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Research Article
Non-steroidal Anti-inflammatory Drug, Ibuprofen Adsorption Using Rice Straw Based Biochar

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Abstract

Background: Adsorption of non-steroidal anti-inflammatory drugs ibuprofen (IBP) by straw based biochars was studied. **Methodology:** In this study, rice straw was pyrolyzed at different temperatures (400-600°C) and were characterized by elemental analysis, Brunauer Emmett Teller (BET) surface area and particle size distributions. Ibuprofen adsorption kinetics and mechanism were studied. Increasing pyrolysis temperature of biochar decrease its ash content, yield, acidity, total hydrogen and oxygen contents while biochar density, total carbon, nitrogen and basicity decreased for the reason of pyrolytic volatilization during pyrolysis. Ibuprofen adsorption have been found to be accelerated and reproduced by pseudo-second-order kinetic equation. **Results:** Results revealing that pyrolysis of straw allows obtaining biochars samples appropriate for the treatment of liquid waste solution that contaminated by pharmaceutical compounds. **Conclusion:** Pyrolysis temperature was found significantly effective on physicochemical properties of the produced biochars.

Key words: Ibuprofen, adsorption, biochar, characterization

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Recently, presence of pharmaceutically active compounds in aquatic environment is one of the evolving subjects in environmental chemistry. Investigations showed that these compounds are not biodegraded in the environment and also frequently not removed throughout wastewater management[1]. Non-steroidal anti-inflammatory drugs (NSAIDs) are intensively and widely used worldwide as important drugs to treat inflammatory conditions. Unfortunately, NSAIDs frequently pass through digestive system and go to water systems through human waste. Detectable NSAIDs have been found in the environment[2] causing significant degenerative, renal and necrotic changes on vertebrates[3].

Ibuprofen is one of the "Essential drugs" itemized by the World Health Organization and so, ibuprofen is one of the most frequently detected pharmaceuticals in the environment[3], with high concentration (ug L^{-1}). Ibuprofen was the 2nd NSAID and the 3rd used drug regarding to packs sold number[4] in 2009. Due to extensive incidence of ibuprofen in water environments, it is possible for ecological problem to be happened[5]. The IB in water has been shown to influence invertebrates and vertebrates reproduction[6], fungal and bacterial species growth[7], genetic and systemic damage to some mussels, fish species[6] and cytogenetic properties in freshwater bivalves[8]. Ibuprofen was consider water frame directive consider ibuprofen as urgent pollutant to be measured in aquatic environment and removed.

Adsorption becomes an attractive and alternative method for wastewater treatment, if using low cost adsorbent that no need pre-treatment step like activation before adsorbent application[9]. Furthermore, biochars have strong sorption affinities for various contaminants.

Low-cost biochar is the material produced from various biomass by its pyrolysis in inert environment[10], has recently received major attention as an effective adsorbent of several inorganic and organic pollutants both water and soil[11] because of its good characteristics containing high surface density of functional groups as well as its condensed structure. All of these characteristics are covered by various factors including type of the precursor and preparatory condition like pyrolysis temperature and time. Production of biochars from different invasive plant species waste is advantageous for agricultural waste management[12,13].

Previous studies showed that biochars is comparable to activate carbon in the adsorption of organic pollutants[14]. Therefore, more studie are needed for biochar preparation for specific enviromentail problem application to be alternative adsorbent to other adsorbents[15]. Thus, in this study, simple, easy and cheap method using steam pyrolysis was developed the preparation of biochar with high sorption capacities of biochars prepared[16].

In the resent years, effective steam pyrolysis method was developed of the preparation of biochar from pecan shell to remove cupper from aqueous solutions. In spite of this, the importance of steam-carbonized biochar in the adsorption of organic pollutants has not been investigated in the literature and requires continuous study.

Lately, numerous studies have investigated ibuprofen removal of using activated carbons[17-20]. However, little work has been done on ibuprofen removal by biochars[21-24]. In this study, rice straw biomass was converted to biochar to simultaneously address two environmental issues i.e., (a) Economically feasible removal of agricultural by-products and avoid bad environmental impacts of direct burning of straw and (b) Preparation of innovative and environment friendly material for pollutants removal. The purpose of this study was to inspect the effect of pyrolysis temperature on characteristics and chemical composition of biochar produced rice straw to evaluate its suitability for ibuprofen removal as NSAIDs drug.

