

1           **Efficient pollutants removal by amino modified nanocellulose**  
2                                   **impregnated with iron oxide**

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29 *Materials*

30 All the chemicals used in this study were of analytical grade or p.a. chemicals. PEG-6-  
31 arm amino polyethylene glycol (PEG-NH<sub>2</sub>, Mr≈15000 g mol<sup>-1</sup>) (Sunbio, South Korea) was used.  
32 The following chemicals, p.a. quality, were supplied from Sigma Aldrich: sulfuric acid, glacial  
33 acetic acid, toluene, perchloric acid, maleic anhydride (**MA**), tetrahydrofuran (THF),  
34 *N,N*-dimethylformamide (DMF), coupling agent *N,N'*-diisopropylcarbodiimide, sodium  
35 hydrogencarbonate (NaHCO<sub>3</sub>) and iron(II) sulfate heptahydrate (FeSO<sub>4</sub>•7H<sub>2</sub>O). Deionised water  
36 (DW) with 18 MΩ cm resistivity was used. The As(V), As(III), nickel and cadmium standard  
37 solutions (Sigma Aldrich), 1000 mg L<sup>-1</sup>, were further diluted with deionised (DW) to the  
38 required concentration. Adjustment of pH was accomplished with 0.1 M NaOH and 0.1 M HNO<sub>3</sub>  
39 (Sigma Aldrich).

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41 *Adsorbents preparation*

42 *Nanocellulose (NC) isolation*

43 The **NC** was isolated from cotton microfiber (20 g) by treating with sulfuric acid (200  
44 cm<sup>3</sup>, 64 wt.%) at temperature <40 °C for 24 h.<sup>1</sup> Product was diluted with 800 cm<sup>3</sup> of deionised  
45 water (DW), neutralized to pH 6, and three cycles of centrifugation/DW water washing were  
46 applied. After dialyzing for 48 h, nanocellulose was filtered by using polytetrafluoroethylene  
47 (200 nm) filter membrane, and named **NC**.

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49 *The NC modification with maleic acid anhydride (NC-MA)*

50 **NC** (10 g) was dispersed in the mixture of glacial acetic acid (100 cm<sup>3</sup>), toluene (130  
51 cm<sup>3</sup>) and perchloric acid (0.5 cm<sup>3</sup>) by the use of ultrasound. Solution of **MA** (5 g) in 45 cm<sup>3</sup> of  
52 toluene was added drop-wise into reaction mixture for 15 minutes under sonication, and reaction  
53 was continued on magnetic stirrer for 1 h at room temperature. Raw product was washed  
54 thoroughly with toluene and ethanol, and dried.<sup>2</sup>

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56 *NC-MA modification with PEG-NH<sub>2</sub>*

57 Dispersion of **NC-MA** (10 g) in the 50 mL dry DMF was added slowly into solution of 1  
58 g of PEG-NH<sub>2</sub> in 50 ml dry DMF. After addition of 2 g of *N,N'*-diisopropylcarbodiimide in 20  
59 mL DMF reaction was carried out by ultrasonic treatment for 30 min (5 min/5 min

60 sonication/mixing cycles), and continued with magnetic stirring at 20-25 °C for 3 h. The product  
 61 was then diluted with 300 ml of methanol, vacuum-filtered with 0.05 µm pore size PTFE filter  
 62 membrane, and washed extensively with excess methanol. The PEG-NH<sub>2</sub> functionalized NC  
 63 (NC-PEG) was freeze/dried by keeping freshly obtained material at -30 °C for 24 h, followed by  
 64 freeze drying at -50 °C maintaining 0.05 mbar for 24 h, and process was finished at -70 °C and  
 65 0.01 mbar for 1 h material treatment. In that way obtained porous NC-PEG substrate was used  
 66 for subsequent precipitation of iron oxide.

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68 *Optimization of adsorbent preparation*

69 The coded and operational values of the selected variables are shown in Table SI,  
 70 together with the experimental plan, which comprised 16 experimental runs plus six replicates on  
 71 the central point.

72 **TABLE SI.** Experimental plan for RSM and experiment results for adsorbent NC-PEG/FO ( $m/V$   
 73  $= 100 \text{ mg dm}^{-3}$ ,  $C_{i[\text{As(V)}]} = 0.5 \text{ mg g}^{-1}$ ,  $T = 25 \text{ °C}$ ,  $\text{pH} = 6$ ).

