**Facile activation of sludge-based hydrochar by Fenton reagent for ammonium adsorption in aqueous media**

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**Highlights**

* We report the facile activation of hydrochar by Fenton oxidation.
* We investigate NH4+ adsorption by activated hydrochar.
* For activated hydrochar, the maximum adsorption capacity for NH4+ is 30.77 mg g−1.
* The NH4+adsorption capacity of a synthetic effluent from an anaerobic membrane bioreactor was lowered by up to 33±3%.
* Saturated activated hydrochar gradually desorbs NH4+.

**Graphical abstract**

**Abstract**

This research investigates ammonium (NH4+) adsorption on hydrochar activated by Fenton oxidation and evaluates its desorption potential. The hydrochar was produced from raw sludge, and the Fenton activation was done with different concentrations of H2O2 and H2O2/Fe2+ and several activation times. The activated hydrochar surface properties were analyzed by attenuated total reflection Fourier transform infrared spectroscopy, high-resolution x-ray photoelectron spectroscopy, Brunauer–Emmett–Teller (BET) surface analysis, and scanning electron microscopy. We investigate the NH4+ adsorption isotherms and kinetics and how competing ions affect the adsorption capacity and NH4+ desorption. The results show that activation occurs within a few minutes when using a relatively low concentration of reagents and no extensive post-treatment steps. Following hydrochar activation, the concentration of the acidic groups and the BET surface area both increase, but the morphology remains essentially constant. The Langmuir isotherm model fits the equilibrium data of NH4+ adsorption onto activated hydrochar, and the pseudo-second-order model fits the adsorption kinetics. The maximum adsorption capacity is 30.77 mg g−1. The adsorption of NH4+ from the effluent of a synthetic anaerobic membrane bioreactor (i.e., adsorption in the presence of competing ions) decreases by up to 33±3%. Desorption experiments demonstrate that NH4+ recovery from the activated hydrochar is 33±5% and 67±2% following three consecutive steps with ultrapure water and 2 M KCl, respectively. These results indicate that facile Fenton oxidation is a promising alternative for hydrochar activation and that activated hydrochar can be used as a low-cost adsorbent for NH4+ remediation in wastewater treatment processes.

**Keywords**: hydrochar; activated hydrochar; ammonium adsorption; nitrogen recovery

1. **Introduction**

Wastewater treatment plants produce a large amount of sludge (Grobelak *et al.*, 2019; Shehu *et al.*, 2012), which is a potential source of pollution and can pose public health risks (Bertanza *et al.*, 2016; European Commission, 2001; Shehu *et al.*, 2012) and must therefore be disposed of appropriately. Thus, the management of wastewater sludge imposes an environmental and economic burden on society (Jimenez *et al.*, 2010; Papa *et al.*, 2017). Conversely, wastewater sludge offers significant potential for the recovery of carbon, energy, and nutrients (Gherghel *et al.*, 2019; Raheem *et al.*, 2018; Van Loosdrecht and Brdjanovic, 2014). Consequently, over the past several years, interest has grown in valorizing wastewater sludge (Fytili and Zabaniotou, 2008; Raheem *et al.*, 2018).

One common valorization scheme is the thermochemical conversion into valuable solid porous coal-like materials called “char” (Gao *et al.*, 2020). Char can take the form either of biochar, which is formed by dry pyrolysis at elevated temperatures (300–650 °C) (Kambo and Dutta, 2015), or hydrochar, which is formed by hydrothermal carbonization (HTC) of wet biomass under autogenous pressure. The latter is the focus of the present study (Heidari *et al.*, 2019; Wang *et al.*, 2018). The HTC process has several advantages over dry pyrolysis thermal pretreatments such as pyrolysis: no prior drying is needed, and the process is performed at a relatively low temperature (180–260 °C) (Kambo and Dutta, 2015). In addition, compared with biochars, hydrochars typically have higher energy density and carbon content, and a lower content of ash, alkali metals, alkaline-earth metals, and heavy metals (Kambo and Dutta, 2015; Wang *et al.*, 2018; Z. Zhang *et al.*, 2019). In addition to char, HTC produces a significant aqueous phase and a limited amount of gas. The aqueous phase is typically rich in nutrients and can potentially be used for agriculture (Mau *et al.*, 2019; Belete *et al.*, 2019) as a liquid substrate for the HTC process (Z. Xu *et al.*, 2019) or for anaerobic digestion (Poerschmann *et al.*, 2014).

