New amino groups functionalized porous carbon for strong chelation ability towards toxic heavy metals

Zakaria ANFAR\textsuperscript{1,2,3,*}, Abdallah AMEDLOUS\textsuperscript{4}, Mohammed MAJDOUB\textsuperscript{4}, Abdella AIT El FAKIR\textsuperscript{1,2}, Mohamed ZBAIR\textsuperscript{5}, Hassan Ait AHSAIN\textsuperscript{6,7}, Amane JADA\textsuperscript{2,3,*}, Noureddine El ALEM\textsuperscript{1}

\textsuperscript{1}Laboratory of Materials & Environment. Ibn Zohr University, Agadir, 80000, Morocco.
\textsuperscript{2}Institute of Materials Science of Mulhouse. Haute Alsace University, Mulhouse, 68100, France.
\textsuperscript{3}Strasbourg University, Strasbourg, 67081, France.
\textsuperscript{4}Laboratory of Materials, Catalysis & Valorization of Natural Resources. Hassan II University, Casablanca, 20650, Morocco.
\textsuperscript{5}Laboratory of Catalysis & Materials Corrosion. Chouaib Doukkali University, El Jadida, 24000, Morocco.
\textsuperscript{6}Chemical and biochemical sciences, Mohamed VI Polytechnic University, Lot 660-Hay Moulay Rachid, Benguerir, Morocco.
\textsuperscript{7}Laboratoire de Chimie Appliquée des Matériaux, Centre des Sciences des Matériaux, Faculty of Sciences, Mohammed V University in Rabat, Morocco.

*Corresponding author: zakaria.anfar@uha.fr and amane.jada@uha.fr
1. **Chemicals Reagents**

The digestate was collected after Co-anaerobic digestion of agri-food organic wastes, and washed with tap water and distilled water. Then, the washed sample was oven dried at 100 °C for 24h. Porous carbon (PC) was prepared using the activated digestate with H$_2$SO$_4$ (pH =2) and pyrolyzed under an N$_2$ atmosphere (200 cm$^3$/min) at 350°C for 3 hours. Ethylenediamine, Alginate, NaCl, KCl, CaCl$_2$, MgCl$_2$ and H$_2$SO$_4$ were acquired from Sigma-Aldrich. Lead(II) nitrate (Pb(NO$_3$)$_2$, 99.999%) and copper(II) chloride (CuCl$_2$, ≥ 99.995%) were purchased from Sigma-Aldrich. pH values of the solutions were controlled with HCl (Merck Millipore) and NaOH (Merck Millipore) solutions. All chemicals were used as received and all solutions were prepared with distilled water.

2. **Regeneration and mass recovery of adsorbent**

The renewability of adsorbent is a crucial factor in practical application. Therefore, five cycles of adsorption-regeneration experiments were carried by using HCl (0.1N). The mass recovery of adsorbent was employed to evaluate the renewability and durability of PC-ED/1.5 and F-PC-ED/1.5. However, the mass recovery of PC-ED/1.5 and F-PC-ED/1.5 was calculated by the following equation:

$$\text{Mass recovery (\%)} = \frac{m_{e, \text{regenerated}}}{m_{e, \text{fresh}}} \times 100\%$$

Where $m_{e, \text{regenerated}}$ and $m_{e, \text{fresh}}$ refer to the mass amounts of recoverable and fresh adsorbents, respectively.

3. **Characterization techniques**

The in situ electrostatic behavior of different systems were assessed by evaluating the solid surface potential through the use of Müteck PCD 02 apparatus. The Dynamic Light Scattering (DLS) was used to measure the adsorbent particle size in aqueous dispersed medium by using Coulter Model N4S. Further, Transmission Electron Microscopy (TEM) type Philips CM 200, 20–200 kV was used in the present work. In addition, the adsorbents morphologies were analyzed using scanning electron microscopy (SEM, JEOL, JSM -IT200). RAMAN
Spectroscopy type Horiba model Labram BX40 with CCD detector operating at laser line of 532 nm was used to determine the D and G bands. X-ray photoelectrons spectroscopy (XPS) was carried out by using XPS VG SCIENTA, Model SES-2002 and Thermo Fisher Scientific ESCALAB 250Xi. The surface area (SBET) was determined by the nitrogen adsorption and desorption isotherm were measured using an AUTOSORB-1. The Fourier Transform Infrared spectra were obtained in the mid infrared region (400-4000 cm\(^{-1}\)) using a Shimadzu 4800S. X-Ray diffraction patterns were collected on a PANalytical MPD X'Pert Pro diffractometer operating with Cu Kα radiation (Kα=0.15418 nm).