No.	$C_{[\text{FeSO}_4]}$ , $X_1$ , $\text{mol dm}^{-3}$	$C_{[\text{NaHCO}_3]}$ , $X_2$ , $\text{mol dm}^{-3}$	Obtained capacity As(V), $\text{mg g}^{-1}$
1.	0.35	0.32	2.039
2.	0.21	0.22	3.142
3.	0.21	0.22	3.142
4.	0.09	0.17	1.605
5.	0.35	0.05	2.440
6.	0.12	0.50	2.273
7.	0.12	0.50	2.273
8.	0.23	0.17	2.975
9.	0.21	0.22	3.209
10.	0.04	0.32	1.805
11.	0.35	0.05	1.471
12.	0.29	0.15	3.311
13.	0.35	0.50	2.106
14.	0.04	0.32	1.905
15.	0.18	0.05	2.340
16.	0.04	0.05	1.471

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78 *Characterization of the adsorbents*

79 Analysis of textural properties of obtained materials was performed by using Brunauer-  
80 Emmett-Teller (BET) method for the determination of the specific surface area, the Barrett-  
81 Joyner-Halenda (BJH) method for the determination of the mesoporosity parameters. The X-ray  
82 diffraction (XRD) (BRUKER D8 ADVANCE) was used for phase and structural analysis of  
83 adsorbents. The morphology of the obtained powders and sintered samples was characterized by  
84 scanning electron microscopy (JEOL JSM-6390 LV). The powders were crushed and covered  
85 with gold in order to perform recording of SEM images. Fourier-transform infrared spectra  
86 (FTIR) were collected on BOMEM (Hartmann & Braun) spectrometer and were employed to  
87 determine the surface groups and its interactions with arsenate. The pH values at the point of  
88 zero charge ( $\text{pH}_{\text{PZC}}$ ) of the samples, *i.e.* the pH above which the total surface of the samples is  
89 negatively charged, were measured using the pH drift method.<sup>3</sup> Quantification of the available  
90 amino group was determined by applying Kaiser test ( $DA_{\text{Kaiser}}$  – degree of amination obtained by  
91 Kaiser test,<sup>4</sup> and by volumetric method.<sup>5</sup> The acid value (AV) was determined according to  
92 ASTM D664 standard, and presented as  $\text{mg KOH g}^{-1}$  of the specimen. The arsenic concentrations  
93 in the solutions after the adsorption and kinetic experiments were analyzed by inductively  
94 coupled plasma mass spectrometry (ICP-MS), using an Agilent 7500ce ICP-MS system  
95 (Waldbronn, Germany).

96 *Adsorption and kinetic experiments in a batch system*

97 Batch experiments were conducted in  $10 \text{ cm}^3$  polyethylene bottles in  $100 \text{ mg dm}^{-3}$   
98 suspension with  $10 \text{ cm}^3$  of arsenic solution of certain concentration, time period, temperature and  
99 pH value. Time dependent batch experiments were determined in  $1 \text{ mg dm}^{-3}$  solution for cations  
100 and  $0.5 \text{ mg dm}^{-3}$  for As(V) solution during 5, 10, 15, 30, 45, 60 and 120 min. This study revealed  
101 that 60 minutes was sufficient for quantitative removal of pollutants. The effect of pH value on  
102 As(V) removal was studied with an initial As(V) concentration of  $0.5 \text{ mg dm}^{-3}$  varying the pH in  
103 the range 2-12. Adsorption isotherm and thermodynamic parameters were evaluated by varying  
104 initial concentration ( $C_i$ ) of cation (1, 2, 3, 4, 5, 6 and  $7 \text{ mg dm}^{-3}$ ) and oxyanions concentration  
105 ( $0.1, 0.2, 0.5, 1, 2, 5$  and  $10 \text{ mg dm}^{-3}$ ) and temperature (25, 35, 45 °C). Batch experiments were  
106 performed under classical mixing using magnetic stirrer Heidolph MR 3001. After adsorption

