

### Electronic supporting information

Phosphorus adsorption by a modified polyampholyte-diatomaceous earth material containing imidazole and carboxylic acid moieties: batch and dynamic studies. †

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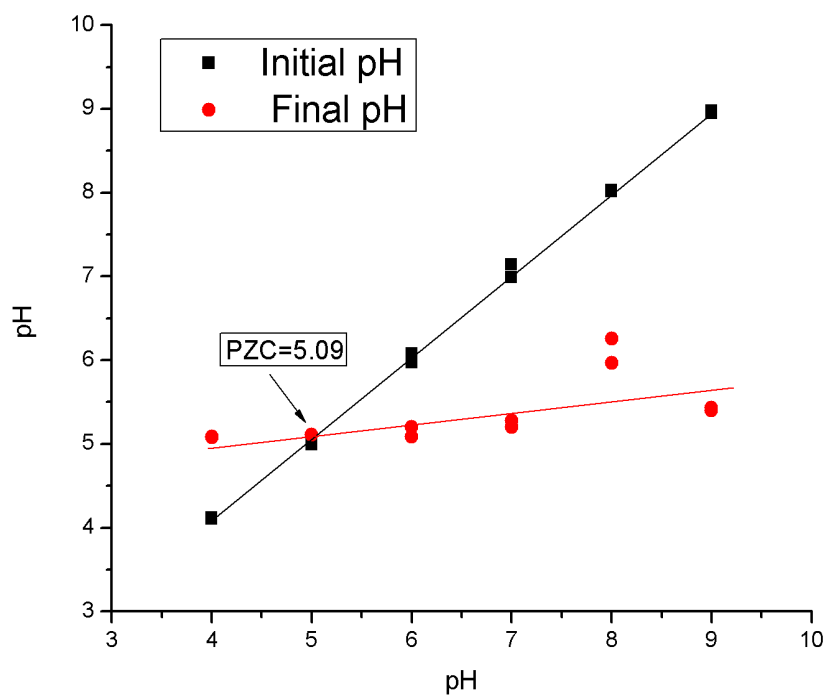
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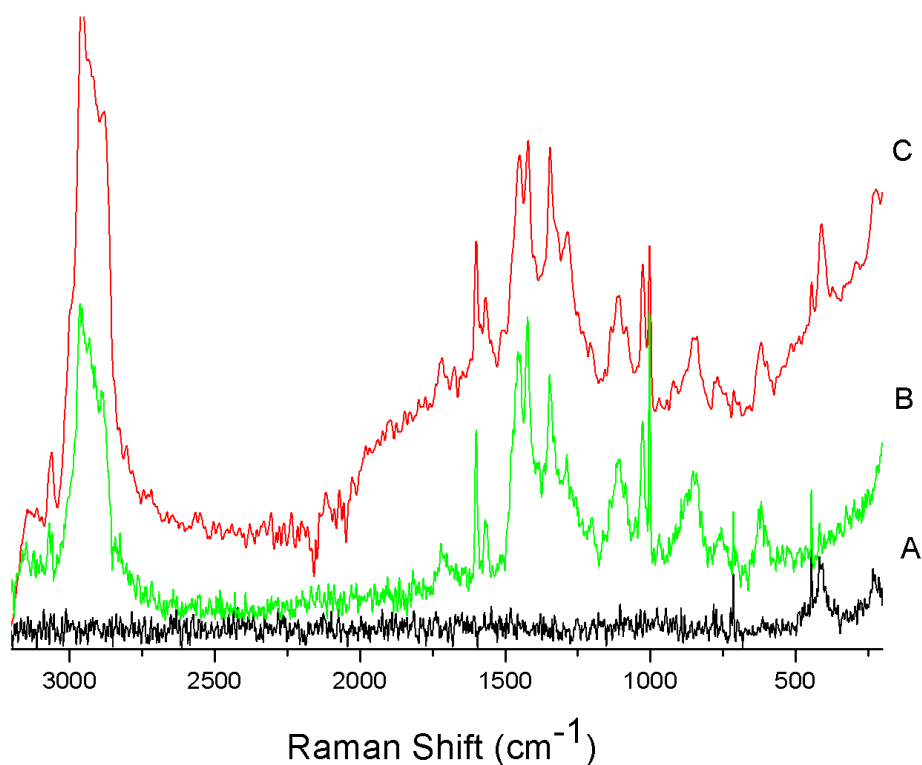


