INFLUENCE OF POINT OF ZERO CHARGE (PZC) IN BOILER ASH USED TO REMOVE PARACETAMOL FROM AQUEOUS SOLUTIONS

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ABSTRACT

Pharmaceutical residues have been becoming a public health concern, due to excessive use and improper disposal. Paracetamol stands out for being one of the best-selling and due to its incomplete adsorption, being released through urine into sewage treatment systems. Efficient removal of paracetamol is necessary, understanding the effects of parameters and removal mechanisms. Adsorption is a great technique, and the adsorbent must be cheap and easily accessible. This work aimed to evaluate the application of sugarcane bagasse ash from industrial boilers in the bioremediation of water contaminated with paracetamol by means of adsorption. The tests were carried out to find a best condition for apply the biomass, considering the charges available through the Point of Zero Charge (PZC). Furthermore, tests with pure and mixture paracetamol solution (with ibuprofen) were performed. The PZC obtained was 8.08. The boiler ash exhibited better removal of 72.38% of in pure solution and pH 5. This value decreased to 66.63% with the addition of ibuprofen in the same pH. When changing to pH 11, the mixture decreased in removal efficiency of approximately 16.5%. These results of the batch study can help identify the characteristics that favor the remove of paracetamol using a low-cost adsorbent.

Keywords: Pharmaceuticals 1. Adsorption 2. pH 3. Waste 4.

1 INTRODUCTION

There is a recent concern due to the presence of different pharmaceutical residues in the environment, mainly contaminating aquatic systems, which can lead to adverse effects on ecosystems, altering environmental dynamics and increasing toxicity risks[1]. Pharmaceuticals are emerging contaminants that affect aquatic life physiologically, even at trace levels. Paracetamol is one of the most used analgesics and antipyretics for treating fever and pain. In Brazil, non-steroidal anti-inflammatory drugs (NSAIDs) represent approximately 45% by mass of drugs sold[2]. Its detection in various water bodies has raised global concerns, necessitating efficient removal from water. Adsorption is widely recognized as an effective and cost-efficient technique for the removal of organic pollutants from water bodies, especially when compared to other approaches. Choosing an appropriate adsorbent is critical for successful adsorptive water treatment. Over the past few years, researchers have employed a diverse range of adsorbent materials to remove organic pollutants from water[3]. A recurring problem in adsorption processes is related to the charge of the materials used, as each particle initially possesses a surface charge, which can be positive, negative, or neutral. This charge is influenced by the pH value of the suspension, thus determining the point of zero charge is crucial. It represents the pH at which positive and negative charges balance out. This information is essential for assessing the optimal pH[4]. In this context, boiler ash, a non-traditional adsorbent, has emerged as a cheaper and more effective option. Therefore, the objective of the work was to determine the point of zero charge that indicates the pH value at which the surface of the material is neutral for removing paracetamol from an aqueous solution, verifying its efficiency. Furthermore, an X-ray diffraction (XRD) analysis helped in the evaluation of this process.

2 MATERIAL & METHODS

The determination of the Point of Zero Charge (PZC) was based on the method proposed in the literature[5]. Initially, 30 mg of sieved boiler ash with a diameter smaller than 100 µm were weighed and then placed in 30 mL of deionized water. The pH was adjusted with hydrochloric acid (0.1 mol L^{-1}) and sodium hydroxide solutions (0.1 mol L^{-1}) according to the 11 different initial pH values proposed 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. After 24 hours, the pH was measured again. The pH was measured on a pHmeter model PG1800 from Gehaka.

The adsorption tests that evaluated the removal of paracetamol in aqueous solution were based on the proposal found in the literature[6] and carried out with boiler ash with a diameter smaller than 100 um, 3% (m/v) of adsorbent material and two different pHs, chosen from the PZC tests. This choice of pH was based after determining the point of zero charge, opting for two different pHs, one above and one below the charge neutrality point of the solution. Furthermore, two types of aqueous solutions were tested, one with only the presence of paracetamol and the other with paracetamol and ibuprofen, aiming to verify whether the presence of another molecule could interfere with the adsorption of the drug under study. The values of the quantity of adsorbent material and particle diameter were based on preliminary tests. Experimental tests were carried out in a shaker, with a rotation of approximately 150 rpm and room temperature (25 ± 2 ºC), for a period of two hours. The initial and resulting solutions were quantified by UV-Vis spectrometry.

To evaluate the structure of the adsorbent material (boiler ash), XRD was collected on a Rigaku Miniflex 600 diffractometer using Cu Kα radiation (40 kV, 15 mA). The X-ray diffractograms were recorded from 10 to 70º with a step of 0.02º.

3 RESULTS & DISCUSSION

The choice of pH 5 and 11 was determining based on the point of zero charge. Figure 1a shows the relationship between the initial and final pH of the solutions. It was possible to establish that the Point of Zero Charge (PZC) by making an arithmetic average of the points at which the final pH remained constant. The value obtained for boiler ash was 8.08.