Hydrochars have been investigated in many environmental applications, such as for solid fuel (Wang *et al.*, 2018), soil amendment, carbon sequestration, and environmental remediation (Gronwald *et al.*, 2016; Huangfu *et al.*, 2020; Sun *et al.*, 2020; Tasca *et al.*, 2019) as well as for producing high-value carbon materials for electrochemical energy storage (Sevilla and Fuertes, 2016). Hydrochar is also being investigated because the functional groups on its surface make it a potential low-cost adsorbent of various contaminates (Huang *et al.*, 2020; Takaya *et al.*, 2016; Xinbo Zhang *et al.*, 2020; Xueyang Zhang *et al.*, 2020). However, the concentration of these functional groups and the surface area of hydrochars are generally low [the Brunauer–Emmett–Teller (BET) surface is less than 9.1 m2 g−1], so its adsorption capacity is relatively low (Sun *et al.*, 2015; Xue *et al.*, 2012).

The adsorption capacity of hydrochars can be enhanced in various ways, the most common of which is chemical activation of hydrochars using a base (e.g., KOH) or acid (e.g., H2SO4) in combination with heating to high temperature (He *et al.*, 2016; X. Zhang *et al.*, 2019). However, acid or base activation processes require significant quantities of chemicals, a long activation time, and tedious post-treatment steps (Fernandez *et al.*, 2015; X. Zhang *et al.*, 2019). Consequently, other activation methods have been investigated in recent years (Vithanage *et al.*, 2017), including catalytic *in situ* activation during HTC production (Chu *et al.*, 2020; Ledesma *et al.*, 2018). In addition, post-treatment methods have been investigated, such as thermal treatment (Huang *et al.*, 2020) and microwave-assisted processes (Gaudino *et al.*, 2019) and the use of CO2 (Xueyang Zhang *et al.*, 2020), potassium salts (Sevilla and Fuertes, 2016), sulfate salts (Wei *et al.*, 2020), or urea (Xiao *et al.*, 2020). A facile alternative to activate hydrochar involves using hydrogen peroxide and enhances the sorption of heavy metals such as lead (Xue *et al.*, 2012), reportedly because of the greater concentration of oxygen-containing functional groups, particularly carboxyl groups, on the hydrochar surfaces.

Another environmentally friendly and facile activation method for enhancing biochar (from dry pyrolysis) sorption capacity is by using a Fenton reagent, which is a mixture of hydrogen peroxide and a ferrous salt as catalyst (H2O2/Fe2+) and has been tested numerous times in recent years (Gu *et al.*, 2013; Huff and Lee, 2016; Mia *et al.*, 2017; Wang *et al.*, 2015). One advantage is that Fenton-activated biochar enhances the sorption capacity of methylene blue (Huff and Lee, 2016) due to the formation of functional groups on the carbon surface, which in turn is caused by the radicals that form during the Fenton reaction.

One interesting application of low-cost waste-derived adsorbent is the adsorption of nutrients (i.e., ammonium and phosphate) from wastewater effluent. In this case, the adsorbent is applied to “polish” the effluent before it is discharged or reused. Since the adsorbent is inexpensive, regeneration is unnecessary (Fang *et al.*, 2018; Takaya *et al.*, 2016). In addition, the saturated adsorbent can potentially be applied directly to soils as a nutrient (Chen *et al.*, 2017; Puga *et al.*, 2020; Takaya *et al.*, 2016; D. Xu *et al.*, 2019).

The present research thus studies the use of Fenton oxidation for facile activation of hydrochars from domestic sludge and measures the capacity of hydrochars to adsorb and desorb NH4+.

1. **Materials and methods** 
   1. *Hydrochar preparation and activation*

The production of hydrochar from HTC of raw sludge is described in detail by Belete *et al.* (Belete *et al.*, 2019). Briefly, domestic sludge from the Yeruham township (Southern Negev region, Israel) wastewater treatment plant was collected and introduced into an HTC reactor at a solid : water ratio of 1 : 3, and hydrochar was produced at 210 °C for 4 h. The hydrochar was rinsed with ultrapure water (Milli-Q water, Millipore, USA) to remove residual impurities and then oven-dried at 105 °C for 24 h before storage in a desiccator until further use.

The hydrochar was activated by soaking 10 g of hydrochar powder (particle size < 850 µm) in 200 mL of pH 4 Fenton reagent solution (30% H2O2/Fe2+) at different H2O2/Fe2+ ratios (10 : 0, 10 : 1, and 10 : 2), peroxide concentrations (25–200 mM, H2O2), and reaction times (30, 90, and 180 min). The mixed solution was mechanically shaken at 160 rpm at room temperature. Upon the completion, each sample was centrifuged at 5000 rpm (TGL20M-II centrifuge, Kaida, China), and the resulting solid product was rinsed three times with ultrapure water to remove residual H2O2. The sample was then dried in an oven at 105 °C to produce the activated hydrochar (AH), hereinafter referred to as AH*x*-*y* where *x* and *y* are the H2O2 concentration and activation time, respectively.