4. Optimization of Cu(II) and Pb(II) adsorption onto PC-ED/1.5

In the present work, the optimization of Cu(II) and Pb(II) adsorption onto PC-ED/1.5 was investigated using the response surface methodology (RSM), which allows the establishment of relationships between independent variables and their responses using a polynomial equation (Eq. (1))\(^5,6\). Firstly, the ranges of variables were obtained from preliminary screening experiments of kinetics and isotherm studies at pH 6 and 25°C (Table S2). Then, Central Composite Design (CCD) was chosen to investigate the linear, quadratic and interaction effects of three independent variables (Table S3). The total number of experiments (N) can be calculated according to Eq. (2).

\[
Y = b_0 + \sum_{i=1}^{n} b_iX_i + \sum_{i=1}^{n} b_i^2X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij}X_iX_j
\]

Eq. (1): Where, \(Y\) is the removal efficiency of Cu(II) or Pb(II), \(x_i\) and \(x_j\) are coded values of the factors (i and j range from 1 to k), \(b_0\) is the intercept coefficient of model, \(b_i, b_{ij}\), and \(b_{ij}\) are interaction coefficients of linear, quadratic, and the second-order terms, respectively. In Eq (1) \(n\) is the number of independent parameters (\(n=3\) in this study), \(k\) is expressed as the number of parameters. \(C_o (=6)\) is the number of central points.

Based on statistical results, the ANOVA of models have p-values<0.5 indicating their significant (Table S5)\(^7\). In addition, \(R^2\) values confirms the significance of the model and show good consistency between observed and predicted values (Table S5)\(^8\). Also, Table S5 shows that 9 out of the 9 model terms were significant for Cu(II) and Pb(II) adsorption onto PC-ED/1.5 include: A, B, and C square terms of A, B, and C and interaction terms of all factors. Based on these results, the quadratic model equations describing the relationship between the
removal of Cu(II) and Pb(II) adsorption onto PC-ED/1.5 and the experimental variables was given below (Eqs. 3 and 4) :

Eq. (3) : \% Removal of Cu(II) onto PC-ED/1.5 = 85.11 – 8.40A + 4.56B + 3.73C + 0.27A^2 – 1.59B^2 + 1.31C^2 – 0.44AB + 0.34AC – 1.29BC

Eq. (4) : \% Removal of Pb(II) onto PC-ED/1.5 = 89.05 – 4.91A + 2.14B + 0.67C + 0.84A^2 + 0.63B^2 + 0.74C^2 + 1.41AB + 1.59AC – 0.69BC

The optimum experimental variables suggested by the RSM for optimum removal of Cu(II) and Pb(II) adsorption onto PC-ED/1.5 were presented in Table S6. RSM in combination with CCD matrix allow the determination of these optimums, and the obtention of the 3D surface plots to illustrate the effect of processing parameters (Figure S7). To verify the precision of optimum removal, experiments using the above-mentioned values were conducted. From the experiment (Table SS), the values of Cu(II) and Pb(II) adsorption are closed to the predicted values. The results show that the proposed model used in this study is suitable and usable to describe the aqueous adsorption of Cu(II) and Pb(II) adsorption onto PC-ED/1.5.
Table S1. Mathematical models used in this work to fit the data.

| Equations | Utility | Description | Ref. |
|------------|---------|-------------|------|
| $Q_{e,t} = \frac{(C_0 - C_{e,t}) \times V}{m}$ | adsorption capacity | $C_0$ (mg/L) and $C_{e,t}$ (mg/L) are the initial and equilibrium concentrations, respectively. $m$ (g) is the weight of adsorbent and $V$ (L) is the volume of Cu (II) or Pb (II) solution. | 9 |
| $R(\%) = \left( \frac{C_0 - C_{e,t}}{C_0} \right) \times 100$ | Removal efficiency | | 10 |
| $Q_t = Q_{cal}(1 - \exp^{K1t})$ | Pseudo-first-order | $Q_e$ and $Q_t$ are the adsorbed Cu (II) or Pb (II) amounts at equilibrium and at times $t$, respectively. $K_1$: the rate constant. | 11 |
| $Q_t = \frac{(K_2Q_{cal}^2)}{(1 + K_2Q_{cal}^t)}$ | Pseudo-second-order | $K_2$: rate constant | 12 |
| $Q_e = \frac{Q_mK LC_e}{1 + K_LC_e}$ | Langmuir isotherm | $K_L$: direct measure of the intensity of the adsorption process; $Q_m$: maximum adsorption capacity. | 13 |
| $Q_e = \frac{1}{K_fC_e^n}$ | Freundlich isotherm | $K_F$: adsorption capacity; $n$: intensity of adsorption; $1/n = 0$: irreversible; $1/n > 1$: unfavorable. $0 < 1/n < 1$: favorable. | 14 |
| $\ln Q_e = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$ | Van’t Hoff equation | where $R$ is the universal gas constant ($8.3145$ J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature (K), | 15 |
Table S2. Characteristic thermodynamic parameters.

