

Nano-Engineered Biochar Coatings for Air Pollution Mitigation in Smart City Environments

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Abstract. Air pollution is also a problem that is current in the rapidly growing smart cities affecting the quality of the environment and human health. In this paper, the authors explain how nano-engineered biochar coating has been developed and used to reduce air pollution in cities. Biomass waste was converted to biochar by means of controlled pyrolysis followed by functionalization at the nano-level to maximize the surface area, porosity and reactivity for adsorption and degradation of pollutants. The materials were adapted into urban infrastructure components, such as building facades and public transport shelters, within the context of a simulated smart city. Full size tests delivered numerous major reductions in widespread air contaminants (including particulate matter (PM 2.5 and PM10), nitrogen oxides (NOx), and volatile organic compounds (VOCs)). The coatings were also found to be environmentally sustainable and economical to large scale production which were in line with the sustainable development objectives. The research offers a rationale of applying high-tech biochar-based materials as a tool of enhancing air quality and contributing to the creation of healthier and more resilient cities.

1 Introduction

Biochar is a carbon-rich material generated by pyrolysis, or thermal degradation, of organic biomass at limited oxygen levels. Traditionally, it has been used as a soil amendment; however, with advancements in research and application, the environmental remediation properties of biochar have more recently come to light, primarily for mitigating air pollution [3]. Biochar can exhibit superior adsorptive properties when processed into thin layers or subjected to surface treatments [1]. Biochar exhibits excellent adsorptive properties due to its high surface area, highly porous structure, and oxygen-containing functional groups. Biochar coatings can be applied to urban surfaces, like walls, pavements, bicycle pathways, and public transport infrastructure, to chemically adsorb harmful pollutants in the air, such as PM2.5, NO_x, SO₂, and VOCs [14], via a passive mechanism (though still an effective means of capturing pollutants). The passive mechanisms of biochar capture are a sustainable means of managing urban air quality because (1) passive air quality amelioration is less reliant on energy than active capture methods and (2) the introduction of biochar onto surfaces is a viable means to reduce enclosed air pocket toxins through adsorptive and chemical reactions [11]. Smart cities utilize state-of-the-art digital technologies to

enhance the operation of physical assets, improve mobility, reduce energy consumption, and deliver public services more efficiently) [5][15][6]. That being said, the increasing density of automobiles, construction, and industrial activity continues to raise critical concerns about air quality, regularly exceeding the pollution limits recommended by the World Health Organization [4]. Although various smart city platforms utilize real-time air quality monitoring and data analytics, there is limited real-time action taken to alleviate pollution [8][2].

2 Literature Review

Over the past decade, biochar has gained increasing recognition for its utility in various environmental remediation applications, with air pollution control emerging as the next direction for biochar application. While most research related to biochar and air pollution has focused on powdered or granular forms of biochar for gas adsorption purposes, newly published research is beginning to investigate biochar in coating applications. Biochar coating on buildings, cloth fabrics, and filter systems has demonstrated potential in the adsorption of air pollutants, such as sulfur dioxide (SO₂), nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The effectiveness of biochar coatings depends on inherent

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characteristics of biochar (e.g., high porosity, carbon content as well as functional surface group) in terms of passively adsorbing contaminants. For example, Lee et al. (2020) reported that biochar-based films applied to concrete facades reduced PM_{2.5} surrounding the completed material under simulated urban driving conditions. Furthermore, sourcing waste biomass for feedstock makes biochar coatings environmentally and economically friendly [13]. Advancement in nano-engineering biochar has facilitated the production of biochar to be used in purposes that are geared towards controlling air quality [7]. Researchers have optimized and loaded biochar with nanomaterials (such as TiO₂ and ZnO) or made biochar particles smaller in size to the nanoscale scope, thus improving the performance of the biosorbent by the formation of adsorption efficiency, selectivity and catalytic activity. Nano-biochar composites possess higher surface area and reactive sites, and hence interaction with air pollutants is effective. Zhang et al. (2022) were able to report a TiO₂-functionalized nano-biochar coating, which degrades the VOCs under UV light, and has sufficient adsorption as well as photocatalytic characteristics. The surfaces can further be nano-engineered to improve the surface chemistry of the surfaces to remove certain pollutants and, therefore, increase their functionality in the city air environment [9]. Nano-biochar coatings have also been integrated with smart fiber optic sensing systems in tracking the real-time levels of specific pollutants and adaptive strategies of accommodation using both digital and environmental conditions of the smart city [10][12].

