombohedral boron nitride (r-BN), hexagonal boron nitride (h-BN), wurtzite boron nitride (w-BN), and cubic boron nitride (c-BN). BNNSs are one of the shape types of BN. Today, hexagonal boron nitride (h-BN) is a crucial material for scientists (Revabhai et al., 2022).

The synthesis of h-BN can be synthesized by using two routes. They are low-temperature growth and high-temperature growth. Solvothermal synthesis is a subtopic of low-temperature growth. It can carry out an autoclave with a mixture composed of boron, nitrogen precursors, and a liquid solvent under 500 °C temperatures. On the other hand, atmospheric pressure high-temperature synthesis is a subtopic of high-temperature growth. This process can be conducted in a horizontal tube under a nitrogen gas atmosphere at high temperatures (up to 1800 °C temperatures) with metal solvents such as Ni-Cr. Maestre et al. (2021) expressed that important select accurate temperature and solvent to obtain large h-BN crystals (Maestre et al., 2021).

H-BN has outstanding properties such as high thermal conductivity, stability under several chemical and thermal conditions, high electrical insulation, low density, huge surface area, and high corrosion resistance (Revabhai et al., 2022; Wang et al., 2019). Because of its properties, h-BN has been extensively researched in hydrogen storage, CO₂ capture, water purification, and desulfurization (Xiong et al., 2020).

H-BNNSs (2D) formed via exfoliation of bulk h-BN (3D). The aim of size changing of the material from 3D to 2D is to obtain uniform dispersion. However, it has known that the exfoliation of bulk h-BN is more complicated than the exfoliation of graphite. Several methods can be used for exfoliation. These are electrochemical peeling, high-shear mixing, chemical exfoliation, liquid phase exfoliation, molten hydroxide etching, ball milling, and shock chilling. Wang et al. (2019) synthesized H-BNNSs from h-BN by using hydrothermal exfoliation at 180 °C with a high exfoliation yield (55 %) (Wang et al., 2019).

3. Performance of BNNSs on Adsorption of Cationic and Anionic Dyes

Singla et al. (2015) tested their BNNSs in the adsorption of an anionic (methyl orange) and a cationic dye (brilliant green). They synthesized BNNSs by using a nitrogen atmosphere at 900 °C. 0.9 nm for average thickness and 0.3 nm for lattice interplaner distance of the nanosheets found utilizing high-resolution transmission electron microscopy (HRTEM). For both dyes, the researchers found that an increase in initial dye concentration caused a

decrease in removal efficiency. This situation occurred due to decreasing adsorption sites of the adsorbent. Because methyl orange, as an anionic dye, has a negative charge, a decrease in pH enables increasing removal efficiency. So, the optimum pH was found as 4. However, for positively charged brilliant green, the optimum pH reached 6. Especially for a brilliant green, 1 min adsorption was enough to achieve maximum adsorption (Singla et al., 2015).

Wang et al. (2018) designed a few layers BNNSs through direct-exfoliation of h-BN. The researchers defined their synthesis method as inexpensive and green to synthesize BNNSs. Because the researchers studied not using at high temperatures, vacuum, sonication or harmful solvents. Yield of exfoliation founded as 15%. Average thickness of BNNSs obtained as nearly 1.5 nm using Atomic force microscopy (AFM) characterization. For adsorption tests, the researchers tested the nanosheets in Rhodamine B as a cationic dye removal. The tests carried out with an 5 mg adsorbent, and 10 mg per litre initial dye concentration. After 10 min, the adsorbent reached adsorption equilibrium (30 mg/g) (Wang et al., 2018).

Wang et al. (2020) obtained BNNSs by calcination boron acid and urea under nitrogen atmosphere. They studied methylene blue as a cationic dye. They reused the adsorbents after washing them with ethanol and calcination in air at 400 °C. They found that, for methylene blue, the nanosheets exhibited nearly 100% removal efficiency after just 20 min. Reusability tests showed that adsorption capacity decreased the adsorbent used again from 100% to 70%. And this value remained unchanged during up to three cycle (Wang et al., 2020).

Ikram et al. (2020) collected h-BNNSs by using sonication. After that, they loaded Nickel with different ratios (2.5-10%) on them via hydrothermal method. Catalytic activity tests showed that the synthesized adsorbent had 10% nickel reached 99% methylene blue degradation in 1 min in the presence of NaBH₄ (Ikram et al., 2020).

Kumar et al. (2022) synthesized interesting adsorbent included h-BNNSs removing methylene blue as a cationic dye and acid orange as an anionic dye in the water. They created hexagonal boron nitride-based magnetic aerogel. Because the adsorbent had zero surface charge and several functional groups, it performed good adsorption against the specific dyes. The adsorbent showed 415 for methylene blue and 286 mg/g for acid orange adsorption capacity (Kumar et al., 2022).