* 1. *Characterization*

The functional groups of the hydrochar and AHs were determined by Fourier transform infrared (FTIR) spectroscopy (Bruker Optics, Germany), equipped with a single-reflection Ge crystal for attenuated total reflectance (ATR, Pike technologies) in the range of 4000–650 cm−1 (30 scans, 4 cm−1 resolution). The composition and functional groups of AH were also characterized by using high-resolution x-ray photoelectron spectroscopy (HR-XPS) with a monochromator and the Al *K*α source of an ESCALAB 250 microscope (ThermoFisher Scientific, USA). The morphology and structure of the activated char were also characterized by HR scanning electron microscopy (HR-SEM, JSM-7400F, JEOL, Japan). The BET surface areas were determined by using a Quantachrome (NOVAtouch 4LX) gas sorption analyzer at 77 K with nitrogen as the sorbate. The iron concentration in the samples was measured following microwave acid digestion (Milestone Ethos Up) (Mayda *et al.*, 2020), which involved mixing a 150 mg of dried sample in each microwave vial with 9 mL 70% HNO3 and 1 mL 30% H2O2 for 30 min of digestion at 200 °C. The digested sample was filtered by using a 0.45 µm membrane filter (Millex-GV, Millipore), and the iron concentration was measured by using inductively coupled plasma optical emission spectrometry (ARCOS ICP-OES, Spectra, Germany).

* 1. *Adsorption and desorption experiments*

To estimate the adsorption capacity, 0.2 g of adsorbent was introduced into a 100 mL ammonium-chloride solution in a 250 mL Erlenmeyer flask. Solution concentrations were 10–150 mg NH4+ L−1. Erlenmeyer flasks were shaken in a thermostatic shaker at 160 rpm for 12 h at a constant temperature of 25 °C. In all adsorption experiments, the solution pH was adjusted to 7 by adding HCl. The amount of NH4+ adsorbed (qe, mg g−1) and the removal efficiency (%) were calculated by using (Chen *et al.*, 2017; Takaya *et al.*, 2016)

(1)

(2)

where *C*0 and *Ce* (mg L−1) are the initial and equilibrium NH4+ concentrations, respectively, *V* is the solution volume (L), and *M* is the adsorbent mass (g).

The ammonium concentration was measured after filtration (0.45 µm, Millex-GV, Millipore) by using the standard distillation method (APHA, 2005).

The adsorption kinetics was executed in triplicate with the initial NH4+ concentrations of 20, 40, and 80 mg L−1 at time intervals of 0.5–12 h. To elucidate the adsorption mechanism, the kinetic data were fit to pseudo-first-order, pseudo-second-order, and Elovich equations.

To determine how competing ions affect NH4+ adsorption, a similar set of experiments was conducted with a synthetic salt solution mimicking the effluent from an anaerobic membrane bioreactor (Grossman *et al.*, 2019). The solution composition was Ca2+ (155 mg L−1), K+ (290 mg L−1), Mg2+ (30 mg L−1), Na+ (390 mg L−1), PO43− (14 mg L−1), and SO42− (40 mg L−1).

The protocol for desorption experiments is described by Takaya *et al.* (2016). Briefly, hydrochars were first soaked in 40, 60, and 80 mg NH4+ L−1 solutions as described above. Next, the saturated hydrochars were centrifuged at 5000 rpm (TGL20M-II centrifuge, Kaida, China), gently washed with deionized distilled water to remove residual solution and re-soaked in ultrapure water or 2 M KCl solution at pH 5. Each desorption experiment was conducted in three 24 h cycles. After each cycle, the NH4+ contraction in the solution was measured by the distillation method, and the deposition was evaluated by the release ratio, which is given by

×100%, (3)

where *C*i and *Cn* refer to the initial and final (after *n* cycles of desorption) concentration of adsorbed NH4+, respectively.