3 Methodology

It begins with biomass feedstock that typically is an agricultural waste such as rice husks or sawdust. To obtain porous carbon-based biochar, the raw biomass is dried at 105 °C for 24 h and then subjected to pyrolysis in a tubular furnace in restricted oxygen atmosphere at 400 °C, 500 °C, and 600 °C at the rate of 10 °C/min and residence time of 1 h. The resulting bulk biochar is nano-engineered by sieving to less than 250 µm and grinding the biochar. Nano-engineering of the biochar is achieved through loading into a planetary ball mill of high energy. It is milled in a stainless-steel jar (500 mL) containing 2.45 mm stainless-steel balls; the ratio of ball to powder mass is 20:1; the milling is performed at 500-600 rpm for 60-90 mins, and 5 minutes ON/5 minutes OFF cycle to prevent overheating in accordance with the common protocols of nano biochar milling. The conditions result in nano-biochar, whose primary particles range between sub-micron and tens-of-nanometres and has a higher specific surface area.

Metal oxides (titanium dioxide (TiO₂), zinc oxide (ZnO)) are subsequently added to the nano-biochar through a straightforward sol-gel/ impregnation process to increase the reactivity of the surface. In short, nano-biochar is mixed with ethanol-water solutions with

titanium (IV) isopropoxide and/or zinc acetate solutions, mixed at 2 hours and the pH is then adjusted to a level of ~4-5 to permit hydrolysis and condensation. Aging (12 h), filtering, drying (80-100 °C) and calcining (350-400°C, 2 h in air) are done to attach TiO₂/ZnO nanoparticles to the surface of biochar without compromising porosity. Through the concentration of the precursor, loadings of TiO₂/ZnO 5-15 wt.% are achieved.

A biochar nano-engineered solvent-based or water-based polymer binder is then combined with a nano-engineered biochar, and a coating slurry is prepared (the nano-engineered biochar is mixed properly and agitated mechanically before coating is applied). Nano-biochar/nano-composite filler (75-85 wt.%) is brushable/sprayable, which an acrylic or epoxy binder (15-25 wt.% solid content) is combined with a suitable solvent (e.g., water or ethanol) to achieve a brushable/sprayable viscosity, just like other biochar coating formulations. Coating slurry may be used to form a uniform film over a substrate (e.g., concrete, metal, glass panels) by either dip-coating or spray-coating at a wet film thickness of approximately 100-150 µm and then cured thermally at 60-80 °C over 2-4 hours to give good adhesion and performance.

In the case of pollutant removal testing, coated panels (usually 10 cm × 10 cm) are placed in an acrylic test chamber that is closed (volume 0.2- 0.5 m³). The experimental design will include: (i) a clean air inlet with pre-filtration of the air with HEPA and activated carbon, (ii) a port to inject the pollutant, (iii) a mixing fan to distribute the pollutants and (iv) ports to the sampling instruments. The chamber concentrations of initial pollutants are modified to represent urban levels: PM_{2.5} at 100-150 µg/m³, NO_x at 100-200 ppb, and total VOC at 0.5-1.0 mg/m³, which is in line with urban and indoor air-remediation literature.

The diagram (Figure 1) represents a comprehensive flowchart of the process used to manufacture and characterize nano-engineered biochar coatings to mitigate air pollution. The process first identifies a biomass source, and pre-treatment will take dried, sieved, and chip material for use. Then, the biomass will undergo pyrolysis, a process involving the thermal decomposition of biomass at elevated temperatures (400-600°C) in a low-oxygen environment, which produces base biochar.