4. Conclusion

Synthetic or textile dyes are carcinogenic, and hazardous for humans and aquatic ecosystems. Compared to the other methods, adsorption comes to the forefront thanks to its easy feasibility. For dye adsorption, several materials can be applied. They are CNTs, graphene oxide, MOFs, COFs, mesoporous silica, and porous carbon. Because of so many unique properties, nanomaterials have gained attention for the adsorption processes. One of the eminent properties, it is enough to use a small amount of nano adsorbent in dye adsorption. H-BN is a prominent member of BNs. H-BNNSs (2D) synthesize via exfoliation of bulk h-BN (3D). Since it can be hard to synthesize H-BNNSs with high yield, there are low-amount of studies in the literature about dye degradation using these materials. In this review, several studies which were about anionic and cationic dyes removal with h-BNNSs presented. So, this material has the advantage of cleaning a dye solution within a few minutes. It was noticed that the researchers have studied developing a hybrid form of the h-BNNSs with other materials, and new synthesis methods of h-BNNSs against climate change. And, it seemed the research gathered mainly in methylene blue degradation for h-BNNSs adsorbents among water-soluble textile dyes.

Nowadays, researchers have started to synthesize h-BNNSs as solvent-free. Less solvent used in nanomaterial synthesis has gained importance for the environment. Also, it has been recently popular to create magnetic h-BNNSs with magnetic metals to increase their adsorption capability and collect the adsorbent in simple way from an aqueous medium.

References

1. **Bangari, R. S., Yadav, A., Awasthi, P. & Sinha, N. (2022).** Experimental and theoretical analysis of simultaneous removal of methylene blue and tetracycline using boron nitride nanosheets as adsorbent. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 634, 127943. Doi: <https://doi.org/10.1016/j.colsurfa.2021.127943>
2. **Fard, R.F., Sar, M.E.K., Fahiminia, M., Mirzaei, N., Yousefi, N., Mansoorian, H.J. & Ghadiri, S.K. (2018).** Efficiency of multi walled carbon nanotubes for removing Direct Blue 71 from aqueous solutions. *Eurasian journal of analytical chemistry*, 13(3). Doi: <https://doi.org/10.20933/ejac/85010>

