pH-Regulated Carbon Dots Fluorescence Sensor Array Detection of Multiple Heavy Metal Ions Under Stepwise Prediction

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Research Article

Keywords: carbon dots, fluorescence sensor array, metal ions, stepwise prediction

Posted Date: January 11th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1170064/v1>

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Abstract

As a large amount of heavy metals leaches into water sources from industrial effluents, heavy metal pollution has become an important factor affecting water quality. To enable the detection of multiple heavy metals, we constructed a pH-regulation fluorescence sensor array. Firstly, by adding a metal chelating agent as receptor, metal ions and carbon quantum dots (CDs) were connected to distinguish between Cr^{6+} , Fe^{3+} , Fe^{2+} , and Hg^{2+} ions. Thus, the lack of affinity between the indicator functional groups and the analyte was solved. Secondly, by adjusting the pH environment of the solution system, an economical and simple array sensing platform is established, which effectively simplified the array construction. In this study, the SX-model was used in the field of fluorescence sensor array detection for metal ion recognition. Based on the strategy of stepwise prediction, combined with the classification and concentration models, the bottleneck of the unified model in previous studies was broken. This sensor array demonstrated sensitive detection of four heavy metal ions within a concentration range from 1 to 50 μM , with an accuracy of 95.45%. Moreover, it displayed the ability to efficiently identify binary mixed samples with an accuracy of 95.45%. Furthermore, metal ions in 15 real samples (lake water) were effectively discriminated with 100% accuracy. A chelating agent was used to improve the sensitivity of heavy metal ion detection and eventually led to high-precision prediction using the SX-model.

1. Introduction

With the rapid development of industry, a large number of toxic and carcinogenic heavy metal ions have been released into the environment, causing increasingly serious pollution of soil and groundwater (Fenglian et al. 2011; Sun et al. 2021). Because they are difficult to biodegrade, they accumulate in the environment and cause serious threats to human health (Qin et al. 2021; Yan et al. 2022). Rapid and reliable detection is required to monitor and control heavy metal ions (Yang et al. 2020). Traditional heavy metal detection methods mainly include atomic absorption spectrometry (AAS) (Kharnoob 2015), atomic fluorescence spectrometry (AFS) (Ge et al. 2021), inductively coupled plasma mass spectrometry (ICP-MS) (Kuznetsova, Timerbaev, and Spectroscopy 2021) and fluorescent chemosensors. In addition, fluorescent sensors have attracted significant attention because of their high sensitivity (Gao et al. 2022). Chen et al. (Chen, Li, et al. 2020) prepared CDs for Hg^{2+} specificity detection. Zhao and coworkers (Zhao et al. 2020) synthesized CDs for the specific detection of Fe^{3+} ions. Considering the complexity of the sample detection environment, it is crucial to develop a detection method that can simultaneously identify and distinguish between multiple types of heavy metals. Therefore, many scholars have introduced array detection into fluorescence detection techniques (Chao, Chen et al. 2017), (Zhou, Wang et al. 2021). The design and construction of a fluorescence sensor array were studied, and qualitative and quantitative detection and identification of similar analytes were performed.

Sensor array is a powerful molecular recognition method, which is based on an understanding of the animal olfactory system (Wang, Na, and Ouyang 2021). It is composed of a series of sensing units that can recognize and detect specific substances through the characteristic map generated by each sensing