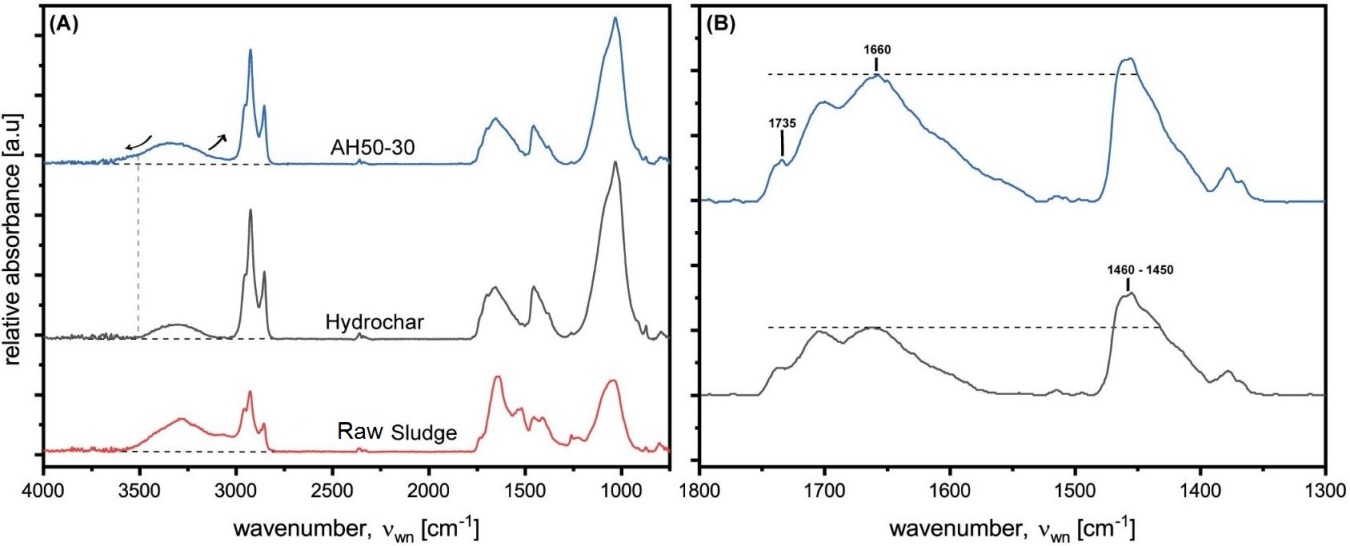
All experimental analyses were done in triplicate, and the results are presented as the mean and standard deviation.

1. **Results and discussion**

*Characterization of activated hydrochar*

The raw sludge, hydrochar, and Fenton-activated hydrochar (AH50-30) were characterized by using ATR-FTIR (**Fig. 1**; note that all AH have similar FTIR spectra; see **Fig. S1** in the supplementary information). HTC of hydrochar changes the FTIR spectrum with respect to that of the raw sludge: the broad peak in the range 2800–3600 cm−1, which is indicative of carboxylic acid and hydroxyl groups, and the bands in the range 1550–1650 cm−1, which are ascribed to the presence of amide motifs, decrease following HTC. In addition, the peak in the range 2800–3500 cm−1 blueshifts, indicating an increased presence of hydroxyl groups (Sun *et al.*, 2015; Wahab *et al.*, 2010). Furthermore, following HTC, the peak ratio in the hydrochar spectrum for the three typical CH, CH2, and CH3 bands at 2800–3000 cm−1 increases substantially compared with that of other peaks, which is attributed to an increase in hydrochar carbon content (Elaigwu and Greenway, 2016), whereas the bands of the carbonyl groups in the range 1700–1750 cm−1 become stronger. All of these changes are likely due to dehydration and decarboxylation during the HTC process (Mau *et al.*, 2016; Tasca *et al.*, 2019).

Although only minor differences generally appear between the FTIR spectra of AH50-30 and hydrochar, note that the peaks for carboxylic-acid derivatives in the range 1700–1750 cm−1 (Wahab *et al.*, 2010) and the C–O peak at 1030 cm−1 (Sun *et al.*, 2015) are stronger in the AH50-30 spectrum than in the hydrochar spectrum (**Fig 1B**). These changes suggest that the multitude of the different compounds found in the hydrochar in these regions is transformed into a set of single distinct groups in AH50-30. Furthermore, the bands for the carboxylic acid OH stretch and hydroxyl in the range of 2500–3800 cm−1 clearly broaden and extend into the CH region for AH50-30 compared with the hydrochar (as emphasized by the dashed lines in **Fig 1A**), which indicates newly created carboxylic acid motifs (Tasca *et al.*, 2019; Wahab *et al.*, 2010).



**Fig.1**. (a) ATR-FTIR spectra of raw sludge, hydrochar, and activated hydrochar [produced at 10 : 1 mole ratio H2O2/Fe2+, 50 mM at 30 min (AH50-30)]. (b) High-resolution ATR-FTIR spectra of hydrochar and of AH50-30. The dotted lines in the OH and CH region of the HC and AH50-30 spectra are visual guides. The spectra were baseline corrected to a parabolic function using a Savitzky–Golay filter to account for ATR distortion.

