SUPPLEMENTARY MATERIAL TO

Efficient pollutants removal by amino-modified nanocellulose impregnated with iron oxide

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EXPERIMENTAL DETAILS

Materials

All the chemicals used in this study were of analytical grade or p.a. chemicals. PEG-6-arm amino polyethylene glycol (PEG-NH$_2$, *Mr* $\approx$ 15000 g mol^{-1}, Sunbio, South Korea) was used. The following chemicals, p.a. quality, were supplied from Sigma Aldrich: sulfuric acid, glacial acetic acid, toluene, perchloric acid, maleic anhydride (MA), tetrahydrofurane (THF), *N,N*-dimethylformamide (DMF), coupling agent *N,N′*-diisopropylcarbodiimide, sodium hydrogencarbonate (NaHCO$_3$) and iron(II) sulfate heptahydrate (FeSO$_4$·7H$_2$0). Deionized water (DI) with resistivity of 18 MΩ cm was used. The As(V), As(III), nickel and cadmium standard solutions (Sigma Aldrich) with initial concentration of 1000 mg L^{-1}, were further diluted with DI water to the required concentration. The adjustment of pH was accomplished by using 0.1 M NaOH and 0.1 M HNO$_3$ (Sigma Aldrich).

Adsorbents preparation

Nanocellulose (NC) isolation. The NC was isolated from cotton microfiber (20 g) by treating it with sulfuric acid (200 cm^3, 64 wt. %) at temperature < 40 °C for 24 h.[1] The product was diluted with 800 cm^3 DI water, neutralized to pH 6, and then three cycles of centrifugation/DI water washing were applied. After

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dialyzing for 48 h, the nanocellulose was filtered by using a polytetrafluoro-ethylene (200 nm) filter membrane, and was named NC.

NC modification with maleic acid anhydride (NC-MA). The NC (10 g) was dispersed in mixture of glacial acetic acid (100 cm^3), toluene (130 cm^3) and per-chloric acid (0.5 cm^3) by usig ultrasound. A solution of MA (5 g) in 45 cm^3 of toluene was added drop-wise into the reaction mixture for 15 min under sonic-ation, and the reaction was continued on magnetic stirrer for 1 h at room tem-perature. The raw product was washed thoroughly with toluene and ethanol, and dried.[2]

NC-MA modification with PEG-NH$_2$. A dispersion of NC-MA (10 g) in 50 mL dry DMF was added slowly into solution of 1 g of PEG-NH$_2$ in 50 ml dry DMF. After addition of 2 g of *N,N′*-diisopropylcarbodiimide in 20 mL DMF the reaction was carried out by ultrasonic treatment for 30 min (5 min/5 min sonic-ation/mixing cycles), and continued with magnetic stirring at 20-25 °C for 3 h. The product was then diluted with 300 ml methanol, vacuum-filtered with 0.05 μm pore size PTFE filter membrane, and washed extensively with excess of methanol. The PEG-NH$_2$ functionalized NC (NC-PEG) was freeze-dried by keeping the freshly obtained material at –30 °C for 24 h, followed by freeze--drying at –50 °C and pressure of 0.05 mbar for 24 h, and at final treatment of the material at –70 °C and 0.01 mbar for 1 h. The obtained in this way porous NC-PEG substrate was used for subsequent precipitation of iron oxide.

Optimization of the adsorbent preparation

The coded and operational values of the selected variables are shown in Table S-I, together with the experimental plan, which comprised of 16 experi-mental runs plus six replicates on the central point. Each experiment (except the central point) was performed in duplicate. The output variable was the adsorption capacity. The data obtained in these experiments were fitted to a second-order polynomial equation and the coefficients of the response function and their statis-tical significance were evaluated by the least squares method using commercial software Design-Expert, Software Version 9 (Stat-Ease Inc., 2021 E. Hennepin Ave., Suite 480, Minneapolis, MN, USA). The Fisher test was used to determine the adequacy of the model and the Student Distribution to evaluate the signific-ance of the coefficients.

The optimization goals were defined in relation to the maximum adsorption capacity of NC-PEG/FO. In that sense, the optimization procedure, performed according to the experimental plan, presented in Table S-I of the Supplementary material, revealed that the optimal adsorbent performance was achieved at the experimental conditions given in Fig. S-1. Used materials were obtained accord-ing to optimized procedure. The maximum adsorption capacity with respect to As(V), was obtained at 12 % iron loading on NC-PEG (Fig. S-1b).