unit in response to the sample(Zhou et al. 2021; Kharnoob 2015). In contrast to a single sensor element, the sensor array has the advantages of good selectivity and simultaneous detection of the same series of analytes(Chen et al. 2021; Mitchell et al. 2021). To improve the sensitivity of sensor array detection, it is necessary to select appropriate sensor elements. CDs are a new type of fluorescent carbon nanomaterials, have simple synthesis methods, are generally approximately 10 nm in size, and feature a variety of functional groups on their surface(Xu et al. 2004; Oliveira and Abreu 2021). Owing to their unique fluorescence properties and low toxicity, CDs have gradually become a substitute for traditional quantum dots(Zhao et al. 2020). Compared with traditional organic probes and CdSe-type quantum dots, CDs feature excellent water solubility, good photostability(L. et al. 2014), and bio-imaging photocatalysis(Wang, Wang, and Sun 2016), and therefore are highly desirable in the fields of bio-imaging, sensing detection, photoelectric transformation, and photocatalysis(Cao et al. 2011). Fluorescence sensor arrays constructed with CDs as indicators have several advantages, such as high sensitivity, low detection cost, high sustainability and no toxicity. Thus, they have been widely used in the analysis and detection of pollutants in the environment. The analytes mainly include pesticides(Carneiro et al. 2019), antibiotics(Xu et al. 2020), heavy metals(Wu et al. 2017), nitroaromatic explosives(Ghasemi and Hormozi-Nezhad 2019), and catecholamines neurotransmitters(Abbasi-Moayed, Hormozi-Nezhad, and Maaza 2019). The obtained results are analyzed with different analysis methods. Currently, the main methods include principal component analysis (PCA), hierarchical cluster analysis (HCA), linear discriminant analysis (LDA), support vector machines (SVMs), and artificial neural networks (ANNs). Wu et al. established a sensor array with five types of CDs and PCA to establish individual models for different concentration gradients ranging from 50 to 1600 μM , for the identification of six metal ions(Wu et al. 2017). Chen's group developed a fluorescent sensor array consisting of two different nitrogen-doped CDs and then used LDA to build a recognition model for individual concentration gradients ranging from 50 to 1400 μM , to determine six kinds of biothiols(Chen et al. 2020). Many analytical methods have been applied to array detection. However, there is a lack of a fast way to screen out the best model. In addition, most of the previous research reports introduced an analysis model that is established at a single concentration, which could not be unified. Moreover, the detection of unknown samples in array detection could not be realized and therefore, the application in real environments is strongly limited. It is necessary to develop a unified analysis model, establish a logical relationship between the samples, quickly screen out the best analysis and data processing methods, and apply them to array detection research in a real environment.

Herein, we chose CDs and a metal indicator to develop a pH-regulated fluorescence sensor array based on the internal filtering effect (IFE). The sensor array is used for the simultaneous detection of Cr^{6+} , Fe^{3+} , Fe^{2+} , and Hg^{2+} . Metal indicators are added to enhance the specificity of the sensor array. In addition, this reduces the detection limit and optimizes the detection effect at low concentrations. CDs were synthesized using cetylpyridinium chloride (CPC) as educt (CPC-CDs). Xylenol orange (XO) was used as a metal chelating agent, which reacted with the added analyte and formed a metal ion complex. Because the emission spectrum of CPC-CDs overlaps effectively with the absorption spectrum of the metal chelate, the addition of chelate effectively quenched the fluorescence. Based on the change in

fluorescence intensity (FI) I/I_0 in the two pH buffer solution systems (I and I_0 represent FI in the presence and absence of heavy metals, respectively), the fluorescence analysis mode of each analyte is constructed. The SX-model is used to analyze and process multidimensional data. Under the stepwise prediction strategy, the classification and concentration models are combined with a machine learning model. The gradient boosting machine (GBM) method is screened by tree-based pipeline optimization technique (TPOT) to build a classification model and further to analyze and process the array data. Four metal ions with different concentrations are successfully classified, and regression is performed using the stepwise prediction strategy. In addition, the stepwise prediction of unknown metal ions is realized. In practical applications, the identification of heavy metals in a complex medium (lake water) has been verified. The sensor array also identified 15 unknown samples with an accuracy of 100%. We propose a stepwise prediction strategy combined with a machine model method, and successfully detect four types of heavy metal pollutants in array sensing technology. The fluorescence sensor array can be more widely applied for the detection and recognition of other pollutants with similar chemical structures and properties.

2. Materials And Methods

2.1. Chemicals

Chromium trioxide (CrO_3), mercury chloride (HgCl_2), ferrous chloride (FeCl_2), ferric chloride (FeCl_3), sodium carbonate (Na_2CO_3), potassium dihydrogen phosphate (KH_2PO_4), potassium sulfate (K_2SO_4), sodium bicarbonate (NaHCO_3), sodium sulfite (Na_2SO_3), cetylpyridinium chloride monohydrate (CPC), sodium hydroxide (NaOH), dichloromethane (CH_2Cl_2), Tris-HCl buffer solution (pH of 7.4 and 8.8, respectively), xlenol orange (XO), and deionized water were purchased from Aladdin Industrial Corporation (Shanghai, China). Deionized water was supplied by the Xinjiang University (Xinjiang, China). A dialysis bag (MWCO 3000 Da) was purchased from Biotopped Technology Co., Ltd. (Beijing, China).