The changes in elemental composition brought by hydrochar oxidation under various activation conditions were measured by XPS. The main change in elemental composition is in the C/O ratio, which decreases from 5.01 in the hydrochar to C/O < 3.9 for all AHs because of the increased concentration of oxygen groups on the AH surface (**Table 1).** However, only a small decrease in the C/O ratio occurs upon increasing the activation time (50 mM H2O2, 5–30 min), which suggests that the activation time can be very short (several minutes) compared with over 2 h for most activation methods (**Table S**1). In addition, the decrease in C/O with increasing H2O2 concentration (25, 50, and 200 mM) indicates that activation can be accomplished by using a relatively small amount of reagents. The effects of hydrochar oxidation on the oxidation states of the carbon species were further analyzed by HR-XPS. Hydrochar carbon contains four functional groups: C–C/C–H, O–C=O, C=O/O–C–O, C–O, and C=O/O–C–O (see **Table 2**) (Li *et al.*, 2020; Luo *et al.*, 2017; Safari *et al.*, 2019). No new groups form after activation, but the relative abundance of each group changes significantly (**Tables 2**). The HR-XPS results for carbon show that, with increasing H2O2 concentration, the relative fraction of the oxygen-containing groups (i.e., O–C=O, C=O, and O–C–O) increases, whereas the concentration of the C–C/C=C/C–H groups decreases. Overall, XPS confirms that H2O2/Fe2+ activation increases the concentration of oxygen-containing groups in hydrochar.

**Table** 1. Elemental composition (in atomic percent) obtained by XPS of hydrochar and activated hydrochars (AHs).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | %C 1*s* | %O 1*s* | %N 1*s* | %Fe 2*p* | C/O |
| Hydrochar | 79.47 | 15.86 | 4.56 | 0.12 | 5.01 |
| AH25-30 | 75.70 | 19.64 | 3.84 | 0.83 | 3.86 |
| AH50-5 | 72.53 | 22.52 | 3.74 | 1.21 | 3.22 |
| AH50-10 | 70.90 | 24.42 | 2.95 | 1.74 | 2.90 |
| AH50-30 | 70.84 | 24.15 | 3.56 | 1.46 | 2.93 |
| AH200-30 | 69.24 | 26.02 | 2.82 | 1.92 | 2.66 |

We also analyzed how activation affects the hydrochar surface area and morphological properties. The results show that, upon activation, the BET specific surface area increases slightly from 2.06 m2 g−1 in the raw sludge to 3.82 m2 g−1 in the hydrochar and 5.18 m2 g−1 in AH50-30. Different surface morphologies detected by SEM (see **Fig. S**2) suggest that, following HTC and hydrochar activation, raw sludge differs from hydrochar, although not significantly, which is consistent with the results of previous studies (Huff and Lee, 2016).

**Table 2.** Results of HR-XPS of carbon and oxygen in raw sludge, hydrochar, and activated hydrochars [produced at a 10 : 1 mole ratio (H2O2/Fe2+)].

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | C 1*s* composition (%) | | | |
| C–C/C=C/C–H | C–O/C=O/O–C–O | C=O/O–C–O | O–C=O |
| 284.75 eVa | 286.46 eVa | 287.84 eVa | 288.71 eVa |
| Raw sludge | 42.73 | 27.79 | 16.14 | 13.35 |
| Hydrochar | 44.37 | 40.38 | 11.55 | 3.71 |
| AH25-30 | 42.62 | 19.55 | 17.24 | 20.61 |
| AH50-5 | 64.26 | 22.25 | 7.09 | 6.42 |
| AH50-10 | 41.23 | 31.09 | 20.39 | 7.29 |
| AH50-30 | 52.73 | 34.52 | 5.53 | 7.23 |
| AH200-30 | 34.54 | 30.35 | 19.33 | 15.79 |

a The carbon peaks were identified based on (He *et al.*, 2015; Luo *et al.*, 2017; Safari *et al.*, 2019).

* 1. *Effect of activation conditions on* NH4+ *adsorption*

We now discuss how H2O2 concentration, activation time, and H2O2/Fe2+ ratio affect the adsorption capacity of hydrochar. The adsorption capacity depends nonmonotonically on peroxide concentration (at a 10 : 1 ratio of H2O2/Fe2+, 30 min reaction time) and peaks at 50 mM H2O2 (**Table 2**). The lower adsorption at peroxide concentrations less than 50 mM is probably not strongly related to acidic groups on the AH, as seen in the HR-XPS results discussed above. The lower adsorption at 200 mM peroxide concentration might be due to the formation of Fe complexes between Fe ions and acidic groups on the AH, which would limit the degree of oxidation during the activation (Kang *et al.*, 2002) and occupy NH4+ adsorption sites during the adsorption step (Lee *et al.*, 2005). This hypothesis is supported by the much higher iron concentration in AH200-30 (0.046 mg mg−1) than in AH50-30 (0.022 m mg−1) that was measured following char digestion by ICP-OES (**Table S2**) and by XPS (**Table 1**). The activation reaction time (10 : 1 H2O2/Fe2+ and 25–50 mM H2O2) has no significant effect on the adsorption capacity of AHs (**Table S**3), as also evinced by the XPS results. Moreover, of the three H2O2/Fe2+ materials studied, the highest adsorption capacity is for H2O2/Fe2+ =10 : 1 (50 mM H2O2, 30 min reaction time) (**Table S3**). Based on these results, AH AH50-30 was used in the subsequent experiments.