| T°C | Δ\(\mathcal{G}\) (kJ mol\(^{-1}\)) | Δ\(\mathcal{H}\) (kJ mol\(^{-1}\)) | Δ\(S\) (J K\(^{-1}\) mol\(^{-1}\)) |
|-----|-------------------------------|-----------------|-----------------|
| 25  | -0.46                         |                 |                 |
| 35  | -1.11                         |                 | 64              |
| 45  | -1.76                         |                 | 64.74           |

Adsorption of Pb(II) onto PC-ED/1.5

| T°C | Δ\(\mathcal{G}\) (kJ mol\(^{-1}\)) | Δ\(\mathcal{H}\) (kJ mol\(^{-1}\)) | Δ\(S\) (J K\(^{-1}\) mol\(^{-1}\)) |
|-----|-------------------------------|-----------------|-----------------|
| 25  | -0.91                         |                 |                 |
| 35  | -1.59                         |                 |                 |
| 45  | -2.27                         | 19.31           | 67.87           |
| 35  | -2.88                         |                 |                 |
| 45  | -4.50                         |                 |                 |
Table S3. Experimental variables, their actual and coded values in CCD design

| Factor                                      | Experimental Field |
|---------------------------------------------|--------------------|
| Concentration of Cu(II) or Pb(II) (mg/L): A | -α  -1  0  +1  +α |
| Adsorbent dose of PC-ED/1.5 (mg): B         | 6.6  10  15  20  23.4 |
| Time of adsorption reaction: C              | 66.4  80  100  120  133.6 |
Table S4. CCD experimental design and obtained values of responses

| Run | A   | B   | C   | PC-ED/1.5 R, % - Cu | PC-ED/1.5 R, % - Pb |
|-----|-----|-----|-----|---------------------|---------------------|
| 1   | 10  | 20  | 80  | 84                  | 96.7                |
| 2   | 20  | 20  | 80  | 70.4                | 83.8                |
| 3   | 10  | 30  | 80  | 94.9                | 98.8                |
| 4   | 20  | 30  | 80  | 75.7                | 87.9                |
| 5   | 10  | 20  | 120 | 92.2                | 97.3                |
| 6   | 20  | 20  | 120 | 76.1                | 87.1                |
| 7   | 10  | 30  | 120 | 94.1                | 93.0                |
| 8   | 20  | 30  | 120 | 80.1                | 92.1                |
| 9   | 6.6 | 25  | 100 | 99.9                | 99.8                |
| 10  | 23.4| 25  | 100 | 69.1                | 80.7                |
| 11  | 15  | 16.6| 100 | 67.3                | 83                  |
| 12  | 15  | 33.4| 100 | 91.2                | 96.3                |
| 13  | 15  | 25  | 66.4| 70.1                | 87.9                |
| 14  | 15  | 25  | 133.6| 90                  | 92                  |
| 15  | 15  | 25  | 100 | 85                  | 89                  |
| 16  | 15  | 25  | 100 | 85.3                | 89.1                |
| 17  | 15  | 25  | 100 | 85.1                | 89.2                |
| 18  | 15  | 25  | 100 | 85.2                | 89.3                |
| 19  | 15  | 25  | 100 | 85.3                | 89.1                |
| 20  | 15  | 25  | 100 | 85.2                | 89                  |
Table S5. Significance of regression coefficients.

