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Affinity of boron nitride nanomaterials towards antibiotics established by exhaustive experimental and theoretical investigations

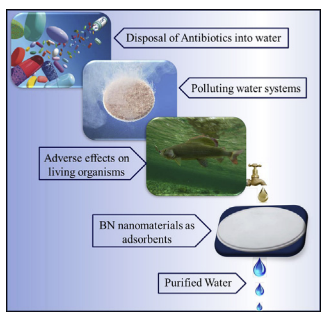
Preeti Singla, Neetu Goel, Sonal Singhal *

Department of Chemistry and Centre of Advanced Studies in Chemistry, Panjab University, Chandigarh 160014, India

HIGHLIGHTS

- Morphologically different BN nanomaterials were explored in adsorption applications.
- Efficient adsorption and removal of antibiotics were noticed.
- Adsorption processes best fitted to Langmuir adsorption isotherm.
- The kinetic studies fitted well into the pseudo-second-order kinetic model.
- Insight interactions were investigated by theoretical studies.

GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceutical pollutants are the emerging class of contaminants due to their prevalence and persistence in the aquatic environment. In this regard, boron nitride (BN) nanomaterials with two different morphologies have been constructed via solid state high temperature annealing approach. Excellent adsorbent properties of as prepared BN nanomaterials have been explored by adsorbing two different antibiotics i.e. ciprofloxacin (CIP) and norfloxacin (NOR) over their surfaces. High surface area consisting negative charge has been revealed by the BET and zeta potential analysis. Effect of various experimental parameters like contact time, pH, adsorbent dosage and initial antibiotic concentration on the adsorption process has been discussed in detail. The adsorption experiments performed at various pH has resulted the maximum adsorption at pH between 4 and 6. Adsorption isotherms have also been incorporated to evaluate the nature of adsorption. Out of Langmuir and Freundlich isotherm models, earlier one offers best fitting into the experimental data suggesting that the adsorption is monolayer. Furthermore, the kinetics studies established that the adsorption process follows pseudo-second-order kinetic model. In addition, theoretical studies have also been included for insight knowledge of nature of interactions between adsorbate and adsorbent using density functional theory formalism. These results demonstrate the great potential of BN nanomaterials for the water purification systems.

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1. Introduction

The widespread applications of pharmaceuticals in the veterinary and human medicines increase their production globally to enhance the quality of life [1,2]. Recently, the extensive use of pharmaceutical and their constantly growing residual and metabolites have emerged as a new class of contaminants [3,4]. The significant sources of pharmaceuticals include drug manufactures and hospitals [5]; in addition, their excretion from humans/animals and improper disposal of expired or unused medicines in the water provides them another entrance into the environment [1,6]. Their presence in water has grabbed the attention of researchers owing

* Corresponding author.
E-mail address: sonal1174@gmail.com (S. Singhal).

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to their ability to impart stringent effects on growth and reproduction of aquatic organisms [7]. Among all pharmaceuticals, the occurrence of antibiotics in the aquatic environment may pose critical threats to humans and the ecosystem, albeit at low concentration, as they may induce the proliferation of antibiotic resistant bacteria [8].

Fluoroquinolones (FQs) are one of the most commonly prescribed antibiotics to humans and animals because of their less resistance, high potency and broad antibacterial spectra [9,10]. Chemically, norfloxacin (NOR; 1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1H-quinoline-3-carboxylic acid) and ciprofloxacin (CIP; 1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-yl-quinolone-3-carboxylic acid) are widely administered synthetic antibiotic drugs belonging to first and second generation of FQs class respectively. Their basic mode of action to kill bacteria is their interference with enzymes like inhibition of DNA gyrase and topoisomerase IV [11]. Owing to the brilliant therapeutic properties, CIP and NOR are not only used as disease-fighting agents but are also explored in the agriculture industries as prophylactics and growth promotants [12]. Thus their high utilization across the world increase their concentration in the aqua-system that inevitably cause a serious threat to the ecosystem as CIP and NOR are highly stable, water soluble and bio-nondegradable.

Removal of these toxic antibiotics from the water system has gripped a great concern of the researchers nowadays. As in the wastewater treatment plants, mineralization of pharmaceuticals into innocuous products was not complete, therefore, the recent studies have reported a few methods of mitigating antibiotic contamination including biodegradation, volatilization, hydrolysis, chemical oxidation and adsorption [13,14]. Among these treatments, adsorption process acquires a special importance owing to inexpensive nature and ease of operation [15]. In the earlier studies, different materials have been applied to adsorb FQs including soils [16,17], magnetite [18], birnessite [19], kaolinite [20], montmorillonite [12,21], clay minerals [22] and carbon nanomaterials [23–25].