**Table 2**. Hydrochar and AH (10 : 1 molar ratio H2O2/Fe2+) NH4+ adsorption capacity at different initial adsorption concentrations.

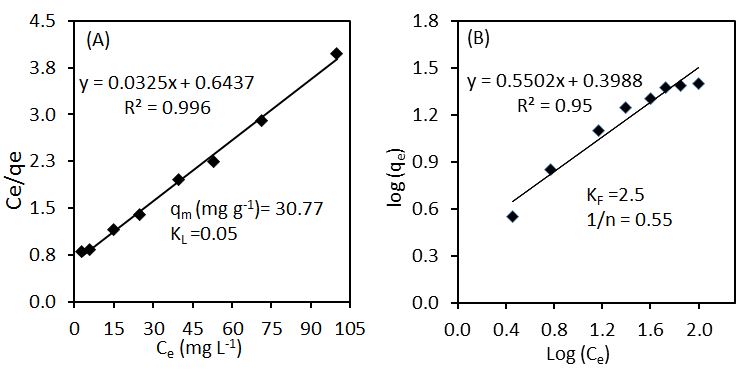
|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *C*0 (mg L−1) | Adsorption amount qe (mg g−1) | | | | |
| Hydrochar | Activated hydrochar | | | |
| at 25 mM | at 50 mM | at 100 mM | at 200 mM |
| 20 | 3.7 | 5.1 | 7.1 | 4.2 | 4.1 |
| 40 | 4.6 | 9.2 | 12.7 | 8.0 | 7.0 |
| 80 | 6.0 | 13.3 | 20.2 | 14.0 | 12.7 |
| 100 | 6.4 | 19.0 | 23.6 | 18.3 | 12.9 |
| The adsorption capacity of AH50-30 differs significantly from the others (*p* < 0.05); the standard deviations range from 0.2 to 2.0. | | | | | |

* 1. *Isotherm studies*

The experimental NH4+ adsorption data were fit to the two common Langmuir and Freundlich isotherms (**Text S1**). The Langmuir model (regression coefficient *R*2 = 0.996) fits the adsorption data better than does the Freundlich model (*R*2 = 0.950) (**Fig. 2**), as typically found for NH4+ adsorption due to the saturation of the available exchange sites on the AH50-30. The Langmuir model gives a maximum adsorption capacity qm = 30.77 mg mg−1, which is relatively large compared with the adsorption reported for many other materials, such as zeolites, biochars, and hydrochars (**Table S4**). The essential features of a Langmuir isotherm can be expressed in terms of adsorption based on a dimensionless separation factor *R*L, which is given by (Hall *et al.*, 1966; Zhang *et al.*, 2011)

(4)

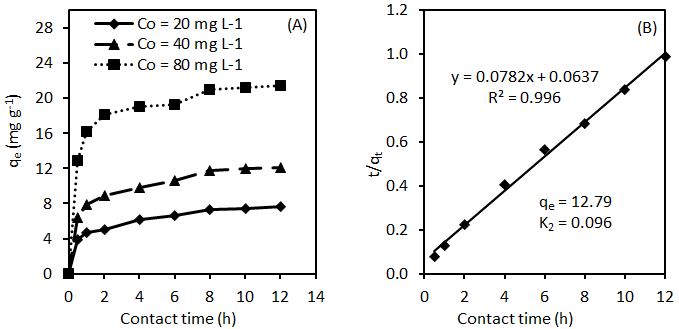
The separation factor *R*L indicates whether the isotherm favors adsorption (0 < RL < 1), does not favor adsorption (RL > 1), or predicts linear adsorption (*R*L = 1) or irreversible adsorption (RL ≈ 0). For a NH4+ concentration in the range 10–150 mg L−1, a calculation gives *R*L = 0.66–0.12 for AH50-30, which favors adsorption This promotion of adsorption increases with increasing NH4+ concentration (Cui *et al.*, 2016; Togue Kamga, 2019; Yusof *et al.*, 2010). The Freundlich model also fits well with the NH4+ adsorption (**Fig. 2B**), which underlines the heterogeneous nature of the exchange sites (Ma *et al.*, 2011), with 1/*n* = 0.55, indicating favorable adsorption (Yusof *et al.*, 2010).