|                  | Adsorption of Cu (II) onto PC-ED/1.5 |          | Adsorption of Pb (II) onto PC-ED/1.5 |          |
|------------------|--------------------------------------|----------|--------------------------------------|----------|
|                  | Model coefficients | P-value  | Model coefficients | P-value  |
| b₀               | 85.11                  | <0.0001  | b₀                    | 89.05    | <0.0001 |
| b₁               | −8.40                  | <0.0001  | b₁                    | −4.91    | <0.0001 |
| b₂               | 4.56                   | <0.0001  | b₂                    | 2.14     | <0.0001 |
| b₃               | 3.73                   | <0.0001  | b₃                    | 0.67     | <0.0001 |
| b₁₋₁             | 0.27                   | 0.00033  | b₁₋₁                 | 0.84     | <0.0001 |
| b₂₋₂             | −1.59                  | <0.0001  | b₂₋₂                 | 0.63     | <0.0001 |
| b₃₋₃             | 1.31                   | <0.0001  | b₃₋₃                 | 0.74     | <0.0001 |
| b₁₋₂             | −0.44                  | 0.00013  | b₁₋₂                 | 1.41     | <0.0001 |
| b₁₋₃             | 0.34                   | 0.00044  | b₁₋₃                 | 1.59     | <0.0001 |
| b₂₋₃             | −1.29                  | <0.0001  | b₂₋₃                 | −0.69    | <0.0001 |
| R²               | 0.915                  |          | R²                    | 0.889    |          |
Table S6. Optimum values of the factors studied for optimal aqueous adsorption of Cu and Pb adsorption onto PC-ED/1.5.

| Adsorption of Cu onto PC-ED/1.5 | Adsorption of Pb onto PC-ED/1.5 |
|--------------------------------|--------------------------------|
| Optimum values | % found by experience | % found by the model | Optimum values | % found by experience | % found by the model |
| 10.2            | 10.2                | 9.9                     | 9.9            | 91.7                  | 92.9                   |
| 24.5            | 91.7                | 92.9                   | 25.7           | 95.8                  | 95.7                   |
| 90              | 90                  | 90                     |                |                      |                        |
Table S7. Comparative study of our prepared adsorbent PC-ED/1.5 and other functionalized materials.

| Adsorbent                                                                 | Metal ions | adsorption capacity | Ref |
|--------------------------------------------------------------------------|------------|---------------------|-----|
| PC-ED/1.5                                                                | Pb(II)     | 140 mg g⁻¹          |     |
|                                                                          | Cu(II)     | 123 mg g⁻¹          | This work |
| EDTA-functionalized bamboo activated carbon (BAC@SiO₂-EDTA)              | Pb(II)     | 123.45 mg g⁻¹       | 16  |
|                                                                          | Cu(II)     | 42.19 mg g⁻¹        |     |
| Mesoporous carbon nitride functionalized with melamine-based dendrimer amine | Pb(II)     | 196.34 mg g⁻¹       | 17  |
|                                                                          | Cu(II)     | 199.75 mg g⁻¹       |     |
| Biowaste-derived char with amino functionalization (PBC@SiO₂-NH₂)        | Pb(II)     | 120 mg g⁻¹          | 18  |
|                                                                          | Cu(II)     | 30 mg g⁻¹           |     |
| Aminopropyl-modified mesoporous carbon (CMK-3)                           | Pb(II)     | 3.5 mmol g⁻¹        | 19  |
|                                                                          | Cu(II)     | 8.6 mmol g⁻¹        |     |
| Amino-functionalized carbon nanotube-graphene (MWCNT-PDA/GO)             | Pb(II)     | 350.87 mg g⁻¹       | 20  |
|                                                                          | Cu(II)     | 318.47 mg g⁻¹       |     |
| EDTA functionalized magnetic graphene oxide (EDTA-mGO)                    | Pb(II)     | 508.4 mg g⁻¹        | 21  |
|                                                                          | Cu(II)     | 301.2 mg g⁻¹        |     |
Figure S1. The influence of the amount of ethylenediamine on the adsorption rate of Cu (■) and Pb (■).
Figure S2. BET analysis of PC, PC-ED/1.5, after and before adsorption of Cu and Pb onto PC-ED/1.5.
Figure S3. Effect of time and kinetics studies of Cu(II) and Pb(II) adsorption onto PC-ED/1.5.
Figure S4. Effect of concentration on the adsorption of Cu(II) and Pb(II) onto PC-ED/1.5 at differentness temperature
Figure S5. a) Freundlich and b) Langmuir models for the adsorption of Cu(II) and Pb(II) onto PC-ED/1.5.
Figure S6. Adsorption data fitted using Van’t Hoff equation of Cu(II) and Pb(II) adsorption onto PC-ED/1.5.
Figure S7. Response surface and contour plots of the aqueous adsorption of Cu(II) and Pb(II) adsorption onto PC-ED/1.5.
Figure S8. FTIR of PC-ED/1.5 after and before Cu (II) and Pb (II) adsorption
Figure S9. Effect of Alginate matrix and functionalization on the adsorption of Cu(II) and Pb(II) onto F-PC-ED/1.5.
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