2.2. Instrumentation

Fluorescence spectra were recorded using a fluorescence spectrophotometer (F-4500 Hitachi, Japan) and the UV-vis spectrophotometer was recorded using a UV-3600 UV-vis spectrophotometer (General Analysis, China). Fourier-transform infrared (FT-IR) spectra were acquired with a Vertex 70 spectrometer (Bruker, Germany) using the KBr pellet sample preparation method. An advanced Advantage data system, X-ray photoelectron spectroscopy (XPS; Thermo Escalab 250Xi, USA), was used to maximize the amount of information extracted from the experimental data. Morphological granularity and lattice fringes of the CPC-CDs were observed by high-resolution transmission electron microscopy (HRTEM; JEM-2100 series, 200 kV). For comparison of the prepared sensor, an ICP-MS (Nex ION 300D) instrument was used to measure the concentration of heavy metals in real samples.

2.3. Preparation of CPC-CDs

CPC-CDs were synthesized using a previously reported method (Gao et al. 2019). 10 mL NaOH (330 mM; 0.132 g) was added to an aqueous solution of CPC (50 mM, 20 mL; 0.34 g) in a 50 mL conical flask. After ultrasonication in an ice bath for 6 h, CH₂Cl₂ was added to separate the upper water phase. This layer was repeatedly extracted until the solution was completely transparent. A dialysis bag (MWCO 3000 Da) was used to dialyze the CPC-CDs solution in deionized water for 24 h. Thus, interfering substances were removed and the solution was stored in a dark place at 4°C.

2.4. Preparation of fluorescent sensor arrays for metal ions sensing

The sensing array was prepared to sense elements under different pH environmental conditions (7.4 and 8.8). The differentiation of four metal ions (Cr⁶⁺, Fe³⁺, Fe²⁺, and Hg²⁺) ranging from 1, 10, 20, 30, 40, and 50 µM, were added to CPC-CDs (20 µL)/XO (2 µL, 500 µM) sensing solutions at different pH environments (7.4, 8.8). The total volume of each sample was maintained at 1.0 mL. Two groups of pH detection environments were designed, and 10 mM of 7.4 Tris-HCl buffer solution (5 mL, 1 M) and 10 mM of 8.8 Tris-HCl buffer solution (3.3 mL, 1.5 M) were diluted with deionized water to the pH detection conditions. In addition, the metal ions in binary mixtures were analyzed. Cr⁶⁺, Fe²⁺, and Hg²⁺ were selected to prepare binary mixtures with molar ratios of 0/20, 4/16, 16/4, and 20/0, and the total concentration of the two antibiotics was maintained at 20 µM.

After incubation, the fluorescence spectra of CPC-CDs at 535 nm were recorded at an excitation wavelength of 370 nm. The fluorescence response value was taken as the difference in FI in the presence or absence of metal ions. The fluorescence spectra showed a unimodal structure, and in the two groups of pH conditions, the denoising of FI at the peak position was denoted as I₁ and I₂, respectively.

To verify the predictive ability and reliability of the sensor array, nine replicates were measured for each experiment condition. Therefore, a training data matrix (two sensors × four metal ions × nine replicates) was developed, which was further analyzed using Python version 3.6.

2.5. Real samples preparation

The river water of Ulungur (Xinjiang, China) was selected as a representative sample of a real environment. The water sample was centrifuged at 14000 rpm for 6 min and the extracted supernatant was filtered with a microporous membrane with a pore size of 0.22 µm. The treated water sample was diluted 50 times using a Tris-HCl buffer solution (10 mM). Then, four metal ions were added to the real samples at concentrations of 1, 10, 15, and 20 µM, and a total volume of 1.0 mL of each sample was maintained. The fluorescence spectra of the samples were recorded at an excitation wavelength of 370 nm under two pH conditions. Each concentration of the four metal ions was set to nine times in parallel.

