Enhancing adsorption capacities of municipal sewage sludge-derived biochar: a comparative study of chemical and physical activation methods for improved removal of penconazole and acetamiprid

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1. Background and purpose of the work

Municipal sewage sludge is a waste of major concern currently in Europe. The elevated generation, intricate composition and biotoxin nature of that sludge poses challenges for achieving safe treatment. However, this complexity also unveils significant potential for the development of biochar to be applied as adsorbent of pollutants presents in wastewater. Biochar synthesized at standards conditions present moderate adsorption capacity. Thus, it is necessary exploring alternative, economical and practical activation methods for the improvement of sludge biochar adsorption capacities and convert it in a competitive environmental solution.

This study aims to compare the adsorption of two microcontaminants (each with a different K_{ow}) using biochar activated through H_3PO_4 (chemical method) and CO_2 (physical method), at high pyrolysis temperature (900ºC) or low pyrolysis temperature (300ºC). The investigation includes the analysis of adsorption kinetics and isotherms, fitting them to suitable models. Also, the effect of water matrix and reusability was explored.

2. Material and methods

The sludge coming from anaerobic digestor of urban wastewater treatment plant at Barcelona (Spain) was oven dried and sieved to 0.16 mm. 3 g of sludge was weighed and placed in a muffle furnace, and it was pyrolyzed under N_2 atmosphere at 300 ºC or 900 ºC during 2 hours and then washed with water until pH was neutral. Those pristine biochars were called B3 and B9, respectively. Then, those materials were activated. For physical process, pristine biochar was loaded to the oven an activated under CO_2 atmosphere at 800 ºC for 1 hour. Those material were called B3C and B9C. For chemical activation, 1 g of B3 or B9 biochar was mixed with 10 mL phosphoric acid solution (85% H_3PO_4: Ultra pure water = 1:10, w:w) for 2 h and washed until the supernatant was neutral. Those materials were named B3P and B9P. Some preliminary tests were run and those activated materials which show a best adsorption capacity were chosen for further comparison. Those were B3C and B9P.

Adsorption capacities were estimated through batch adsorption experiments in solutions of 100 mg of biochar/L of different volume, with an initial pesticide concentration of 10mg/L. The solutions were shaken for 72 hours at 25 ºC until equilibrium, measuring the concentration through High-Performance Liquid Chromatography (HPLC). Biochars were characterized using elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis and porosimetry.

3. Results and discussion

Main results of the study are shown in figure 1. Firstly, figure 1(a) shows the adsorption capacity for the four materials tested. Pristine biochar B3 present a moderate adsorption which is clearly improved by activation step. Pristine B9 presents a good adsorption capacity, probably due to the high pyrolysis temperature applied during its synthesis. Its adsorption is also enhanced after activation with phosphoric. CO_2 and H_3PO_4 activate the biochar by oxidizing the carbon skeleton and metal on the surface of the biochar, respectively. The oxidation of CO_2 causes small pores in the surface carbon structure; H_3PO_4 dissolves the surface ash and coagulates, reducing protrusions. According to results, physical activation induces a small improvement in the adsorption capacity, but chemical activation combined with high pyrolysis temperature produced a notable increase in adsorption capacity. Thus, the adsorption of Penconazole (PEN) by B9P was 50.51 mg/g, increasing the adsorption performance by 73.55% compared to the untreated sludge biochar B9. The activation did not enhance the adsorption effect of Acetamiprid (ACE) significantly, proving that B9P is especially suitable for the adsorption of hydrophobic materials as PEN. Adsorption results fits with BET measurements. B3 and B9 presented areas of 1.8 and 60 m^2/g respectively. B3C BET area was increased up to 16 m^2/g and B9P up to 152 g/m^2, which correlates directly with the adsorption values found for the 4 materials.

Kinetic experiments were also conducted, measuring the concentration of ACE and PEN over time (figure 1(b)). Experimental results were fitted to pseudo-first and pseudo-second order kinetics. Both show a good agreement with the experimental results but pseudo-second order kinetics exhibits a better fitting. Isotherms for both pollutants and activated materials were also conducted (figure 1(c)). Results were fitted to well-established models as Langmuir, Freundlich and Temkin model. PEN and ACE adsorption was better predicted by Langmuir model. The pseudo-second-order kinetic and the Langmuir model fitting results propose that the adsorption process is a monolayer adsorption process dominated by chemisorption.

