Biochar Production from Domestic Sludge: A Cost-effective, Recycled Product for Removal of Amoxicillin in Wastewater

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Abstract: Due to the broad spectrum, antimicrobial activity, Amoxicillin is one of the extensively used antibiotics. Amoxicillin ends up in the wastewater stream by direct or indirect disposal pathways which ultimately affect the aquatic ecosystem. Conventional wastewater treatment plant cannot remove it completely. Hence our objective was to produce sludge derived biochar and use it as an adsorbent for removal of amoxicillin. Effective biochar was obtained at 300°C produced from the sludge of the domestic wastewater treatment plant. 100 ppm amoxicillin solution spiked in biochar was kept for 180 mins in an orbital shaker and every 30 minutes the filtrate was checked in UV spectrophotometer. A steady decreasing gradient was obtained for absorbance of amoxicillin after 30 minutes. Further scanning electron microscopy showed significant morphological change in biochar obtained before and after spiking amoxicillin. Our preliminary assessment suggests that biochar can be exploited as an effective treatment technique to remove amoxicillin from wastewater. Moreover, we suggest that utilization of domestic sludge for commercial application in treatment plants can reduce the load of domestic waste in the open dumpsites.

Keywords: Amoxicillin, sludge, biochar, UV spectroscopy, Scanning Electron Microscopy.

1. Introduction
Ubiquitous presence of antibiotics in the environment has instigated concern in the scientific community from the beginning of 21st century [1]. In 2010, India consumed 12.9 billion
antibiotic pills. During 21st century the antibiotic usage across the globe rose by 36 per cent and in India, the count went up by 62 per cent, from 8 billion pills in 2001 to 12.9 billion in 2010 [2]. Antibiotics can end up into the environment via various point and non-point sources such as biomedical waste, pharmaceutical wastewater from industries, treated and untreated wastewater, sludge, agricultural and aquaculture activities [1,3]. Such pharmaceutical compounds, once released in the environment is characterised by certain degree of persistence depending on the structure of the compounds. Bio-accumulation of antibiotics even in small quantities may cause serious problems to both humans and animals in long run [5]. Bacteria may get resistant to the antibiotics over a period of time and in turn disrupt the human immune system [6].

Inability of the conventional Wastewater Treatments Plants (WWTP), Sewage Treatment Plants (STP) and Water Treatment Plants (WTP) to remove Emerging Pollutants of Concern (EPOCs) such as antibiotics has been found to be a major source of surface water pollution [7]. Hence treatment of wastewater has gained enormous importance in the past few decades due to rising pollution of surface water with untreated wastewater.

Widely used antibiotic, amoxicillin, is a drug of beta lactam category. Presence of amoxicillin in WWTP & STP effluent across the globe indicates the incapability of the conventional plants in removing it efficiently, and eventually may contaminate freshwater resources [8,9]. Though data from the Indian subcontinent is scarcely reported, studies done in a STP in the capital city of India, New Delhi, showed that only 50% amoxicillin can be removed by conventional methods [10].

Various techniques like solvent extraction, flotation, gravity sedimentation, coagulation, oxidation, precipitation, evaporation, distillation and adsorption are used for the treatment of wastewater. Among the waste treatment techniques, adsorption is more advantageous because of its simplicity, low cost of operation, and absorbent, as well as large options of adsorbents available [11]. The main objective of the present study were to (i) producesludge derived biochar (ii) find the optimum parameter for production of the most efficient sludge-derived biochar and (iii) removal of amoxicillin by the sludge derived biochar.

2. Materials And Method

2.1 Chemicals and Sludge Sampling
Amoxicillin standard (99% pure) was purchased from Sigma Aldrich, USA. Millipore water was used from MilliQ plus system (Elix Technology inside, USA). All other reagents used were of High Performance Liquid Chromatography (HPLC) grade. Sludge samples used for Biochar preparation was collected from sludge drying bed after secondary treatment from SRM wastewater treatment plant (SRM Nagar, Chennai, India) in pre-washed zip lock covers. The sludge samples were stored at -20°C until further processed.