3. Fraga, T.J.M., da Silva, L.F.F., de Lima Ferreira, L.E.M., da Silva, M.P., Marques Fraga, D.M.D.S., de Araújo, C.M.B. & da Motta Sobrinho, M.A. (2020). Amino-Fe₃O₄-functionalized multi-layered graphene oxide as an ecofriendly and highly effective nanoscavenger of the reactive drimaren red. *Environmental Science and Pollution Research*, 27, 9718-9732. Doi: <https://doi.org/10.1007/s11356-019-07539-z>
4. Ikram, M., Hassan, J., Imran, M., Haider, J., Ul-Hamid, A., Shahzadi, I. & Ali, S. (2020). 2D chemically exfoliated hexagonal boron nitride (hBN) nanosheets doped with Ni: synthesis, properties and catalytic application for the treatment of industrial wastewater. *Applied Nanoscience*, 10, 3525-3528. Doi: <https://doi.org/10.1007/s13204-020-01439-2>
5. Khataee, A., Eghbali, P., Irani-Nezhad, M.H. & Hassani, A. (2018). Sonochemical synthesis of WS₂ nanosheets and its application in sonocatalytic removal of organic dyes from water solution. *Ultrasonics Sonochemistry*, 48, 329-339. Doi: <https://doi.org/10.1016/j.ultsonch.2018.06.003>
6. Krishna Kumar, A.S., Warchol, J., Matusik, J., Tseng, W.L., Rajesh, N. & Bajda, T. (2022). Heavy metal and organic dye removal via a hybrid porous hexagonal boron nitride-based magnetic aerogel. *NPJ Clean Water*, 5(1), 24. Doi: <https://doi.org/10.1038/s41545-022-00175-0>
7. Lan, D., Zhu, H., Zhang, J., Chen, S. Li, Q., Wang, C. & Xu, M. (2021). Adsorptive removal of organic dyes via porous materials for wastewater treatment in recent decades: A review on species, mechanisms and perspectives. *Chemosphere*, 293, 133464. Doi: <https://doi.org/10.1016/j.chemosphere.2021.133464>
8. Liu, T., Anigbor, C.O., Ejimofor, M.I., Menkiti, M.C., Wakawa, Y.M., Li, J. & Jeevanandam, J. (2022). Recent developments in the utilization of modified graphene oxide to adsorb dyes from water: A review. *Journal of Industrial and Engineering Chemistry*, 117, 21-37. Doi: <https://doi.org/10.1016/j.jiec.2022.10.008>
9. Maestre, C., Toury, B., Steyer, P., Garnier, V. & Journet, C. (2021). Hexagonal boron nitride: a review on selfstanding crystals synthesis towards 2D nanosheets. *Journal of Physics: Materials*, 4(4), 044018. Doi: <https://doi.org/10.1088/2515-7639/ac2b87>
10. Massey, A.T., Gusain, R., Kumari, S. & Khatri, O.P. (2016). Hierarchical microspheres of MoS₂ nanosheets: efficient and regenerative adsorbent for removal of water-soluble dyes. *Industrial & Engineering Chemistry Research*, 55(26), 7124-7131. Doi: <https://doi.org/10.1021/acs.iecr.6b01115>
11. Revabhai, P.M., Singhal, R.K., Basu, H. & Kailasa, S.K. (2022). Progress on boron nitride nanostructure materials: properties, synthesis and applications in hydrogen storage and analytical chemistry. *Journal of Nanostructure in Chemistry*, 13, 1-41. Doi: <https://doi.org/10.1007/s40097-022-00490-5>
12. Sharma, J., Sharma, S. & Soni, V. (2021). Classification and impact of synthetic textile dyes on Aquatic Flora: A review. *Regional Studies in Marine Science*, 45, 101802. Doi: <https://doi.org/10.1016/j.rsma.2021.101802>
13. Singla, P., Goel, N. & Singhal, S. (2015). Boron nitride nanomaterials with different morphologies: synthesis, characterization and efficient application in dye adsorption. *Ceramics International*, 41(9), 10565-10577. Doi: <https://doi.org/10.1016/j.ceramint.2015.04.151>
14. Tan, K.B., Vakili, M., Horri, B.A., Poh, P.E., Abdullah, A.Z. & Salamatinia, B. (2015). Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. *Separation and purification technology*, 150, 229-242. Doi: <https://doi.org/10.1016/j.seppur.2015.07.009>
15. Wang, S., Jia, F., Kumar, P., Zhou, A., Hu, L., Shao, X. & Liu, B. (2020). Hierarchical porous boron nitride nanosheets with versatile adsorption for water treatment. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 598, 124865. Doi: <https://doi.org/10.1016/j.colsurfa.2020.124865>
16. Wang, F., Pan, F., Yu, S., Pan, D., Zhang, P., & Wang, N. (2021). Towards mass production of a spherical montmorillonite@ covalent organic framework@ gold nanoparticles heterostructure as a high-efficiency catalyst for reduction of methylene blue. *Applied Clay Science*, 203, 106007. Doi: <https://doi.org/10.1016/j.clay.2021.106007>
17. Wang, X., Yang, Y., Jiang, G., Yuan, Z. & Yuan, S. (2018). A facile synthesis of boron nitride nanosheets and their potential application in dye adsorption. *Diamond and Related Materials*, 81, 89-95. Doi: <https://doi.org/10.1016/j.diamond.2017.11.012>
18. Wang, N., Yang, G., Wang, H., Yan, C., Sun, R. & Wong, C.P. (2019). A universal method for large-yield and high-concentration exfoliation of two-dimensional hexagonal boron nitride nanosheets. *Materials Today*, 27, 33-42. Doi: <https://doi.org/10.1016/j.mattod.2018.10.039>
19. Xiong, J., Di, J., Zhu, W. & Li, H. (2020). Hexagonal boron nitride adsorbent: Synthesis, performance tailoring and applications. *Journal of Energy Chemistry*, 40, 99-111. Doi: <https://doi.org/10.1016/j.jechem.2019.03.002>
20. Yadav, A. & Dindorkar, S.S. (2022). Adsorption behaviour of hexagonal boron nitride nanosheets towards cationic, anionic and neutral dyes: insights from first principle studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 640, 128509. Doi: <https://doi.org/10.1016/j.colsurfa.2022.128509>

21. Yan, Y., Han, H., Dai, Y., Zhu, H., Liu, W., Tang, X. & Li, H. (2021). Nb₂CT x MXene Nanosheets for Dye Adsorption. *ACS Applied Nano Materials*, 4(11), 11763-11769. Doi: <https://doi.org/10.1021/acsanm.1c02339>
22. Yang, Q., Ren S., Zhao Q., Lu R., Hang C., Chen Z. & Zheng, H. (2018). Selective separation of methyl orange from water using magnetic ZIF-67 composites. *Chemical Engineering Journal*, 333, 49-57, 2018. Doi: <https://doi.org/10.1016/j.cej.2017.09.099>