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TABLE S-I. Experimental plan for RSM and experiment results for adsorbent NC-PEG/FO ($m/V = 100$ mg dm^{-3}, $c_{i[As(V)]} = 0.5$ mg g^{-1}, $t = 25$ °C, pH 6)

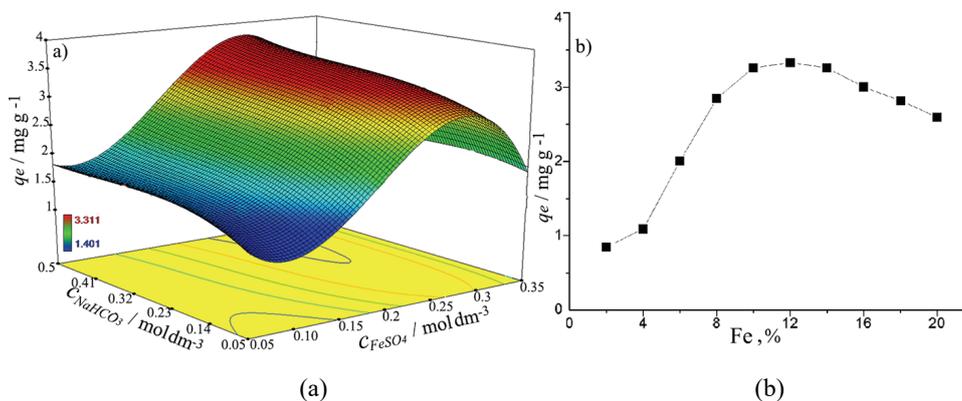| No.	$c_{[FeSO4]}, X_1$ / mol dm^{-3}	$c_{[NaHCO_3]}, X_2$ / mol dm^{-3}	Obtained capacity As(V), mg g^{-1}
1.	0.35	0.32	2.039
2.	0.21	0.22	3.142
3.	0.21	0.22	3.142
4.	0.09	0.17	1.605
5.	0.35	0.05	2.440
6.	0.12	0.50	2.273
7.	0.12	0.50	2.273
8.	0.23	0.17	2.975
9.	0.21	0.22	3.209
10.	0.04	0.32	1.805
11.	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

Fig. S-1. Contour diagram representing NC-PEG/FO adsorbent capacity *vs.* c_{FeSO_4} and c_{NaHCO_3} (a) and NC-PEG/FO capacity *vs.* iron loading for $c_{i[As(V)]} = 0.5$ mg dm^{-3} As(V), $m/V = 100$ mg dm^{-3}, pH 6 and $t = 25$ °C (b).

The NC-PEG-based adsorbent was obtained by modification of hydrophilic NC by performing two-step esterification/amidation reaction, which provided introduction of branched PEG-6-arm structure. The modification of NC to NC-MA, was conducted by using MA with an acid value (*AV*) of 28. It introduced ≈1.50 mmol g^{-1} of carboxylic groups (*AV* = 150). The lower efficiency of the NC-MA modification with PEG-NH$_2$ resulted in 0.12 mmol g^{-1} amino group in NC-PEG. This result indicated that the extent of amidation, due to steric interference of the voluminous PEG-6-arm structure, was significant. The experimental value of 0.12 mmol g^{-1} indicated that, regardless of the lower extent of the NC surface

functionalization, the presented procedure provided a large number of amino groups with high capability for iron binding/precipitation, as well as for cations removal. The significance of the amino group involved in the cation complexation process was recently presented.[3] The high coordination affinity of the amino groups and iron ions, and the higher nucleophilicity of the amino groups at pH > > pH_{PZC} provided conditions for preferable complexation/chelation of iron at the NC surface.[4] Also, the increased number of total basic sites contributed to the uniform/high iron oxide loading.

The optimal deposition of FO onto NC-PEG was obtained by performing two-step FO precipitation. For the NC-PEG/FO production 82.5 cm^3 (0.32 mol dm^{-3}) $FeSO_4·7H_2O$ and 75 cm^3 (0.38 mol dm^{-3}) $NaHCO_3$ solutions were used. The applied methodologies provided beneficial morphology/chemistry with a number of available adsorptive sites on the NC-PEG/FO surface for arsenate removal. It also provided the means for controlled precipitation of hydrous iron oxide (HFO) in goethite form thus creating nano-scaled deposit with improved textural properties.

