

# SIMULTANEOUS ADSORPTION OF AMMONIUM AND PHOSPHATE FROM CONTAMINATED WATER SOLUTIONS BY A NUT RESIDUE BIOCHAR

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## Abstract

Excessive amounts of phosphorous and ammonium discharged in wastewaters threaten the biodiversity of aqueous ecosystem and safety for living organisms. Adsorption is an efficient, environmentally friendly and economically feasible process for the removal of these pollutants. Present study aimed to investigate the potential of a nut residue biochar, physically activated by steam, for simultaneous adsorption of phosphate and ammonium from contaminated water solutions. The performance of biochar was tested as a function of initial ion concentrations, adsorbent dose, contact time and pH. The mechanism of adsorption was examined by carrying out structural and chemical analyses of the material before and after ions adsorption, as well as by applying two isotherm models, simulating the experimental data.

## Experimental

### Preparation and characterization of adsorbent material

The raw materials was almond kernels. These was ground to a particle size < 500 μm. For biochar production, a stainless steel fixed bed reactor system was used. Each sample was devolatilized up to 700°C under nitrogen and activated by steam for 1 h. Characterization of materials was conducted according to European standards CEN/TC335. Structural characterization was carried out by applying the BET method. The chemical functional groups of biochar samples before and after ions adsorption were identified by a Fourier Transform Infrared Spectrophotometer (FTIR).

### Mono-ion and multi-ion kinetic and adsorption experiments

The reagents used were NH<sub>4</sub>OH and KH<sub>2</sub>PO<sub>4</sub>. A series of concentrations 10, 50, 100, 200, 300 mg/L were prepared. The initial pH of the solutions was adjusted to pH=7. The equilibrium contact time was determined from kinetic tests at various time intervals. The filtrates were analyzed for residual NH<sub>4</sub><sup>+</sup> or PO<sub>4</sub><sup>3-</sup> following the methods 3642-SC nesslerization and 3655-5C vanadomolybdo phosphoric of colorimeter Smart 3 by LaMotte.

### Modelling of adsorption data

For adsorption data modeling, the Langmuir  $\frac{C_e}{q_e} = \frac{1}{bC_e} + \frac{C_e}{Q}$  and Freundlich  $\log q_e = \log k + \frac{1}{n} \log C_e$  isotherm models were adopted.

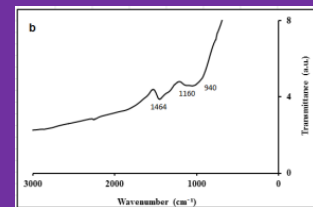
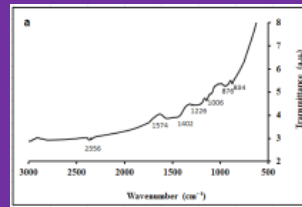
The adsorption efficiency was determined by equation:  $\% \text{Ion removal} = \frac{C_0 - C_e}{C_0} \times 100$

The amount of each ion adsorbed per adsorbent mass unit (uptake) q (mg/g) was calculated by equation:  $q = \frac{(C_0 - C)V}{m}$

## Results

Table 1 Chemical and structural analyses of raw materials and biochar (% dry)

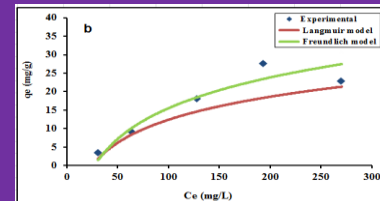
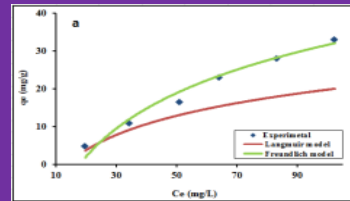
Sample	Volatile matter	Fixed carbon	Ash	C	H	N	O	S	Specific surface area (m <sup>2</sup> /g)	Micropore volumex10 <sup>2</sup> (cm <sup>3</sup> /g)
Raw (AK)	72.0	27.5	0.5	54.0	6.0	0.5	39.0	-	2.5	6.6
Biochar (AKB)	-	97.4	2.6	66.2	1.1	-	30.1	-	660	33.0