Since B9P proves to be a best adsorbent, the rest of study was done only with this material. Matrix effect was then studied and it does not seem to decrease B9P capacities. B9P maintains high adsorption performance over a wide range of pH values from 3-11 (figure 1(d), and in 0.1 M salt solutions (figure 1(e)), which makes it highly interesting for real-world applications. Figure 1(c) only shows ACE but similar results were found for PEN. Lastly, reusability was examined by the detergent of B9P with acetonitrile at the end of each cycle for PEN adsorption. After three washing cycles, the adsorption capacity of the material only decreased by 30% (figure 1(f)).

The remarkable adsorption capacity, versatile applicability in water with diverse conditions, and effective regeneration point to B9P as a promising material for valorizing a challenging waste stream such as digested sludge.

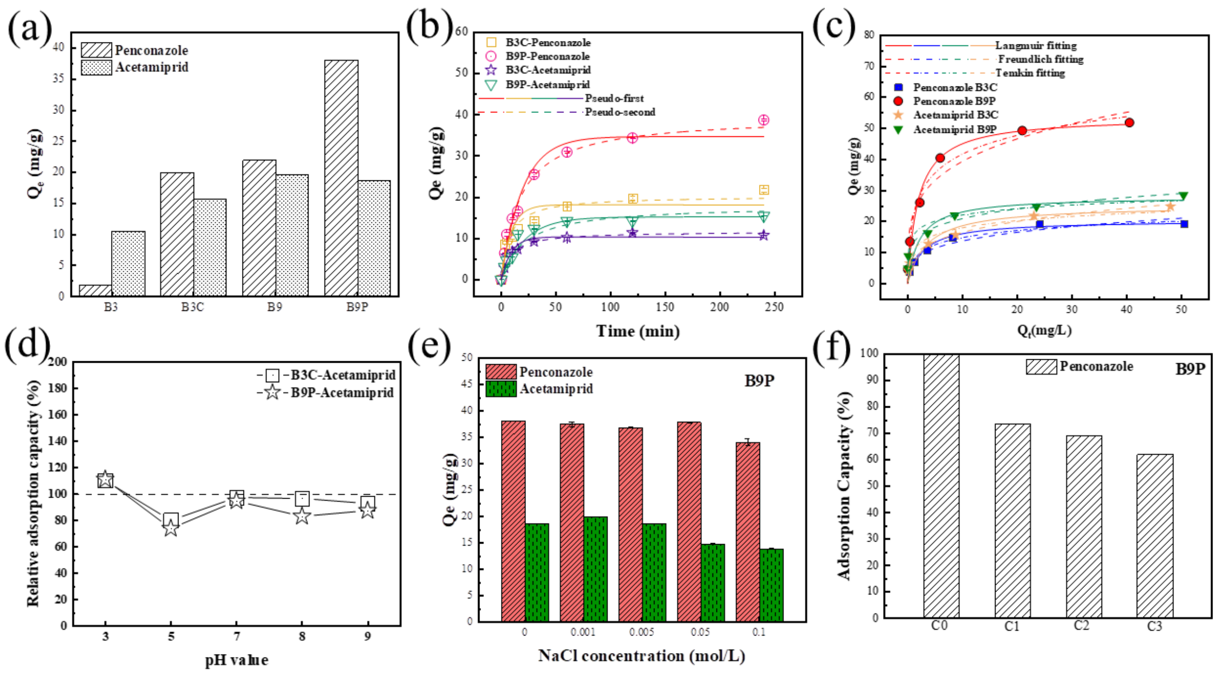

Figure 1. (a) Adsorption capacity of sludge biochar before and after activation; (b) B3C and B9P adsorption kinetics of Penconazole and Acetamiprid; (c) adsorption isotherm of B3C and B9P on Penconazole and Acetamiprid; (d) relative adsorption capacity of B3C and B9P on Acetamiprid at different pHs; (e) B9P adsorption capacity under coexisting salt interference; (f) reusability of B9P for Penconazole adsorption

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