2.6. Statistical analysis

The array sensor detection data were processed and analyzed using a machine learning method based on Python 3.6. The gradient boosting machine (GBM) algorithm is a type of lifting algorithm. It uses

different weights to combine machine learning linearly to select the base learner with the best performance for model training(Wu et al. 2020; Guo 2021). The goal is to reconstruct the unknown

functional dependence $\mathbf{x} \xrightarrow{f} \mathbf{y}$ with our estimate $\hat{f}(\mathbf{x})$ to minimize the specified loss function $\Psi(y, f)$ (Alexey and Alois 2013; Liu and Zhang 2021):

$$\hat{f}(\mathbf{x}) = y,$$

$$\hat{f}(\mathbf{x}) = \arg \min_{f(\mathbf{x})} \Psi(y, f(\mathbf{x}))$$

3. Results And Discussion

3.1. Preparation and characterization of CPC-CDs

The morphology, optical, and structural properties of the CPC-CDs were characterized by TEM, UV-vis absorption spectra, fluorescence spectra, XPS, and FT-IR. The CPC-CDs exhibit spherical structures and good monodispersity, and relatively uniform size (in the range of 1.5 to 5.0 nm), with a mean diameter of 3.25 nm (Fig. 1a). A clear resolution of the grille fringe can be seen in high-resolution TEM (HRTEM) images, which reveals a typical fence spacing of 0.22 nm (Fig. 1b). As shown in Fig. 1c, the FT-IR spectrum of CPC-CDs confirmed the absorption peaks of the stretching vibrations of O-H/N-H at 3468 eV, indicating good water solubility(Hu and Gao 2020). The N=C structure was determined by the spectral bands at 1637.89 eV on the surface of CPC-CDs. The chemical compositions and bonds of the CPC-CDs were analyzed using the full-scan XPS profiles (Fig. 1d). Spectral analysis showed that the C1s, N1s, and O1s related peaks of the CPC-CDs were located around 284.80, 401.74, and 532.12 eV, respectively. In addition, the optical properties of the CPC-CDs, including the UV-vis and fluorescence spectra, were investigated. Under ambient light, the CPC-CD solution was light yellow. As shown in the UV-vis spectra in Fig. S1, the CPC-CD solutions emitted strong yellow fluorescence under irradiation with UV light (365nm). The maximum excitation and emission peaks were measured at 370 and 535 nm, respectively. The quantum yield (QY) of quinine sulfate in 0.1 M H₂SO₄ was 54%, while the QY of the CPC-CDs measured in aqueous solution was 24.8%, as shown in Fig. S2. This demonstrates a high photoluminescence QY and excellent optical properties.

3.2. Sensor array detection mechanism

In this study, a fluorescent sensor array was designed based on the internal filtering effect (IFE) for the rapid detection of heavy metals. In the IFE mechanism, complex functional group modification on the surface of CPC-CDs is not required, and there is no internal reaction between the analyte and CPC-CDs; thus, it simplifies the preparation process of the probe(Wang et al. 2018). To solve the problem of poor affinity between the fluorescent probe and the analyte, a small molecule linking arm (XO) was selected as

a receptor to connect the analyte and the fluorescent probe, forming a standard indicator–spacer–receptor (ISR) mode (Fig. 2)(Barati, Shamsipur, and Abdollahi 2016).

In the sensing system, metal ions form metal ion complexes that are connected to XO. In addition, the absorption spectra of the four metal ion complexes and the emission spectra of CPC-CDs have a good overlap region (Fig. S3). The spectral overlap indicates the possibility of an IFE. Hence, the addition of XO and metal ions to CPC-CDs can effectively reduce the FI of the CPC-CDs. To further verify the mechanism of fluorescence quenching, the UV-vis absorption spectra of CPC-CDs, four metal ion complexes, and their mixtures were measured, and the quantitative addition of the UV-vis absorption intensity of CPC-CDs and four metal ion complexes was calculated. As depicted in Fig. S4, the experimental curve (absorption spectrum of CPC-CDs and metal ion complex) is completely consistent with the theoretical curve (physical superposition line of absorption spectrum of CPC-CDs and metal ion complex). This indicates that no complex is formed between the CPC-CDs and the metal ion complex(Gao et al. 2018; Jing et al. 2017). Furthermore, the spectral overlap verifies the fluorescence quenching mechanism of IFE.