107 experiments, adsorbent was removed by filtration with 0.22  $\mu\text{m}$  PTFE membrane and filtrate was  
108 analyzed on pollutant content. The adsorbent capacity was calculated according to the eq. (S1):

$$109 \quad q = \frac{C_i - C_e}{m} V$$

110 (S1)

111 where  $q$  is adsorption capacity in  $\text{mg g}^{-1}$ ,  $C_i$  and  $C_e$  are initial and final ion concentrations in  $\text{mg}$   
112  $\text{dm}^{-3}$  ( $\mu\text{g dm}^{-3}$ ), respectively,  $V$  is volume of the solution in  $\text{dm}^3$ , and  $m$  is mass of adsorbent in g.  
113 The results of ions adsorption on glass tube wall and filters showed negligible effect on the  
114 reliability of results.

115 To evaluate the regeneration capabilities, after adsorption experiments and washing with  
116 DW, wet adsorbents ( $m/V = 100 \text{ mg dm}^{-3}$ ) were re-dispersed in  $20 \text{ cm}^3$  of regenerator. Different  
117 solutions: NaOH (0.2 or 0.5  $\text{mol dm}^{-3}$ ), NaCl (0.2 or 0.5  $\text{mol dm}^{-3}$ ) or their combination was used  
118 for cation and arsenic elution. The amount of desorbed cations and As(V) was measured after  
119 magnetic mixing for 3 h in a batch system. Five consecutive adsorption/desorption cycles were  
120 performed in triplicate by using both **NC-PEG** and **NC-PEG/FO** adsorbents.

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#### 122 *Adsorption data modeling and statistical analysis*

123 Calculations of kinetic and thermodynamic parameters were obtained by using OriginPro  
124 9.1<sup>®</sup> software. Unknown parameters of the isotherm models were determined using Levenberg-  
125 Marquardt (LM) algorithm and Orthogonal Distance Regression (ODR) algorithm. Levenberg-  
126 Marquardt (LM) algorithm minimizes the residual sum of squares by adjusting fitting parameters  
127 in the iterative process. The residual in LM is the difference between the observed value and the  
128 predicted value of the dependent variable. And the algorithm combines the Gauss-Newton  
129 method and the steepest descent method. Orthogonal distance regression (ODR) algorithm  
130 minimizes the residual sum of squares by adjusting both fitting parameters and values of the  
131 independent variable in the iterative process. The residual in ODR is not the difference between  
132 the observed value and the predicted value for the dependent variable, but the orthogonal  
133 distance from the data to the fitted curve.<sup>6</sup> Considering that values of both axes are affected by  
134 measurement error in the process of experimental data by adsorption isotherm models fitting, the  
135 use of ODR modeling procedure is statistically correct, and can be presented by following eq.  
136 (S2):

$$\text{ODR} = \sum_{i=1}^n \left[ \left( \frac{q_i - \hat{q}_i}{q_i} \right)^2 + \left( \frac{C_{fi} - \hat{C}_{fi}}{C_{fi}} \right)^2 \right] \quad (\text{S2})$$

where  $n$ ,  $q_i$ ,  $\hat{q}_i$ ,  $C_{fi}$  and  $\hat{C}_{fi}$  denote the number of data points, the experimental and the estimated values of adsorption capacity and equilibrium adsorbate concentration, respectively, is suitable for fitting adsorption isotherms when the measurements of initial and final adsorbate concentrations are affected by heteroscedastic error and no replicates were done. In eq. (S2) weighting is performed by  $1/q_i$  and  $1/C_{fi}$  for the  $y$  and  $x$  axes, respectively, and thus at the same time heteroscedasticity is taken into account and the scaling is performed so that dimensionless values, independent of units, can be added together to form the sum of error function.