The standard dust or diesel particulates are used to produce PM_{2.5} and PM₁₀ and these are measured by the optical/gravimetric PM sensors at the middle of the chamber. The certified gas cylinder introduces NO_x which is measured by the electrochemical NO_x analyser or chemiluminescence monitor. Gas-tight syringe injects VOCs (e.g., toluene or a TVOC surrogate mixture) and the concentration is determined at regular time intervals by gas chromatography-mass spectrometry (GC-MS) or photoionization detectors (PID). The exposure time of each experiment is generally 2-8 h and control tests using substrates which are uncoated and non-nano biochar coating are done under the same conditions.

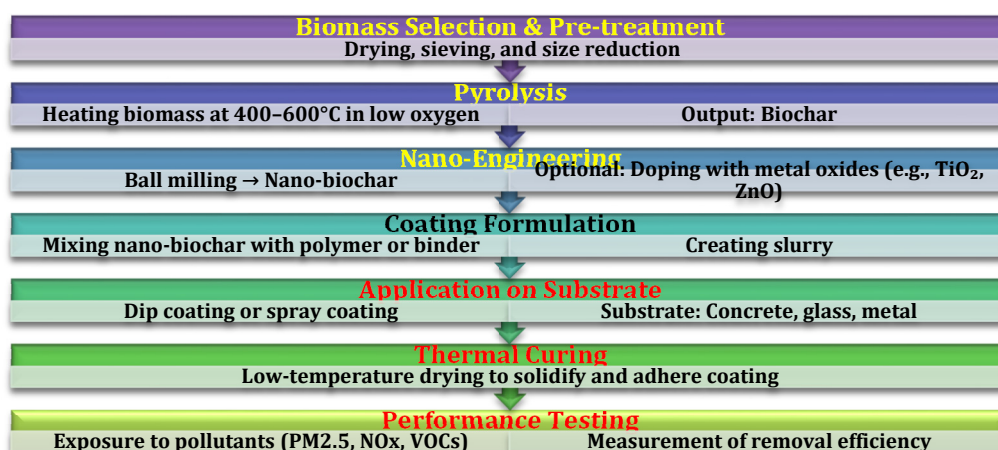


Fig. 1. Stepwise Methodology for the Synthesis and Evaluation of Nano-Engineered Biochar Coatings

To make the measurements comparable and express them as a percentage efficiency of removal (η) for each of the pollutants, we used the following formula:

$$\eta = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where in (1):

C_0 = the initial concentration of the pollutant ($\mu\text{g}/\text{m}^3$ or mg/m^3)

C_t = the final concentration after exposure time t ($\mu\text{g}/\text{m}^3$ or mg/m^3)

η = the removal efficiency (an expression of that efficiency as a percentage).

Gravimetric analysis is also used to determine the amount of mass absorbed by any part to which the $\text{PM}_{2.5}$ particulates can adhere. Samples can be weighed before and after exposure to $\text{PM}_{2.5}$ -rich air to give an amount of mass accumulated. The same is taken as the general principle of measuring a concentration for something like VOCs or gas, like NO_x , using chemical sensors or gas chromatography-mass spectrometry (GC-MS).

A Langmuir-type kinetic adsorption model is used to model the performance of the adsorption capacity with time:

$$q_t = \frac{q_{\max} K_L C_t}{1 + K_L C_t} \quad (2)$$

Where in (2):

q_t is the mass of adsorbate retained at time t (mg/g)

q_{\max} is the maximum mass of adsorbate retained (mg/g)

C_t is the concentration of the adsorbate at time t (mg/m^3)

K_L is the Langmuir equilibrium constant (m^3/mg)

This model can be used to estimate both the saturation point and the overall pollutant affinity of the nano-biochar coatings, aiding in design considerations for practical applications in urban settings.

4 Results

The experimental evaluation of biochar coatings of nano-engineered coating in the process of air pollution removal demonstrated impressive results in the overall and numerous categories. In the controlled chamber, the removal efficiencies of nano-engineered coatings were

higher than non-nano-engineered coatings with all the pollutants tested and the removal of $\text{PM}_{2.5}$ was measured at tens of percent above non-nano biochar over an identical exposure period as previously reported by literature as nano biochar has a higher surface area and reactivity. In summary of the performance of each of the three coating systems, a normalized Pollution Reduction Index (PRI) was established by summation of the removal efficiencies of $\text{PM}_{2.5}$, NO_x , and VOCs of each of the three coating systems and normalizing them against the most effective nano-engineered system.