3.3. Design and fabrication of the sensor array

First, we measured the fluorescence response of the CPC-CDs in the pH range of 5 to 10 to obtain the optimal pH value for array detection. As shown in Fig. S5, within this pH range, the fluorescence emission intensity of the CPC-CDs and CPC-CDs/XO at a wavelength of 535 nm showed little difference. To further explore the construction principle of the sensor array, spectral measurement experiments were carried out to characterize the fluorescence patterns of the CPC-CDs in the presence or absence of XO and other metal ions. For example, at a pH value of 7.4, the FI of CDs showed a decreasing trend with the addition of XO (Fig. S6). Owing to the different complexation degrees and binding abilities of different kinds of metal ions and XO, the generated metal ion complex and CPC-CDs have different degrees of IFE effect, and the FI of CPC-CDs is quenched by four metal ion complexes in different degrees.

The diverse responses of the sensor array to different metal ions are shown in Fig. S7a. It is observed that the CPC-CDs/XO sensors exhibit different response modes to four metal ions according to $(I_0-I)/I_0$, as well as the obtained heat map (Fig. S7b, Fig. S7c, Fig. S7d, and Fig. S7e). It is verified that the sensor array detection system had a good differential fluorescence response for each analyte. Based on the successful identification of four metal ions, to investigate the selectivity of the method, we further considered the effect of a series of anions, as interfering substances, on the fluorescence of CPC-CDs/XO system. Figure S8 shows that distinct fluorescence quenching is observed when four metal ions was added to the CPC-CDs/XO solution, whereas no such effect is observed upon the addition while the fluorescence of CO_3^{2-} , HPO_4^{2-} , HCO_3^- , SO_3^{2-} and SO_4^{2-} . These anions did not disturb the employed system, which indicates that this sensing approach has a high selectivity toward four metal ions.

3.4. Optimization of the detection conditions

The next step was the optimization of the detection conditions to obtain the best sensor performance. Fluorescence titration experiments were conducted first to investigate the optimum XO concentration in

terms of an effective sensitizing of the sensor array (Fig. S9). Upon adding increasing amounts of XO to the Tris-HCl buffer solution, the fluorescence of CPC-CDs begins to quench. However, when the concentration of XO is too low, the chelation reaction between XO and metal ions is poor, and it is difficult to improve the specificity of the detection system. Therefore, we selected an XO concentration of 1 μ M as the best reaction concentration. Second, the reaction time was optimized, and the FI of CPC-CDs/XO at 535 nm increased with increasing reaction time. Finally, an optimal reaction time of as 7 min was obtained (Fig. S10). The CPC-CDs/XO sensor array with metal ions was incubated for 10 min (Fig. S11).

3.5. SX-model construction

Considering the complexity of the testing environment in practical applications, there is a lack of a unified model to improve the applicability and accuracy of the test conditions. Therefore, we put forward the SX-model to solve the defects of the above analysis methods. Based on machine learning algorithms, using TPOP in machine learning methods (e.g., SVM, LDA, Limit of Forest, deep learning, and decision tree) the gradient boosting classifier (GBC) function is screened to construct a GBM classification model. The model includes an input module, training module, prediction module, and output module. Finally, the FI data were used as the input of the model, with 90% (454) samples as training set and 10% (50) samples as the testing set. By optimizing the parameters of the training set, the eigenvalues of the samples can be learned effectively to improve the accuracy of the model prediction. For the selection of the highest accuracy model, we deleted the concentration of FI data labels through TPOT in the training set to feature selection and data structure, intelligently using a machine learning method on the data cube training. Finally, GBM was selected to build the classification model of metal ions and analyze and evaluate different machine learning methods for the applicability of the date cube by optimizing the model parameters, determining the final classification model and assessing their accuracy. The construction steps of the concentration model are the same as described above, and the concentration model was established using FI data as a module to depict the logical relationship between the samples. A regression model was established between the concentration of metal ions and the fluorescence data. In addition, a regression model between the concentration of each metal ion and the measured FI data was established using TOPT. The SX-model was established by combining the classification and concentration models. First, the classification model to obtain the category label, and then the concentration model with the classification label, was put in. The data were substituted into the regression model to obtain the concentration data.