MATERIALS AND METHODS

Preparation of biochar: Rice straw was gathered from Egyptian paddy field and dried at 60°C for 24 h and then chopped to small pieces. The dried samples were settled in a tube furnace. Biochars were prepared at different pyrolysis temperatures in the range from 400-600°C under oxygen-limited environment. The sample was heated with heating rate of 5°C min^{-1} to the required temperature with one hour as hold time. Depends on the pyrolysis temperature (400, 500 and 600°C) the resulting biochars were namely Biochar-300, Biochar-400, Biochar-500, respectively. Biochar yield was calculated, based on dry weight.

Characterization: The ash content was measured by combustion of biochar at 760°C for 6 h according the following equation:

$$\text{Ash contents}(\%) = \frac{\text{Weight of ash}}{\text{Dry weight of biochar}} \times 100 \quad (1)$$

Pore structure characteristization of the resulting biochares were measured using N_2 adsorption isotherm at 77 K. BET (Brunauer-Emmett-Teller) equation was used to estimate biochar surface area. Total pore volume (V_t, 0.95) calculated from amount of N_2 adsorbed on the adsorbent at relative pressure of 0.95 and the mean pore radius from $r_{BET} = 2V_t/S_{BET}$. Pore size distribution of the biochars got by using micrometrics Density Functional Theory (DFT) model to N_2 isotherm.

Biochar pH values were measured using 1:10 biochar/water ratio using pH meter Hanna Instruments pH 2.11. Basic and acidic functional groups were determined using Boehm titration method[25]. The CHN Elemental Analyzer (Carlo-Erba NA-1500) was used to measured elemental analyses including C, H and N. Philips XRG3100 X-ray diffractometer was used to measure the XRD patterns of the prepared biochar materials.

Ibuprofen adsorption: Adsorption experiments conducted through batch technique by mixing and shaking 50 mL of drug solutions of certain concentration (10-100 mg L^{-1}) with 25 mg of biochar in conical flask at a room temperature for fixed time intervals. Samples were separated using syringe microfilter (0.45 μm). Supernatant ibuprofen concentration was measured using UV-visible Spectrophotometer "Shimadzu 2100S" at 220 nm. Adsorption capacity of biochar for ibuprofen (q, mg g^{-1}) estimated using the following equation:

$$q_e = V(C_o\text{-}C_e)/M \tag{2}$$

where and C_e and C_o are equilibrium and initial concentration (mg L^{-1}), respectively, V is solution volume (mL) and M is the biochar dry mass (g).

RESULTS AND DISCUSSION

Characterization of the adsorbents: The yield of biochar decreased from 28.9-21% as temperature of pyrolysis increased from 400-600°C. This could be owing to increased evapouration rate of oragnics with increasing temperature[26]. It was proposed that moisture go out at 220°C, hemicelluloses decompose at temperature range 220-315°C and cellulose decompose at 315-400°C, whereas lignin decompose at 400°C[27]. Generally, the primary thermal degradation of biomass occurs at low pyrolysis temperature. Nevertheless, volatiles were more broken to lower molecular weight compounds at high pyrolysis temperature[28].

Similar to yield, biochars ash content decreases with rising pyrolysis temperature from 400-600°C. This means that increasing pyrolysis temperature can influence on both carbonaceous and inorganics part (insoluble silicate) of samples[29]. The gases emerge through activation may eliminate some of inorganic clusters and greater one could undergoes decomposition throughout extended exposure to high temperature during pyrolysis. The ash content of resultant biochar at different temperatures Biochr-400, Biochr-500, Biochr-600 is higher than that of raw material. Also, it is higher than that derived woody feedstock (2-8%) and from grass (<20%)[30]. This may be due to rice straw has high ash content (especially silicon dioxide) compared to other crop residues[31]. Therefore, rice straw can be preferred for biochar preparation.

Biochar mechanical strength linked to its true density. This means increased biochar with high molecular order has higher mechanical strength than its biomass[32]. True density data showed that transformation of low-density disordered biochars to high-density ones, telling that high temperature lead to increase in true density of produced biochar samples. This could be linked with active decompasion of cellulosic portions and compression processes that leads to increase aromatic carbon clusters contents at high temperature. Biochar formation from various biomass is complex and still confused. Demirbas[33] recommended three reaction mechanisms for pyrolysis step of biomas to produce biochar:

1st stage: Biomass → water+unreacted residue
2nd stage: Ureacted residues → (volatile+gases)+(char)
3rd stage: Char → (volatile+gases)+char

In agreement with such mechanisms, three main steps involve in the formation of biochar. Biochar produced in 2nd stage undergoes chemical rearrangement and furthermore break down to carbon-rich biochar.