**ESI 1.** Final pH vs initial pH of the polyampholyte – DE mixture.

**ESI 2.** FTIR assignments for the FT-IR spectra depicted in Figure 2

	Wavenumber (cm <sup>-1</sup> )				
	A	B	C	D	E
$\nu_{\text{CH}}$		1275,1370	1275,1370	1275,1343, 1400	1275,1343, 1400
<b>C-O-C</b>		1077	1077	1077	1077
$\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$		628, 721, 838, 921, 1450,1560,1638	628, 721, 838, 921, 1450,1560,1638	628, 721, 838, 921, 1450,1560,1638	628, 721, 838, 921, 1450,1560,1638
$\nu_{\text{Si-O-Si}}$ (asymmetric stretching in plane)	1070				
$\nu_{\text{Si-OH}}$	791				
<b>Si-O</b> deformation / <b>Al-O</b> stretching	615				
$\nu_{\text{C=O}}$		1715	1715	1715	1715
-CO2-		1560	1715	1715	1715

**A:** DE, **B:** polyampholyte, **C:** polyampholyte - DE mixture, **D:** polyampholyte - DE mixture after exposure to a P solution at pH 5 and **E:** polyampholyte - DE mixture after exposure to a P solution at pH 7

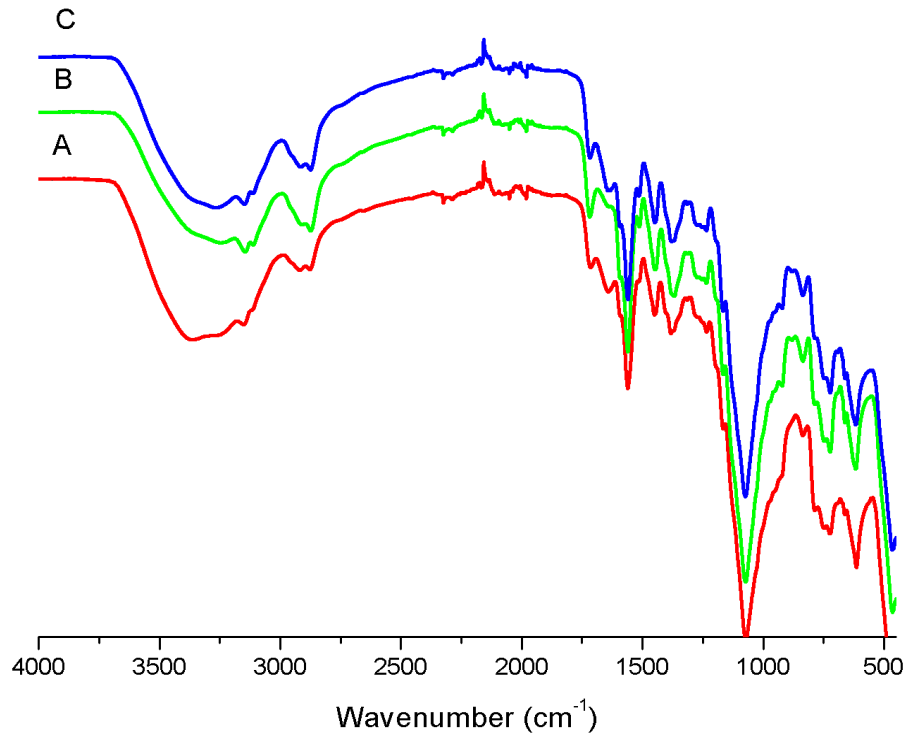


**ESI 3.** FT - Raman spectra of **A:** DE, **B:** polyampholyte, **C:** polyampholyte - DE mixture.

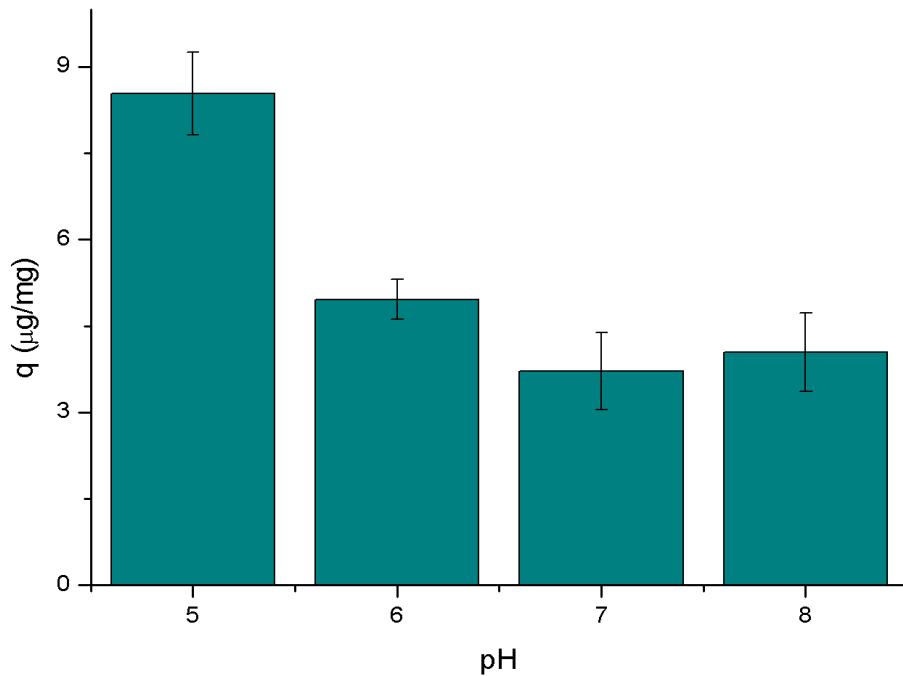
**ESI 4.** Raman assignments for the Raman spectra depicted in Figure 3