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**Fig. 2**. Capacity of NH4+ adsorption onto AH (produced at 10 : 1 mole ratio H2O2/Fe2+, 50 mM at 30 min): (A) linear Langmuir isotherm and (B) linear Freundlich isotherm at *C*0: 0–150 mg L−1.

* 1. NH4+ *adsorption kinetics*

**Figure 3(A)** shows how, for three NH4+ concentrations, the contact time between AH and solution affects NH4+ adsorption onto AH50-30. NH4+ adsorption is high during the first 2 h because of the availability of active adsorption sites on the AH and the high NH4+-concentration gradient (Boopathy *et al.*, 2013). After 2 h, the adsorption rate decreases gradually and reaches equilibrium after approximately 8 h, probably because of the paucity of active site groups for adsorption and the lower concentration gradient (Yusof *et al.*, 2010). As shown in **Fig. 3(A)**, the adsorption capacity as a function of contact time is similar for the three NH4+ concentrations, but the time required to reach equilibrium increases with initial ammonium concentration.

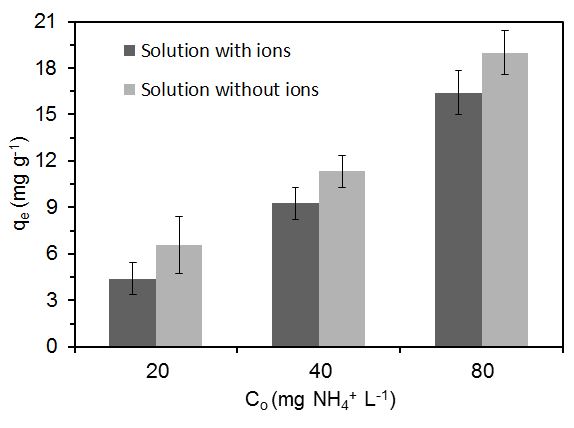


**Fig. 3.** Capacity of NH4+ adsorption onto AH (produced at 10 : 1 mole ratio H2O2/Fe2+, 50 mM at 30 min). (A) Amount of NH4+ adsorbed as a function of contact time, and (B) pseudo-second-order kinetics (*C*0: 40 mg L−1) at *t* = 12 h.

The kinetic analysis can help determine the adsorption reaction (D. Xu *et al.*, 2019). Various adsorption kinetics models (**Text S2**) were used to fit the adsorption kinetics data: the pseudo-first-order model (**Fig. S4A**), pseudo-second-order model (**Fig. 3B**), and the Elovich equation (**Fig. S4B**). The parameters of the kinetics models were calculated from the slopes and intercepts of the respective plots (Yusof *et al.*, 2010), following which the best-fit model was chosen based on the regression coefficients *R*2. As seen in **Figs. 3** and **S4**, the results of the regression analysis with the pseudo-second-order model are more consistent with the experimental NH4+ adsorption data (*R*2 = 0.996) than are the results of the pseudo-first-order model (*R*2 = 0.951) and of the Elovich model (*R*2 = 0.988). Moreover, qe = 12.79 mg g−1 from the pseudo-second-order model is consistent with the experimentally determined qe (12.13 mg g−1). The fit of the pseudo-second-order model suggests that the adsorption rate of NH4+ onto AH is determined by the chemisorption process through electron sharing between the functional groups on the AH50-30 and NH4+ (Boopathy *et al.*, 2013; He *et al.*, 2016; Huang *et al.*, 2015; Vu *et al.*, 2017; Zhu *et al.*, 2012).