The influence of pyrolysis temperature on BET surface areas and total pore volume of prepared biochars are given in Table 1. Biochr-500 give surface area little higher than

Table 1: Pore property, elemental analyses, pH, surface acidity and alkalinity of biochars

Element	Biochr-400	Biochr-500	Biochr-600
S_{BET} (m^2 g^{-1})	71.35	76.2	63.0
S_{mic} (m^2 g^{-1})	51.5	52.8	43.6
$V_{p(0.95)}$ (cc g^{-1})	0.054	0.063	0.052
V_{mic} (ccg, %)	0.03 (55)	0.034 (53)	0.02 (47)
r_{BET} (nm)	1.55	1.6	1.65
H	4.4	3.2	2.9
N	1.1	1.3	1.7
O	49.0	43.6	30.1
C/N	23.2	24.6	28.8
H/C	0.1	0.06	0.02
O/C	1.0	0.84	0.45
pH	9.2	9.3	9.1
Basic gps (meq g^{-1})	6.22	8.13	13.06
Acidic gps (meq g^{-1})	5.6	2.0	1.79
Carboxyl (meq g^{-1})	0.1	0.05	0.1
Lactonic (meq g^{-1})	5.4	1.89	1.5
Phenolic (meq g^{-1})	0.13	0.06	0.18

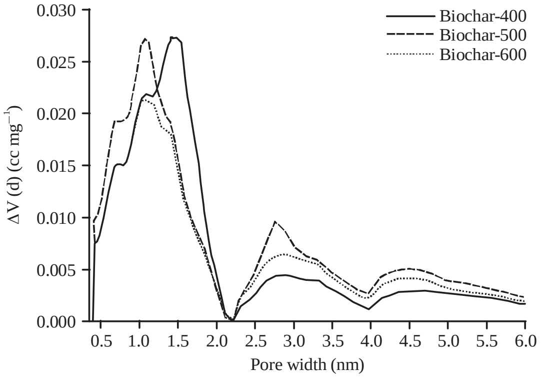

Fig. 1: DFT pore size distribution of biochar samples

Biochr-400 and Biochr-600. These results are completely agreement with total pore volume due to increasing micropore and mesopore volume. However, for pyrolysis temperatures higher than 500°C the surface areas decreased due to burnt off increased amount of biochar, resulting in the conversion of microporosities into mesoporosities or even macroporosities. Upon increasing the pyrolysis temperatures the pore wide increases. Increasing temperature leads to the destruction of pore to larger one, increasing fraction percentage of mesopores and decreasing of micropores (Table 1). Temperature greater than 500°C, pore widening and structural ordering appear to dominate, results in reduction of pore volume and surface area. In addition as a consequence of melting, softening and pyrolysis, pores may be partly blocked[34]. The same trend was observed by Angin[35] for safflower seed-based[35].

The pore size distribution of prepared biochar was studied and results are demonstrated in Fig. 1. It is clear that the samples exhibit wide pore size distribution, from narrow micropores to wide mesopores. The pores of biochar shown one sharp peak at about 1.0 -1.5 in micropore region and two broad peaks at at about 3.0 and 5.0 nm in mesopore region. The results illustrate that pyrolysis temperature appears to affect pore size distribution. The micropore of carbonized Biochr-400 concentrated in peak at 1.5 nm while increasing pyrolysis temperature shifts this peak to lower pore width at 1.0 nm. In mesopore range there are two broad peaks at 2.7 and 4.5 nm, its intensity increased by increasing pyrolysis temperature up to 500°C. This means that increasing pyrolysis temperature enhancing micro and mesoporosity.

Decrease of pore size with rising temperature signifying that reaction through pyrolysis can deteriorate biomass macromolecular structure to give more fragile biochars[36]. This may be due to reduction of tensile strength of precursor materials at high temperature that cause reduction of abrasion resistance[32]. Biochar elemental composition was investigated and is given in Table 1. At high temperature, carbon contents are high, whereas the hydrogen and oxygen content is low. Increasing carbon with increasing temperature due to volatiles release through pyrolysis which leads to removal of the non-carbon species and carbon enhancement[37]. These results show that carbonization degree was enhanced at high temperature[38]. Breaking and damage of weak bond inside the structure of biochar results in losses of oxygen and hydrogen at high pyrolysis temperature[33].