FTIR spectra of (a) biochar before adsorption and (b) after adsorption

Table 2 Removal efficiency of ions during mono-ion and multi-ion adsorption

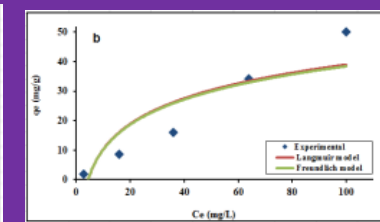
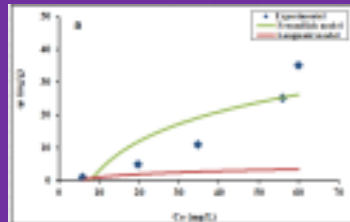
Initial ion concentration (mg/L)	Mono-ion adsorption removal efficiency (%)				Multi-ion adsorption removal efficiency (%)			
	Adsorbent dose 4 g/L		Adsorbent dose 2 g/L		Adsorbent dose 4 g/L		Adsorbent dose 2 g/L	
	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>	NH <sub>4</sub> <sup>+</sup>	PO <sub>4</sub> <sup>3-</sup>
10	26.0	10.0	34.6	9.5	27.1	70.0	36.1	65.0
50	49.2	28.0	64.0	26.5	49.6	68.8	65.0	64.6
100	59.6	36.0	79.5	34.1	55.4	68.0	74.1	64.0
200	59.0	36.0	78.4	34.0	64.1	67.6	85.1	63.8
300	56.3	37.0	74.0	35.2	74.4	66.7	97.4	63.0



Mono-ion adsorption isotherms of NH<sub>4</sub><sup>+</sup> (a) and PO<sub>4</sub><sup>3-</sup> (b) at adsorbent dose 4 g/L

Table 3 Isotherm model parameters of ions for multi-ion adsorption

	Adsorbent dose 4 g/L					
	Langmuir model			Freundlich model		
	Q (m/g)	b (L/mg)	R <sup>2</sup>	k (L/g)	1/n	R <sup>2</sup>
NH <sub>4</sub> <sup>+</sup>	12.392	0.012	0.915	0.053	1.540	0.992
PO <sub>4</sub> <sup>3-</sup>	588.235	0.0009	0.118	0.597	0.955	0.997
	Adsorbent dose 2 g/L					
	Langmuir model			Freundlich model		
	Q (m/g)	b (L/mg)	R <sup>2</sup>	k (L/g)	1/n	R <sup>2</sup>
NH <sub>4</sub> <sup>+</sup>	16.556	0.037	0.805	0.199	1.857	0.837
PO <sub>4</sub> <sup>3-</sup>	2000	0.0004	0.04	0.943	0.972	0.997



Multi-ion adsorption isotherms of NH<sub>4</sub><sup>+</sup> (a) and PO<sub>4</sub><sup>3-</sup> (b) at adsorbent dose 4 g/L

## Conclusions

The results showed that the specific surface area of the adsorbent increased about 260 fold after activation by steam. Adsorption was fast within 30 min, while reached equilibrium after 12 h. The maximum uptake of phosphate was 70% at phosphate concentration 10 mg/L and adsorbent dose 4 g/L, whereas the maximum uptake of ammonium was 74.4% at ammonium concentration 300 mg/L and adsorbent dose 4 g/L. The maximum adsorption capacity of the material increased with a decrease in adsorbent dose to 2 g/L and reached a value of 94.5 mg/g for phosphate and 108 mg/g for ammonium. The experimental data were best fitted by the Freundlich model. Potential mechanisms of adsorption were surface complexation, electron coordination, or electrostatic attraction.