## RESULTS AND DISCUSSION

### *The XRD analysis*

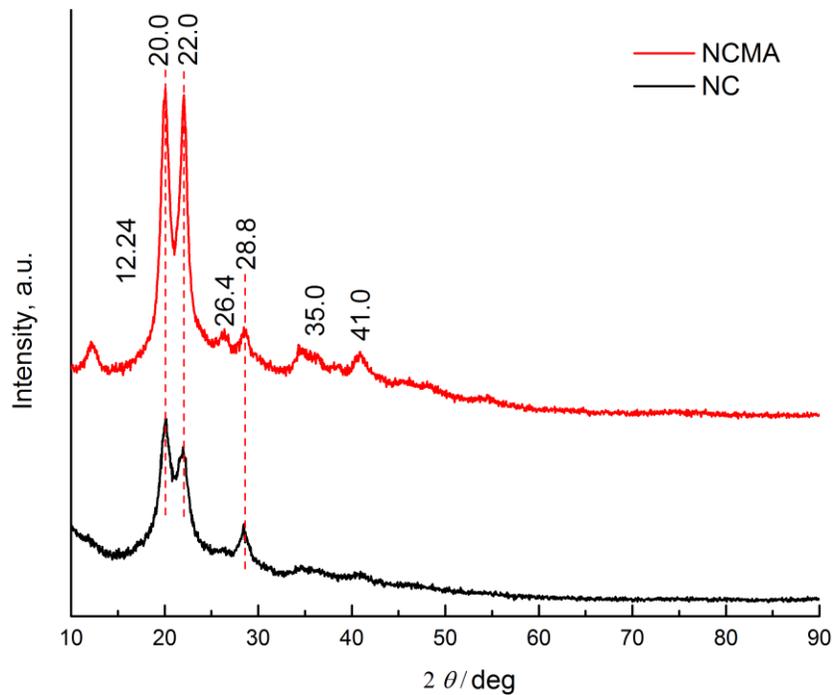
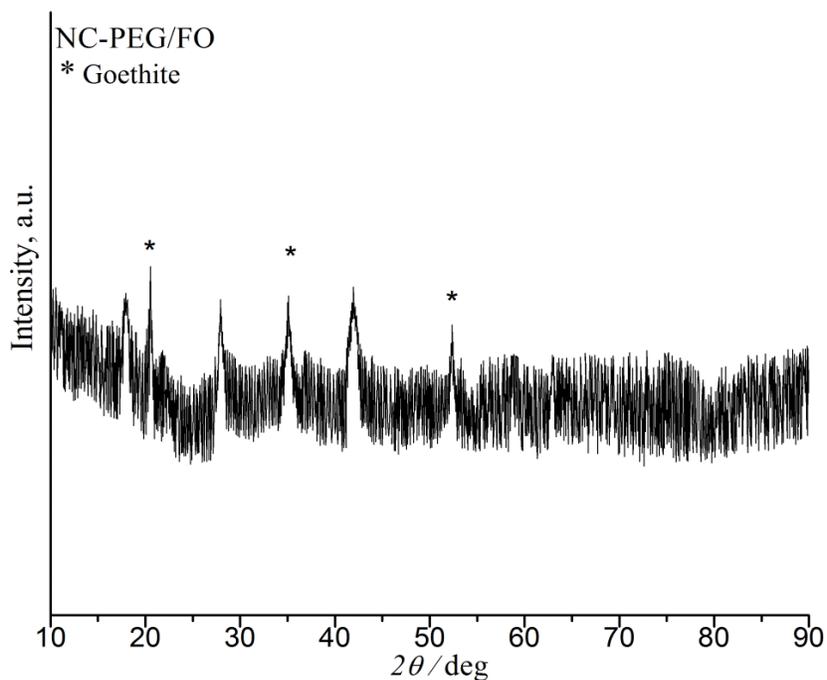


Fig. S1. XRD diffractograms of NC and NCMA<sup>2</sup>



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Fig. S2. XRD pattern of NC-PEG/FO.

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157 The maximum adsorption capacities for As(V) and As(III) by using NC-PEG/FO, as well as  
 158 Cd<sup>2+</sup> and Ni<sup>2+</sup> by using NC-PEG are given in Table

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160 **Table SII.** The maximum adsorption capacities for As(V), As(III), Cd<sup>2+</sup> and Ni<sup>2+</sup>, obtained by  
 161 using Langmuir model

Adsorbent	$q_e / \text{mg g}^{-1}$			
	25 °C	35 °C	45 °C	
NC-PEG/FO	As(V)	26.0	27.4	28.6
	As(III)	23.6	24.3	25.5
NC-PEG	Cd <sup>2+</sup>	37.9	40.9	43.9
	Ni <sup>2+</sup>	32.4	33.7	35.0

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