There is a relative increase in nitrogen content of biochar samples with temperature in this study. This may be due to the nitrogen incorporation into biochar stricter. Nitrogen is resistant to heating and not easily volatilized then Temperature could conserve N in biochars[39].

Biochar structure aromaticity degree and bonding arrangement of the biochar samples can be explained by H/C and O/C elemental ratios. Table 1 shows that H/C and O/C atomic ratios reduced at high temperature which indicating that structural transformations induced by pyrolysis process. Reduction of O/C ratios at high temperature is accompanied with dehydration reactions that lead to hydrophobic biochar[40]. Furthermore, reduction of H/C ratio was connected to carbonization degree. This means that with increasing temperature the biochars became carbonaceous and more aromatic as a result of continuous dehydration and decarboxylation reactions[34]. The decrease of O/C and H/C ratios, down to 0.45 and 0.02 for Biochr-600 may be the reason of increasing carbonization degree inside biochar. Very low O/C and H/C point to that unsaturated carbon is predominate in these biochars. High ratio of H/C (0.1) and O/C (1.0) for biochar-400 may be due to the presence of residual organic matter like carbohydrates[41].

The biochar generated from rice straw contain around 45-65 wt% of carbon and 1.1-1.7 wt% of nitrogen. Then application of our biochar in the soil will increases its fertility by enhancing its carbon content and restoring some nitrogen that may be removed due to stover collection. As clear from Table 1, pyrolysis temperature did not has a great influence on biochar pH values that were around 9.2. These outcomes are in line with literature that most of the dry-pyrolysis biochars are alkaline[42]. Alkaline property of biochar can be considered as one of most important advantages as it can potentially neutralize soil acidity and reduce soil exchangeable aluminum then alleviate its toxicity[18].

The basic nature of biochares can be due to great surface basicity and alkalinity as shown in Table 1. Low temperature produces biochars have higher surface acidity than in those high temperature produced biochares. Also all biochar

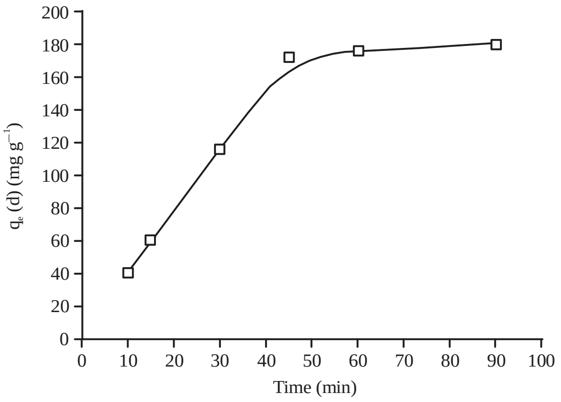

Fig. 2: Effect of time on ibuprofen adsorption by Biochr-500

samples have the three types of surface oxide groups including carboxylic, lactonic and phenolic depending on temperature used for pyrolysis. These finding are in line with many investigators who reported that low temperature produced biochars have several surface oxides, including carboxylic acids that decomposes by heating at higher temperature[43].

Ibuprofen adsorption: Biochr-500 gave high ibuprofen removal, q (56.0 mg g^{-1}) in comparison to Biochr-400 (15.6 mg g^{-1}) and Biochr-600 (5.56 mg g^{-1}). It seems that both porosity and aromaticity play important role in ibuprofen adsorption. Pyrolysis temperature intensely influence on removal of biochar for metals and organics compounds[44]. It has been investigated that trichloroethylene removal by pine-needle based biochar proportionate to pyrolysis temperature (300-700°C) as a result of high biochar surface area, aromaticity and low polarity[45]. Therefore, Biochr-500 was used for the following study to detect effect of various experimental factors on ibuprofen uptake.

Ibuprofen adsorption time-profile in Fig. 2 increases continuously until saturation and equilibrium at 40 min. This proposing formation of monolayer ibuprofen adsorbed layer on Biochr-500 surface short time of adsorption equilibrium considered one of the most significant character cost effective applications of adsorbent in wastewater treatment. As clear from Fig. 2, there are two sections including initial fast ibuprofen adsorption in the time range of 0 and 30 min and then gradual stage until equilibrium without anymore ibuprofen uptake after 40 min. The fast and rapid ibuprofen adsorption may be owing to great quantity of adsorption sites on Biochar-500 surface available to remove ibuprofen from solution. The second slow adsorption stage may be owing to reduction of available sits on the surface of adsorbent to remove ibuprofen. Many investigators got the same trend of adsorption time profile of rapid adsorption followed by slow ones[46-48]. Preliminary slopes of adsorption curve in Fig. 2 demonstrated that ibuprofen adsorption rate using Biochr-500 is significantly based on initial adsorbate concentration and film diffusion is the predominate mechanism for ibuprofen adsorption on Biochar-500.