2.2 Sludge Derived-Biochar preparation
The samples were dried at 105°C for 24 hours using a hot air oven. After drying, the samples were pyrolyzed in a Muffle furnace at 300°C with one hour residence time. After the residence time the samples were allowed to cool down to room temperature. The obtained biochar was stored in air tight container and directly used for subsequent experiment. Special care was taken to prevent the biochar from coming into contact with moisture. And hence the bottles containing the biochar were stored in a desiccator.
2.3 Biochar characterization
Different analytical techniques were used to determine the properties of the prepared Biochar. Moisture content of the sludge sample were calculated using the difference in weight before and after heating using the formula:

\[
\text{Percentage (\%) of moisture} = \frac{\text{Wt. of the sample (before drying)} - \text{afterdrying}}{\text{Wt. of the sample before drying}} \times 100
\]

2.4 Adsorption
Stock solution of Amoxicillin was prepared dissolving 10mg of the standard in 100ml of MilliQ water. To estimate the applicability of the produced sludge Biochar as an adsorbent for amoxicillin, 100 ppm amoxicillin solution was taken with 10 mg of biochar in a standard 100ml conical flask. Shaker was maintained at 180rpm for efficient adsorption result as observed elsewhere [12]. Adsorption experiment was conducted in the stirred (180 rpm) glass reactor with a temperature-controlled incubator at room temperature. Method blank was used as a control sample, consisting of 10mg of biochar mixed with 10 ml of MilliQ water. Seven different flasks including the blank containing the amoxicillin and biochar mixture were kept in the shaker at the same time.

2.5 Absorbance Isotherm Experiment
The relationship between absorbance and aqueous concentration at a given temperature can be regarded as an absorption isotherm. For these adsorption isotherm experiment, the initial concentrations were taken to be 0, 25, 50, 100 ppm solutions. The experiments were conducted at 25 °C. The commonly used absorbance vs concentration isotherm models are in accordance with the Beer Lambert’s Law [13].

2.6 Adsorption Analysis Methods
After every 30mins from the start time one flask was taken out and filtered using 0.2µm Whatman filter paper. The filtrate was analysed using Ultra Violet spectrophotometer (Analytical specord-220 plus). The residues of biochar were dried in hot air oven and checked for SEM results (FESEM).

2.7 Scanning Electron Microscopy
The morphological characterization of biochar was studied by using a high-resolution field emission scanning electron microscope (FEI Quanta FEG 200 SEM). 0.5 g of sample was subjected to FESEM under low vacuum environmental sample mode. Acceleration voltage of 10 kV was used with minimum 10,000× magnification [14] has exemplified the importance of using SEM for surface and morphology study of environmental samples. ImageJ processing software was applied to determine the particle size and study the morphology of the particles. Void size in the biochar is expressed in Ferret’s diameter to avoid approximation in reporting particles with irregular geometry [15].

3. RESULTS AND DISCUSSION

3.1 Biochar Production
Biochar, traditionally, is a charcoal derived from pyrolysis of sludge or thermal degradation of carbon rich compounds. Biochar was produced from the wastewater sludge, after the pre-
treatment of the sludge by following the pyrolysis process. Several studies reported that the wastewater sludge can be a promising source for the production of biochar [16,17,18,22]. Pyrolysis has been used for biochar production elsewhere [10]. The efficacy of the Sludge Derived Biochar depends on the sludge characteristics also on the type of wastewater. The high variation of sludge from different wastewater treatment plant may lead to the high variation in the adsorption of organic pollutants using sludge-derived biochar [20].

3.2 Removal of amoxicillin by sludge-derived Biochar
Amoxicillin peak was observed at 272 nm. Results from UV-Spectrometer clearly showed a steady decrease in the concentration of amoxicillin after 30 minutes (Figure 1). Sludge-derived biochar at 300°C could effectively adsorb the amoxicillin molecules on its surface. Among the 3 sets of Sludge-derived biochar, biochar produced at 300 °C showed the most effective adsorption.