In recent years, while carbon allotropes have received remarkable attention in the field of adsorption; their isoelectronic and isostructural boron nitride (BN) nanomaterials have also been taken into a significant consideration by the scientists to explore their behavior in the adsorption process. The fascinating properties of BN nanomaterials including high thermal stability [26], chemical durability [27] and the most importantly constant and wide band gap with semiconducting nature [28] have proven them more potential candidate over the carbon nanomaterials for a plethora of applications. In the last decade, a few studies have been reported by research cohorts to scrutinize the adsorption behavior of the BN nanomaterials. The porous BN nanosheets have been fabricated by Lei et al. [29] that exhibit great adsorption performance towards a wide range of solvents, oils and dyes. Xue et al. [30] synthesized the mesoporous hexagonal boron nitride fibers and have shown their fast and selective adsorption towards methylene blue. Activated boron nitride has been considered as an effective and excellent adsorbent for various metal ions, organic pollutants and volatile organic compounds by Li et al. [31]. Quick adsorption rate for methylene blue with high adsorption capacity has been exhibited by BN nanocarpets developed by Zhang et al. [32]. BN ultrathin fibrous nanonets fabricated by Lian et al. [33] have been employed for wastewater treatment with excellent performance by ultrafast adsorption of methylene blue. However, till now no literature reports have been focused on the applications of BN nanomaterials towards the adsorption of antibiotics.

The present study accords an effective and advanced adsorbent material for the adsorption and removal of harmful antibiotics i.e. CIP and NOR for the environmental remediation, which has not been explored so far to the best of our knowledge. Adsorption efficacy of BN nanomaterials with two different morphologies has been thoroughly investigated by taking into account the impact of the various experimental factors including drug concentration, pH, time and adsorbent dosage. The interplay between the nanomaterial surface and the adsorbates has been vividly elucidated in terms of adsorption kinetics and isotherms and the study is well supported by theoretical investigations that have been performed within the formalism of density functional theory (DFT).

2. Experimental

2.1. Reagents

Ciprofloxacin hydrochloride (CIP, $\geqslant$98.0%, $C_{17}H_{18}FN_3O_3{\cdot}HCl$) and norfloxacin (NOR, $\geqslant$98.0%, $C_{16}H_{18}FN_3O_3$) were purchased from Sigma Aldrich. Boric acid (H_3BO_3, 99.5%) obtained from Fisher Scientific, Urea ($CO(NH_2)_2$, 99%) and melamine (99%) provided by Central Drug House (CDH) and pure nitrogen gas (>99.9%) were used for the synthesis of the adsorbents. All the Chemicals were used as received without the further purifications. Analytical reagents HCl and NaOH were also used in the experiments to regulate the pH. Fresh aqueous antibiotic solutions were prepared every time. Highly pure water was used in this study generated using Milli-Q water purification system (Millipore).

2.2. Adsorbent fabrication

Two different morphologies i.e. nanoparticles and nanosheets of the boron nitride (BN) nanomaterials have been employed as adsorbents in the current study. The engineering of these morphologies of BN nanomaterials has been carried out by following the previously developed protocol i.e. solid state thermal annealing approach [34]. Highly crystalline and pure boron nitride nanoparticles (BNNP) have been fabricated by the reaction of boric acid with melamine at high temperature i.e. 1400 °C for 2 h in the presence of nitrogen gas. A homogeneous mixture of boric acid and urea have been used as starting material for the fabrication of boron nitride nanosheets (BNNS), which has been heated at 900 °C for 5 h in the nitrogen gas atmosphere to yield highly pure BNNS.

2.3. Adsorption procedure

In order to explore the adsorption behavior of BN nanomaterials towards antibiotics, detailed adsorption studies were performed for CIP and NOR in the aqueous solution. Accurately weighted quantity of CIP and NOR antibiotics were completely dissolved in the deionized water to prepare their stock solution which was diluted to obtain the working solutions of the required concentrations. In the adsorption experiment, 100 ml solution of the antibiotics at specific concentration was poured into the 250 ml beaker containing known amount of BN nanomaterials and immediately subjected to the dispersion using ultra-sonicator for uniformly dispersed solution. Furthermore, continuous stirring of the dispersed solution was done at a constant speed of 500 rpm till the equilibrium reaches. All the adsorption tests were conducted at room temperature. Blank experiments were also conducted in the absence of adsorbents to ensure that there was no degradation and adsorption onto the glass bottle walls, it was purely the effect of adsorbent that decrease the concentration. To analyze the extent of adsorption with time, 4 ml dispersed solution was withdrawn after periodic time intervals and filtered using 0.45 μm nylon syringe filter to separate the adsorbent. The residual concentrations of antibiotic solutions were estimated spectrophotometrically by measuring the absorbance values using UV–vis spectrophotometer. The removal

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