Table 2: Kinetic parameters of ibuprofen adsorption onto Biochr-500

Model	Parameter	Value
Experimental date	q_e,exp (mg g^{-1})	170
Frist-order	K_1 (g mg^{-1} min)	54.2x10^{-3}
	q_e (mg g^{-1})	98
	R^2	0.92
Second-order	K_2 (g mg^{-1} min)	0.23x10^{3}
	q_e (mg g^{-1})	165
	R^2	0.99
Elovich	α (mg g^{-1} min)	5.3
	β (g mg^{-1})	5.4x10^{-3}
	R^2	0.92

Kinetic investigation: One or more combination of chemical, diffusion control and mass transfer can control any adsorption process. Adsorption process modeling and kinetic parameters can measured by investigation of experimental data at several time. To go deep into the mechanism of adsorption of ibuprofen on Biochr-500, experimental results were modeled by means of different kinetic equations containing pseudo first-order, pseudo-second-order and Elovich equations[49,50]. Represented by the following equations:

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1}{2.303} t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

$$q_t = \frac{1}{\beta}\ln\left(\alpha\beta\right) + \frac{1}{\beta}\ln t \qquad (5)$$

q_t (mg g^{-1}) is the quantity of ibuprofen sorbed at time t, q_e (mg g^{-1}) is the quantity of ibuprofen sorbed at equilibrium, k_1 (min^{-1}) is the pseudo-first rate constant, k_2 (g mg^{-1} min) is the pseudo-second-order rate constant, α (mg g^{-1} min) is the Elovich sorption rate and β (g mg^{-1}) is the Elovich desorption constant.

Table 2 illustrate the kinetic adsorption parameters obtained by fitting of adsorption data using these three equations. Correlation coefficients (R^2) were used to judge the fitting of model and agreeing between theoretical values and experimental data. According R^2 values, pseudo-second-order model is more fitting ($R^2 = 0.98$) than first-order model

(R^2 = 0.92) and Elovich kinetic model (R^2 = 0.9) for ibuprofen/Biochr-500 system. Furthermore, calculated pseudo-second q_e values exactly expect adsorption over all working adsorption times. In contrast of the calculated first-order q_e that give too low values compared with experimental one. These results proposed ibuprofen adsorption overall rate on Biochr-500 is covered by process of chemisorption[51] and adsorption rate straight proportionate to No. of active adsorption sites on adsorbent. Biochr-500 has high ibuprofen equilibrium sorption capacity q_e (165 mg g^{-1}), very fast sorption rates (0.23×10^3 g mg^{-1} min) and short equilibrium times (40 min) which identify high affinity degree between ibuprofen and Biochr-500 surface[52].

Ibuprofen adsorption mechanism by Biochr-500: Electrostatic and dispersive interaction are two main mechanism that can control aromatic compounds adsorption from liquid phase on carbons sorbents[53]. Ibuprofen is in solution occur in molecular form, then adsorption can be done through dispersive attractiveness between carbon graphene sheet π orbital and ibuprofen aromatic rings electronic density (π-π interactions)[54]. Moreover, high uptake of Biochr-500 for ibuprofen may be explained by ibuprofen/Biochr-500 electrostatic interaction. Also, ibuprofen can also be adsorbed by the interaction between ibuprofen ring π electrons and positive charge on weak or nonacidic oxygen groups that leads to increase electrostatic attraction and consequently a higher ibuprofen adsorption.

CONCLUSION

Pyrolysis temperature was found to be significantly effective on physicochemical properties of the produced biochars. Yield of biochar decreased with increase pyrolysis temperature. At high pyrolysis temperature, biochar carbonization degree was high that leads to increase carbon content and then their elemental ratios of H/C and O/C decrease. Pseudo-second order kinetic equation gave the highest fitting for ibuprofen sorption kinetic experimentail data. The overall results revealed that the preperaed straw based biochars have adequate properties for pharmaceutical compounds removal.

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