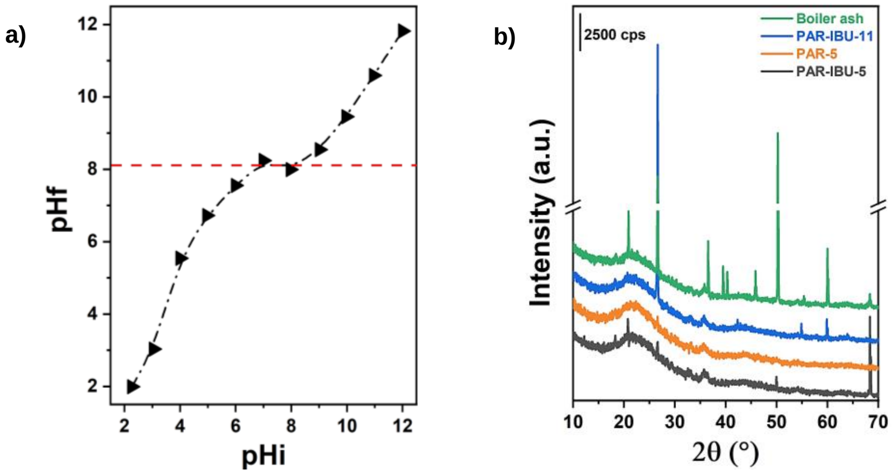

Figure 1 a) Determination of PZC for boiler ash. **b)** XRD of the boiler ash in natura and in two different pHs (5 and 11) and presence of paracetamol or paracetamol and ibuprofen.

When a solid material comes into contact with a liquid solution with a pH below the PZC, the surface is positively charged, and a large number of anions are adsorbed. Thus, adsorbents are more effective for removing, for example, anionic materials. It is known that paracetamol, due to its structure, has a dissociation constant value (pKa) equal to 9.53. Therefore, paracetamol can exist in different forms, which depend on the pH of the solution. Therefore, at pH < 9.53 it is in non-ionized or molecular form and when it is in a solution with pH > 9.53 it is in anionic form. In other words, with a pH above 9.53, almost 20% of paracetamol is in the anionic form [7,8]. Due to this situation, through Table 1 it is possible to verify that at pH 5 (Exp. 3) there was a greater adsorption of paracetamol, possible due to the charges presented by the drug and the surface of the adsorbate.

For the experiments 1 and 2, the removal of paracetamol from a combination of two or more species present (paracetamol + ibuprofen) is known as competitive adsorption. In these cases, the adsorption of the first solute is often negatively affected by the presence of additional solutes in the mixture[9], as can be seen by comparing the results of experiments 1 and 3 in Table 1. In aqueous solutions with a higher pH than PZC, the surface is negatively charged and preferentially adsorbs cations. In this case, adsorbents are more effective for removing cationic materials, and this situation becomes evident when comparing experiments 1 and 2, where in a competitive adsorption, the increase in pH led to a decrease in the removal of paracetamol (molecule of interest - anionic).

Tabel 1: Experimental tests of paracetamol removal using sugarcane bagasse boiler ash. Tests were conducted under three conditions: two with a mixture of paracetamol and ibuprofen at pH 5 and 11 (PAR-IBU-5 and PAR-IBU-11), and another with only paracetamol at pH 5 (PAR-5)

Exp	Condition	Paracetamol Initial concentration (mg L^{-1})	% Removal Efficiency	Adsorptive capacity (mg g^{-1})
1	PAR-IBU-5	32.2	66.63 ± 6.71	0.72
2	PAR-IBU-11	32.2	55.60 ± 4.79	0.70
3	PAR-5	29.2	72.38 ± 2.13	0.60

Adsorbents from the agroindustry have been tested in the adsorption of paracetamol from aqueous solutions and its capacity varies notably depending on the nature of the adsorbent and the experimental conditions. Based on this, it is worth mentioning that paracetamol adsorption is very dependent on the nature, type, surface morphology of the substrate, experimental situation and solution chemistry[10]. For rice husk ash, the point of zero charge (PZC) was found at a value of 8.4. As is known, PZC indicates the net charge of the adsorbent surface in the solution and plays a crucial role in the sorption process. In this case however, the greatest adsorption was found at pH 8.

Regarding adsorptive capacity, boiler ash presented the best value (0.72 mg g^{-1}) for experiment 1, even though it did not have the best removal efficiency. Dehydrated sewage sludge and *P. oceanica* (seagrass species) were studied for paracetamol sorption and obtained values of 0.956 and 1.638 mg g^{-1}, respectively[11]. These values are close to those found in this work, as well as the values for grape stems (1.74 mg g^{-1}), cork skins (0.99 mg g^{-1}) and yohimbe skins (0.77 mg g^{-1}), presented by other authors who also aimed to remove paracetamol from aqueous solutions by some residue without added value (vegetable waste)[12].

The X-ray diffraction (XRD) patterns of boiler ash before and after paracetamol or paracetamol and ibuprofen adsorption in two different pHs (5 and 11) are shown in Figure 1b. The diffractogram of boiler ash indicates a partially crystalline material with an amorphous phase associated with the carbon structure. They reveal three characteristic peaks of the quartz phase (peaks at approximately 20°, 27°, and 50°), and the other smaller peaks indicate the presence of different crystalline phases, such as mullite ($Al_{4.44} Si_{1.56} O_{9.78}$). The XRD analysis exhibited that after adsorption in pH 5 and 11, the intensity of the crystalline phases declined, which can be caused by the extraction/exchange of ions from the adsorbent or the expansion of the structure with the different amounts of paracetamol or paracetamol-ibuprofen molecules. Similar results in the literature13, but using activated carbon as the adsorbent material, demonstrate that the adsorption of paracetamol did not change the structure space of the solid and, therefore, the adsorption process occurred on the surface.

4 CONCLUSION

The value obtained of the Point of Zero Charge (PZC) for the boiler ash was 8.08. Through XRD was observed that after paracetamol adsorption, increased the proportion of amorphous phase in the carbon structure. Therefore, these results demonstrate the possibility of using agro-industrial residue as an efficient adsorbent material for the removal of paracetamol from aqueous solutions, always taking into account the condition of the aqueous phase.

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