Characterization of the adsorbents

The analysis of the textural properties of the obtained materials was performed by using Brunauer–Emmett–Teller (BET) method for determination of the specific surface area and Barrett–Joyner–Halenda (BJH) method for determination of the mesoporosity parameters. X-ray diffraction (XRD, Bruker D8 Advance) was used for phase and structural analysis of the adsorbents. The morphology of the obtained powders and sintered samples was characterized by scanning electron microscopy (SEM, JEOL JSM-6390 LV). The powders were crushed and covered with gold in order to record the SEM images. Fourier-transform infrared spectra (FTIR) were collected on BOMEM (Hartmann & Braun) spectrometer and were employed to determine the surface groups and their interactions with the arsenate. The pH values at the point of zero charge (pH_{PZC}) of the samples, *i.e.*, the pH above which, the total surface of the samples is negatively charged, were measured using the pH drift method.[5] The quantification of the available amino group was performed by applying Kaiser test (DA_{Kaiser} − degree of amination obtained by Kaiser test)[6] and by volumetric method.[7] The acid value (*AV*) was determined according to ASTM D664 standard, and presented as mg KOH g^{-1} of the specimen. Instrument Alpha 1-4 LSC plus, CHRIST was used for freeze-drying of the material. The arsenic concentrations in the solutions after the adsorption and kinetic experiments were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), using an Agilent 7500ce ICP-MS system (Waldbronn, Germany).

Adsorption and kinetic experiments in a batch system

The batch experiments were conducted in 10 cm^3 polyethylene bottles using 100 mg dm^{-3} suspension with 10 cm^3 arsenic solution of certain concentration, set time period, temperature and pH value. The time dependent batch experiments were conducted in 1 mg dm^{-3} solution for cations and 0.5 mg dm^{-3} for As(V) solution for 5, 10, 15, 30, 45, 60 and 120 min. This study revealed that 60 min were sufficient for quantitative removal of the pollutants. The effect of the pH value on the As(V) removal was studied with an initial As(V) concentration of 0.5 mg dm^{-3} and varying the pH value in the range of 2–12. The adsorption isotherm and thermodynamic parameters were evaluated by varying the initial concentration (c_i) of cation (1, 2, 3, 4, 5, 6 and 7 mg dm^{-3}), oxyanions concentration (0.1, 0.2, 0.5, 1, 2, 5 and 10 mg dm^{-3}) and temperature (25, 35 and 45 °C). The batch experiments were performed under classical mixing using magnetic stirrer Heidolph MR 3001. After adsorption experiments, the adsorbent was removed by filtration with 0.22 µm PTFE membrane and the pollutant content in the filtrate was analyzed. The adsorbent capacity was calculated according to:

$$q = \frac{c_i - c_e}{m} V \qquad \text{(S-1)}$$

where q is the adsorption capacity in mg g^{-1}, c_i and c_e are the initial and final ion concentrations in mg dm^{-3} (µg dm^{-3}), respectively, V is the volume of the solution in dm^3, and m is the mass of the adsorbent in g. The ions adsorption on the glass tube wall and filters showed negligible effect on the reliability of the results.

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

Adsorption data modelling and statistical analysis

The calculations of the kinetic and thermodynamic parameters were performed by using OriginPro 9.1$^®$ software. The unknown parameters of the isotherm models were determined using Levenberg–Marquardt (L–M) algorithm and orthogonal distance regression (ODR) algorithm. The L–M algorithm minimizes the residual sum of squares by adjusting fitting parameters in the iterative process. The residual in L–M is the difference between the observed value and the predicted value of the dependent variable. The algorithm combines the Gauss–Newton method and the steepest descent method. The ODR algorithm

minimizes the residual sum of squares by adjusting both the fitting parameters and the values of the independent variable in the iterative process. The residual in the ODR algorithm is not the difference between the observed value and the predicted value for the dependent variable, but the orthogonal distance from the data to the fitted curve.[8] The use of ODR modeling procedure is statistically correct, and can be presented by the following equation:

$$ODR = \sum_{i=1}^{n} \left(\frac{q_i - \hat{q}_i}{q_i} \right)^2 + \left(\frac{c_{fi} - \hat{c}_{fi}}{c_{fi}} \right)^2 \qquad (S-2)$$

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 the adsorption capacity and equilibrium adsorbate concentration, respectively. The ODR modeling procedure 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. (S-2) weighting is performed by $1/q_i$ and $1/c_{fi}$ for the y and x axes, respectively, and thus at the same time the 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.
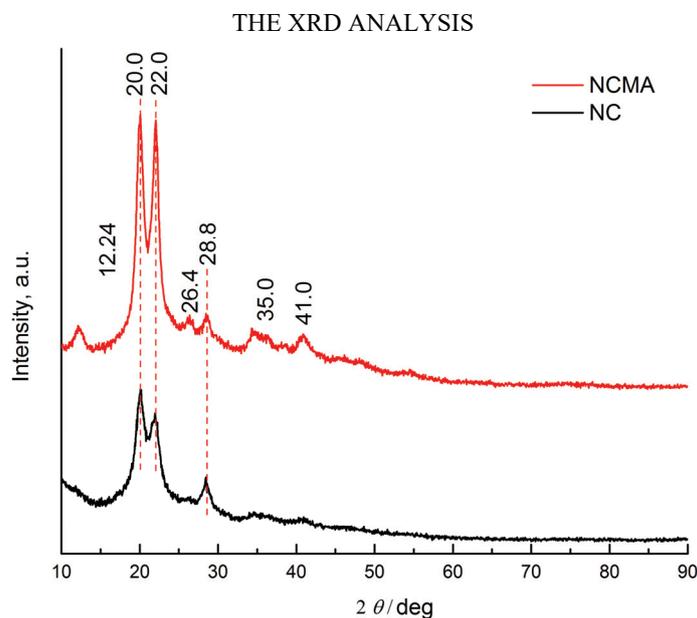
THE XRD ANALYSIS

