Supporting information

Monitoring of Cobalt and Cadmium in Daily Cosmetics Using Powder and Paper Optical Chemosensors

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Instruments

The surface properties including the specific surface area and the pore structure were determined by N₂ adsorption-desorption isotherms which were measured by Automatic surface area and pore size analyzer (BELSORP MINI X) was used to determine Specific surface area (SBET) via adsorption-desorption of N₂ gas at 77 K via applying the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was determined from the adsorption isotherms by using nonlocal density functional theory. Specific surface area (S_BET) was calculated using multi-point adsorption data from linear segment of the N₂ adsorption isotherms using Brunauer-Emmett-Teller (BET) theory. Before the N₂ isothermal analysis, all samples pre-treated at 80°C for 6h and calibrated to 10⁻³ Torr. Small- and wide-angle powder X-ray diffraction (SAXRD, and, respectively) patterns were measured by using X’Pert - PRO – TAM with monochromated CuKα (λ = 1.54060 Å) radiation with diffraction reflections recorded for 2 angles between 5° and 10° corresponding to d- and WAXRD of chemosensors scanned from 4° to 80°. Prior to analysis, the samples were outgassed
at 80 °C for 24 h. The Field emission scanning electron microscopy (FESEM) images were used to investigate the morphologies of Al-MOFs nanorods and obtained by Zeiss Leo Supra55 microscope. Moreover, to record the SEM micrographs, the scanning electron microscope was operated at 20 keV. The samples for FESEM observations were observed with copper coating. Moreover, to record the SEM micrographs, the scanning electron microscope was operated at 20 keV. High resolution transmission electron microscope (HR-TEM, Tecnai G20, FEI, and Netherland) was used for the purpose of imaging and elemental analysis. The absorbance spectrum of the TAM chemosensors were measured by a Shimadzu UV-2600 solid-state UV–vis spectrophotometer.

**Calculation of adsorption capacity**

The adsorption capacity \( Q \), mmol g\(^{-1} \) of the TAM sensor at saturation was deduced by the following equation:

\[
Q_t = \frac{(C_o - C_t) V}{m}
\]  

(S1)

Where \( Q_t \) is the adsorbed amount at saturation time \( t \), \( V \) is the solution volume (L), \( m \) is the mass of silica nanosphere carriers (g), \( C_o \) and \( C_t \) are the initial concentration and the concentration at saturation time, respectively.

**Apparatus and Software.**

Scanning of the color scales was performed with the use of the scanner of LaserJet Pro 400 in color mode RGB 24 bits with resolution 300 dpi and Digital Nikon camera (D3100) to show the good performance using different devices by this simple sensor. The determination of the colorimetric characteristics of the obtained images and transformation of the color coordinates were performed in the Adobe Photoshop CC 2017 (64 Bit) on a personal laptop. Using the “Crop” tool called “Elliptical Marquee Tool” to select an oval region in the middle of the image of the colored sample and the “Histogram” tool used to obtain the average color intensities values of RGB, Red, Green, and Blue of each image. All data were transferred to Microsoft Excel 2016 (64 Bit) spreadsheet for subsequent data analysis and using Origin Pro 2016 (64 Bit) for data plotting.

the color intensity can be also directly related to the absorbance concentration using the following equation:
where for each color X (R, B, G), $A_X$ is the absorbance of X, $I_X$ and $R_X$ are the intensity and the reflectance of light X, respectively, $I_{X,b}=0, I_{X,w}=256$, and C is the concentration of X [1].

Figure S1. Small angle XRD diffraction patterns (SAXRD) of the nanosphere as carrier for the powder optical chemosensors (POCs).
Figure S2. The interference studies of POCs in selective detection of Cd\(^{2+}\) at pH=9 and Co\(^{2+}\) at pH=7.

Table S1. Tolerance concentration limits for interfering ions during recognition of Cd(II) and Co(II) using POCs at optimum conditions.

| Interfering ions | Tolerance limit (mg/L) | Cd(II) | Co(II) |
|------------------|------------------------|--------|--------|
| Na\(^+\), K\(^+\), Cs\(^+\), Mn\(^{2+}\), Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), Cr\(^{3+}\), Ba\(^{2+}\) | 100 | 100 |
| Zn\(^{2+}\) | 85 | 100 |
| Cu\(^{2+}\) | 50 | 66 |
| Hg\(^{2+}\) | 70 | 95 |
| Co\(^{2+}\) | 88 | Ref |
| Cd\(^{2+}\) | Ref | 82 |
| Pb\(^{2+}\) | 95 | 93 |
| Fe\(^{3+}\) | 100 | 100 |
| Ni\(^{2+}\) | 80 | 95 |

Elution and reuses.

The metal ions recovery by elution/desorption operation is an important parameter to evaluate the materials as a cost-effective potential candidate for potential application. To evaluate the exact eluent for regeneration and reusability of the adsorbent, elution experiments were performed using different concentrations of EDTA. A simple treatment using the stripping agent of 0.1 M EDTA was found to effectively remove the Cd\(^{2+}\) and Co\(^{2+}\) ions (i.e. decomplexation) and kept the
remaining functionality of adsorbent for reuse in several cycles. These experiments were carried out several times via liquid-exchange process to release the metal ions and to get “metal–free” sensor surface. The optical chemosensors were reused after regeneration and rinsed with water, respectively, followed by vacuum drying. After multiple regeneration/reuse cycles (i.e. ≥5). The prepared optical chemosensor showed a slight influence on the sensitivity with the increase of the recovery cycles shown in Figure S3. This is evidence indicating that the prepared optical chemosensor for sensing of Cd$^{2+}$ and Co$^{2+}$ ions many times.

![Graph](image)

Figure S3. The elution and regeneration of A) POCs and B) PBCs for multiple cycles where the stripping agent was 0.1 M EDTA.

References

1- Kompany-Zareh, M.; Mansourian, M.; Ravaee, F.; Simple method for colorimetric spot-test quantitative analysis of Fe(III) using a computer-controlled hand-scanner, *Anal. Chim. Acta.* 2002, *471*, 97–104