	Raman Shift (cm <sup>-1</sup> )		
	A	B	C
$\nu_{\text{CH}}$		2957 - 2887	2957 - 2887
<b>C-O-C</b>		1027	1027
$\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$		1109 - 1080	1109 - 1080
Amorphous Si-O bonds	406		406
$\nu_{\text{C=O}}$		1604	1604
$\nu_{\text{C-C}}$		1003- 851- 753 -631	1003- 851- 753 -631
$\nu_{\text{(C-N)}}$		1109	1109
Hetero ring		1571	1571
$\text{CH}_2$		1428 - 1456	1428 - 1456

**A:** DE **B:** Polyampholyte **C:** Polyampholyte – DE.  $\nu$ , stretching



**ESI 5** FT-IR spectra of A: polyampholyte - DE mixture exposed at 25 °C, B: polyampholyte - DE mixture exposed at 37 °C and C: polyampholyte - DE mixture exposed at 40 °C.



**ESI 6.** Adsorption capacity vs pH

## Isotherm adsorption models

Langmuir and Freundlich models have been widely applied to the adjustment of biosorption equilibrium data. The former assumes that a sorbate interacts homogeneously, at homogeneous sorption sites, until a monolayer is formed in the sorbent surface. On the other hand, Freundlich model have proved to describe better the adjustment of sorbents with heterogeneous adsorption sites and dissimilar interactions.<sup>31</sup> Langmuir and Freundlich adsorption isotherms can be expressed using equations (1) and (2) respectively.<sup>32</sup>

$$q_{eq} = \frac{q_m \cdot K_a \cdot C_{eq}}{1 + K_a \cdot C_{eq}} \quad (1)$$

$$q_{eq} = k \cdot C_{eq}^n \quad (2)$$

where  $K_a$  is the adsorption equilibrium constant (L/mg),  $q_m$  is the maximum adsorption capacity (mg/g) and  $k$  and  $n$  are arbitrary parameters. The dimension of  $k$  depends on the value of  $n$ .

The non-linear Sips isotherm equation predicts a monolayer sorption capacity characteristic of the Langmuir isotherm at high sorbate concentrations.<sup>33</sup> On the other hand, at low sorbate concentrations it exhibits a departure from Henry's law such as Freundlich isotherm. It can be represented as:

$$q_{eq} = \frac{q_m (a_s C)^{n_s}}{1 + (a_s C)^{n_s}}$$

If the value of  $n_s$  is equal to 1 then this expression turns to be a Langmuir equation, where  $a_s$  is the adsorption equilibrium constant. Alternatively, as either  $C$  or  $a_s$  approaches 0, this isotherm reduces to the Freundlich isotherm.

The Redlich-Peterson isotherm (R-P) incorporates features of both the Langmuir and Freundlich equations: at low concentrations the R-P isotherm approximates to Henry's law and at high concentrations its behaviour approaches that of the Freundlich isotherm.<sup>33</sup>

$$q_e = \frac{K_r C}{1 + a_R C^{n_R}}$$

When the value of  $n_R$  is equal to 1, the above equation is reduced to the Langmuir Model with their heterogeneity parameters ( $n_s$  and  $n_{rp}$ ) close to a value of 1, while it reduced to a Freundlich isotherm in case the value of  $a_R C^{n_R}$  is much bigger than 1. The ratio of  $K_R/a_R$  indicates the adsorption capacity.

## Dynamic adsorption model

## Thomas model

The Thomas model is another one frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming the second-order reversible reaction kinetics and the Langmuir isotherm. Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small.<sup>34</sup> The Thomas model is given by Equation 3

$$\frac{C_t}{C_0} = \frac{1}{e^{\left(\frac{k_{Th}}{Q} \cdot (q_0 \cdot m) - (C_0 \cdot Q \cdot t)\right)}} \quad (3)$$

where  $k_{Th}$  is the Thomas rate constant,  $m$  is the mass of adsorbent in the column,  $Q$  is the flow rate,  $q_0$  is the adsorption capacity of the column.