Fig. S-2. XRD diffractograms of NC and NCMA.[2]

ADSORPTION ISOTHERMS
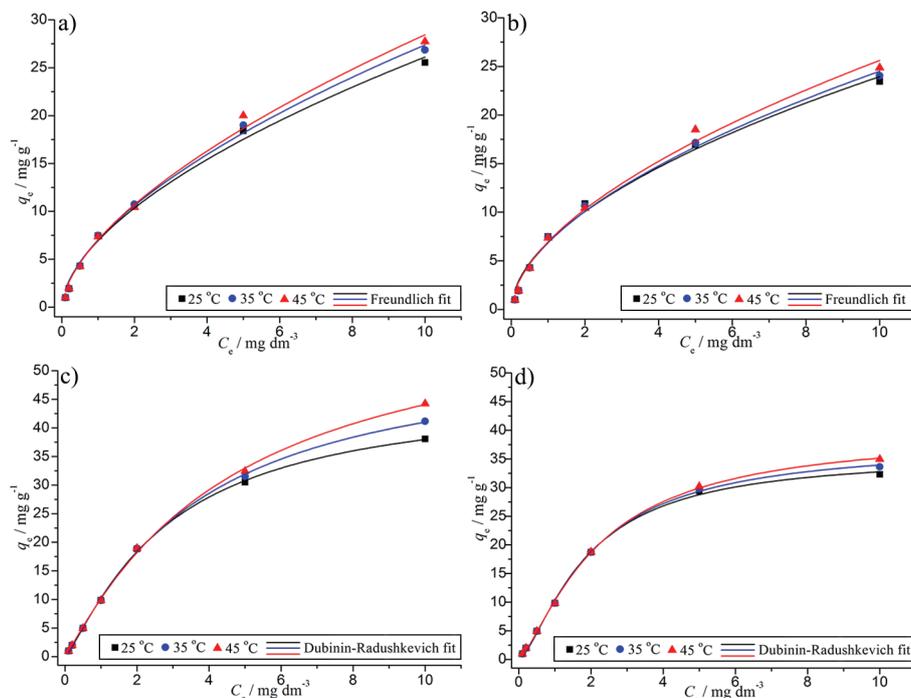

Fig. S-3. Adsorption isotherms and fitting for As(V) (a) and As(III) (b), $m/V = 100$ mg dm^{-3}, $c_i = 0.1, 0.2, 0.5, 1, 2, 5$ and 10 mg dm^{-3}, pH 6.0 ± 0.1, with NC-PEG/FO adsorbent, and Cd^{2+} (c) and Ni^{2+} (d) removal with NC-PEG, $m/V = 100$ mg dm^{-3}, $c_i = 1, 2, 3, 4, 5, 6$ and 7 mg dm^{-3}, pH 6.0 ± 0.1.

TABLE S-II. Results of the fitting for NC-PEG/FO and NC-PEG obtained by using Freundlich and D–R models, respectively

Parameter	NC-PEG/FO					
	As(V)			As(III)		
	t / °C					
	25	35	45	25	35	45
k_f/ mg g^{-1}	11.756	12.134	12.202	11.349	11.375	11.579
$1/n$	0.3516	0.357	0.3631	0.3425	0.344	0.3518
R^2	0.996	0.995	0.992	0.998	0.997	0.996
	NC-PEG					
	Ni^{2+}			Cd^{2+}		
Parameter	t / °C					
	25	35	45	25	35	45
q_m / mg g^{-1}	29.54	30.71	31.88	27.49	27.99	28.48
$\beta \times 10^{-9}$ / mol^2 J^{-2}	7.67	7.63	7.60	7.67	7.65	7.64

TABLE S-II. Continued

Parameter	NC-PEG					
	Ni^{2+}			Cd^{2+}		
	t / °C					
	25	35	45	25	35	45
E / kJ mol^{-1}	8.072	8.092	8.112	8.073	8.083	8.092
R^2	0.998	0.985	0.989	0.992	0.993	0.990

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