3.3 Morphological variation in sludge-derived biochar
Sludge-derived biochar produced at 300°C was found to have a regular wavy pattern with average void size of 0.58 µm in Ferret diameter. It is estimated that the particle to void ratio is on the lower side, exemplifying the fact that specific surface area is high. This infers that the sludge derived biochar is suitable for adsorption of Amoxicillin [10].

![Fig. 1a: Change in absorbance of amoxicillin by UV Spectrophotometer. 1b: Variation in absorbance with respect to time.](image)
Formation of pores with large surface area may accommodate the adsorbate. Antibiotics particularly amoxicillin has a good affinity for adsorption and they are adsorbed over the surface of sludge-derived biochar. Previous studies also have proved that biochar is a first-class adsorbent as it has strong adsorption ability for organic pollutants including atrazine, sulfamethoxazole, phenanthrene, phenols, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls [15,16,21,22,23]. The distinct pattern observed in biochar before adsorption was not visible after the adsorption of amoxicillin. The particle size after the adsorption has been reduced indicating the filling up of void spaces. Previous research shows that the sludge derived biochar has relatively large Brunauer–Emmet–Teller (BET) specific surface areas that were beyond 110.0 m²g⁻¹ [8,9,10].

4. CONCLUSION
Efficient removal of amoxicillin by adsorption in sludge-derived biochar, suggested the possibility to minimise the waste generated at the conventional WWTPs and STPs. This source of Biochar can be exploited as a promising low cost adsorptive medium for the removal of amoxicillin from wastewater. For efficient results care, must be taken that the biochar used must be completely dry. It is recommended that the sludge after the dehydration or fluid bed dryness treatment is most suitable source for biochar production. Pyrolysis temperature is believed to be the most important factor affecting the yield of Biochar produced. Grinding of the Biochar produced maximum sample surface area for adsorption experiment. Analysis showed that the absorbance concentration isotherm model fit well with the experimental data of the produced biochar. These findings suggest a new approach for the pollution control of amoxicillin using low-cost and efficient sludge-derived biochar. The cost incurred by the wastewater treatment plants to treat the sludge is quite high, thus the use of sludge-derived biochar for removal of antibiotics can add a commercial value to the waste sludge. Hence, we suggest that scaling up of this kind of adsorption technique can reduce the load of disposed sludge in the open landfills or dumpsites.

5. ACKNOWLEDGMENT
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Research Interests:
Dr. Chakraborty is working on the environmental occurrence, source identification, fate and behavior of new and emerging pollutants, persistent organic pollutants and trace elements and investigate the inter-media transfer of organic contaminants. Current research focuses on the source apportionment, fate, behavior, and risk assessment of: (a) emerging organic pollutants that are persistent and bio-accumulative and (b) trace elements, in and around hotspots like solid waste dumping grounds and electronic waste recycling units. Assess the potential threat to the ecosystem due to organic contaminants along the coastal length of India. Further she started looking into cost-effective
remediation techniques. She has also received projects grants from DEPARTMENT OF SCIENCE AND TECHNOLOGY-Fast Track Young Scientist SERB (“SR/FTP/EE-44/2012) and MOEF-Call for Proposals during Oct’ 2012

**Key Publications:**

- Passive Air Sampling of Polychlorinated Biphenyls, Organochlorine Compounds, and Polybrominated Diphenyl Ethers in Urban, Rural and Wetland Sites along the Coastal length of India. Zhang, G.; **Paromita Chakraborty**; Sampathkumar, P.; Balasubramanian, T.; Kathiresan, K.; Takahashi, S.; Subramanian, A.; Tanabe, S.; Jones, K. C. *Environmental Science and Technology*; 2008, 42 (22), pp 8218–8223; DOI: 10.1021/es8016667. Impact Factor: 5.33

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