* 1. *Effect of competing ions*

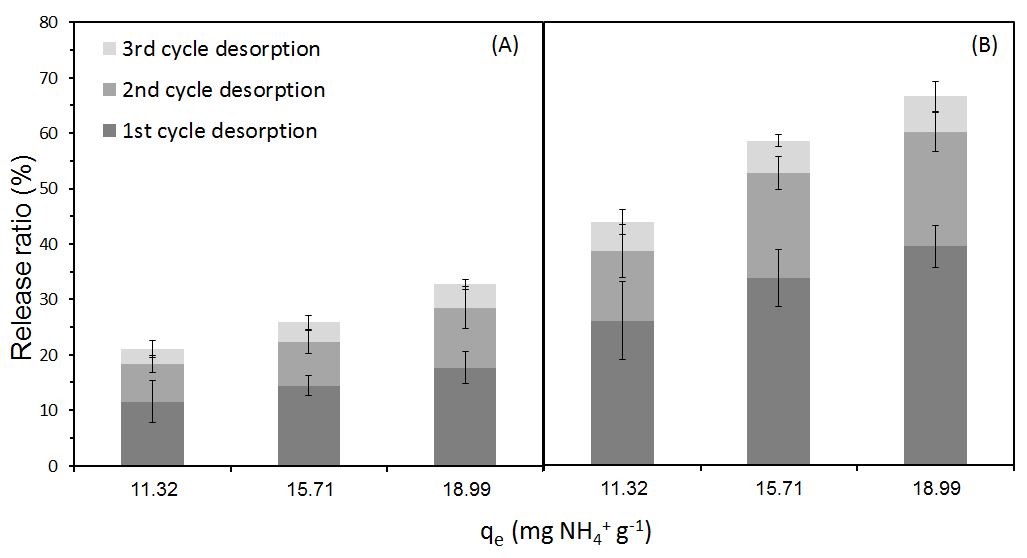
The adsorption capacity of AH50-30 using a synthetic solution that mimics effluent from an anaerobic membrane bioreactor was studied to evaluate how competing ions affect the capacity to adsorb NH4+. The presence of other ions in the solution (Ca2+, Mg2+, K+, Na+, PO43−, and SO42−) may compete against ammonium ions for adsorption onto the functional group, which can decrease NH4+ adsorption (Guaya *et al.*, 2015; He *et al.*, 2016; Huang *et al.*, 2010). **Figure 4** shows that, compared with NH4+ adsorption in deionized distilled water, the capacity of AH50-30 to adsorb NH4+ in the presence of competing ions decreases from 14% ± 4% to 33% ± 3% depending on the initial NH4+ concentration, as found in previous work (Guaya *et al.*, 2015; He *et al.*, 2016; Liu *et al.*, 2010). However, the competing ions only weakly affect NH4+ adsorption, possibly because of the polar groups at the adsorbent surface (Liu *et al.*, 2010; Wahab *et al.*, 2010).

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**Fig. 4**. Capacity qe of NH4+ adsorption onto AH (produced at 10 : 1 mole ratio H2O2/Fe2+, 50 mM at 30 min) in pure water (solution without ions) and in the presence of competing for ions (solution with ions) for three initial concentrations of ammonium. The experiment conditions were 0.2 g AH /100 mL, and a contact time of 12 h.

* 1. *Desorption studies*

**Figure 5** presents the NH4+ desorption for different initial adsorbed concentrations (with qe = 11.32, 15.71, and 18.99 mg NH4+ g−1) following three continuous desorption steps with ultrapure water and 2 M KCl. After the first desorption step, the desorption of NH4+ reaches 17% ± 3% and 40% ± 4% NH4+ with respect to the adsorbed concentration in ultrapure water and 2 M KCl, respectively. Desorption during the second cycle is much less than during the first cycle (up to 11% ± 4% with water and 21% ± 4% with 2 M KCl) and is almost negligible during the third cycle (less than 4% with water and 6% with 2 M KCl). Overall, NH4+ deposition reaches 33% ± 5% and 67% ± 2% with ultrapure water and 2 M KCl, respectively. When the adsorption mechanism involves ion exchange, less NH4+ is released in ultrapure water than in salt solution. However, the incomplete exchange between NH4+ and K+ [as was also reported by others (Ma *et al.*, 2011; Mia *et al.*, 2017; Takaya *et al.*, 2016)] might be due to a low exchange rate or to strong interactions between the NH4+ and AH. In any event, the desorption results suggest that the saturated AH can be used as a slow-release fertilizer, which is currently being investigated.

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**Fig. 5**. Desorption (release ratio) of adsorbed NH4+ in (A) ultrapure water and (B) 2 M KCl at pH 5 with 0.2 g AH (produced at 10 : 1 mole ratio H2O2/Fe2+, 50 mM at 30 min)/100 mL solution. Each cycle is 24 h at room temperature.

1. **Conclusions**

Hydrochar was activated by using the facial Fenton reaction to modify the surface chemistry and thereby enhance its capacity to adsorb NH4+ from aqueous-phase solution. The AH50-30 sample (qe: 23.6 mg g−1) provides optimal activation for NH4+ adsorption. The Langmuir isotherm fits the experimental NH4+ adsorption data and the pseudo-second-order model fits the adsorption kinetics, which suggests that NH4+ is adsorbed via chemisorption. The presence of competitive ions decreases NH4+ adsorption by up to 33% ± 3%. The results of the NH4+ desorption experiments show that NH4+ desorbs by up to 33% ± 5% and 67% ± 2% in ultrapure water and in 2 M KCl, respectively. These findings suggest that AH produced by the facile Fenton-reagent path is a promising low-cost adsorbent for removing NH4+ from the effluent of wastewater treatment plants.

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