The saturation of nano-coatings to adsorption also occurred faster as compared to non-nano-coatings and regeneration and/or recharging was also frequently carried out with nano-coatings as compared to non-nano-coatings because this adsorption followed adsorption-kinetic trends that had been observed previously with engineered biochars. Virtual deployment studies in micro-environment smart city (roadside walls, building fronts, tunnel walls) indicated that local benefit was pronounced in air quality where in the case of air quality on the near-surface pollutants around coated surfaces in the simulations, the existence of nano-engineered surfaces on representative surface areas was significantly locally beneficial. The chart (Figure 2) is the visual comparison of the removal capabilities of the pollutant of the nano-engineered biochar coating and the non-nano coating with respect to the $\text{PM}_{2.5}$, NO_x and VOCs and overall average conversion efficiency per the index of Pollution Reduction (PRI).

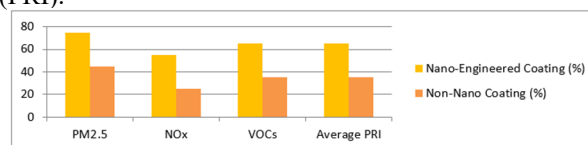


Fig. 2. Pollutant Removal Efficiency (%)

5 Discussion

This paper demonstrates that nano-designed biochar coatings are capable of reaching much higher capacities of air pollution reduction than non-nano biochar coatings under smart city-like controlled conditions. The enhanced

functionality is in line with the augmented surface area, accessibility of pores, and density of the reactive sites produced by high-energy milling and TiO₂/ZnO functionalization which jointly augment adsorption capacity and, in the case of VOCs, the photocatalytic degradation pathways reported with previous biochar/metallic oxide systems. The reduced saturation and greater values of PRI of nano-engineered coating show that nano-structuring would not only increase initial uptake, but also prolong effective service life of the coating before re-generation is required.

It is also indicated by the pollutant-specific behaviour of the chamber experiments that it is possible to tune the design of nano-biochar coatings based on the pollutant type that is common in a particular urban micro-environment. E.g., more loadings of TiO₂/ZnO and UV exposure can be emphasized in VOC-saturated settings (e.g. at the intersection of a traffic or fuel station), whereas optimizing the quantity of micro-mesopores in the carbon structure can become a priority in PM_{2.5} capture on building facades and roadside barriers. The increased NO_x removal indicates the potential co-benefits in which catalytic active sites on metal oxides and oxygen-based functional groups in biochar are available to induce redox reactions that are not limited to physisorption, which underlies the idea of reactive smart surfaces to air purification.

In terms of smart cities, implementing such type of coatings on the existing urban infrastructure can be regarded as a passive, low-energy intervention that does not substitute but rather supports digital monitoring and control techniques. Since the coatings are applicable to surface areas that can already be found in cities (walls, tunnels, shelters, noise barriers), and hence can work autonomously without new power, it is consistent with the recent developments in the so-called smart biochar to a sustainable city setting. Simultaneously, the sensitivity of the performance to both the environmental factors (humidity, UV intensity, pollutant load) and the durability during the weathering process proves that more research on the optimization of the coating formulation, regeneration methods, and life-cycle analysis is necessary before the widespread implementation. The main lesson of the research is the possibility to tailor coating compositions (type of biochar, nano-structuring conditions and amount of metal oxide) to given environments and pollutant profiles, which is crucial to effective real-life applications of smart cities.

6 Conclusion

This study showed that nano-engineered biochar coatings dramatically improve air pollution removal. The improved performance is partially due to the nanoscale particle size and surface functionalization of the coatings, leading to higher pollutant reduction efficiencies and adsorption capacities. This makes nano-engineered biochar coatings a strong candidate for use in smart city applications, given their low-cost, passive, and scalable nature. Our findings support the idea that nano-engineered biochar coatings can meaningfully contribute to urban air quality

improvement. Given their versatility, the coatings could possibly be used as indoor air pollution barrier, and for pollution control in transportation and rural areas without necessary infrastructure. Future research, however, is warranted for investigating long-term durability, regeneration, and real-world performance variability in different environments.

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