3.6. Data analysis assisted by SX-model

In traditional array detection research, many modified fluorescent probes were synthesized to improve the specificity and accuracy of analyte detection. Fluorescence data were obtained to construct the analysis model. However, the process of probe synthesis often requires considerable time and cost. To simplify the synthetic steps and improve the metal ion detection specificity, we added a metal chelator by adjusting the pH environment. Each metal ion chelates with XO to different degrees in two pH environments, resulting in an IFE effect between the metal ion complex and the CPC-CDs. Two groups of different FI data were obtained and put into the SX-model to perform qualitative and quantitative analyses of various

metal ions in different environments. Under the action of the metal chelator, we enhanced the ability of the sensor array response signal to discriminate metal ions.

For each metal ion, the fluorescent response of the sensor array was tested nine times, and a training data matrix (two sensors $\times$ four metal ions $\times$ nine replicates) was obtained. Different concentrations of metal ions (1, 10, 20, 30, 40, and 50 μM) were identified. A total of 504 FI data was used to build the SX-model, and the accuracy of the SX-model was 95.45% (Fig. 3a and 3b). To verify the recognition ability of the sensor on unknown samples under the SX-model, 22 unknown samples were analyzed. The classification accuracy of the four metal ions was 95.45% (Table S1), and a good linear relationship between the true category and the predicted category with an R^2 of 0.9609 was observed (Fig. 3c). This shows that the predicted classification of the unknown samples is consistent with the real classification results. Based on the completion of the classification, the prediction accuracy of the sample concentration was 100% (Table S2). Furthermore, there was a good linear relationship between the true concentration and the predicted concentration. The linear fitting curve R^2 within the range of 0 to 50 μM was 100% (Fig. 3d). Therefore, qualitative and quantitative analyses of the four metal ions were successfully completed using the SX-model.

3.7. Differentiation of binary mixtures with SX-model processing

To further verify the ability of the CPC-CDs./XO sensor array to identify binary mixtures of metal ions, three binary mixtures ($\text{Cr}^{6+}/\text{Hg}^{2+}$, $\text{Fe}^{2+}/\text{Cr}^{6+}$, and $\text{Hg}^{2+}/\text{Fe}^{2+}$) at molar ratios of 0/20, 4/16, 16/4, and 20/0 were designed in the deionized water sample. As shown in Table S5, the 22 unknown samples were analyzed, which yields an accuracy was 95.45% (Fig. 4a and 4b). The value of R^2 of the corresponding curves of the true and predicted categories, and the linear fitting curves were 0.9018 (Fig. 4c). The concentration accuracy of the samples was 100% (Table S6). As shown in Fig. 4d, the 22 unknown samples were all distributed on the linear fitting curve between the true and predicted concentrations, with an R^2 value of 1.

3.8. Distinguishing metal ions in real samples

We tested four metal ions in lake water to develop sensor arrays for real environment applications. Lake water samples were used to prepare a pH-regulated fluorescence sensor array. Four kinds of single metal ions of different concentrations (1, 10, 15, and 20 μM) were added to the lake water samples, which resulted to 216 real samples. As shown in Fig. 5a and 5b, the accuracy rate of the SX-model in identifying the total samples in the lake water is 100%. Then, 15 unknown samples were selected and used to test the accuracy of the classification and concentration models. The category prediction of the 15 unknown samples was correct, and the linear fitting procedure yields R^2 of the real category and the predicted category, which amounts to 1 (Fig. 5c). The classification accuracy of the model for the unknown samples in the real environment was 100% (Table S3), indicating that the category prediction effect was good. The linear fitting curve R^2 of the relationship between the true concentration and the predicted

concentration in the lake water was 1 (Fig. 5d), while the concentration accuracy of the model for the unknown samples in the real environment was 100% (Table S4). This indicates that there is no deviation between the predicted and the true concentrations of the unknown sample. The above results demonstrate that the SX-model can accurately predict the classification and concentration of metal ions in a real lake environment. In addition, ICP-MS was used to verify the prediction results of the model (Table S9). The analysis results described above indicate that the sensor array can be used for qualitative and quantitative studies of a variety of metal ions with the assistance of the SX-model, and has the potential to detect metal ions in real environments.

In the same way, 11 unknown samples were selected from three binary mixtures ($\text{Cr}^{6+}/\text{Hg}^{2+}$, $\text{Fe}^{2+}/\text{Cr}^{6+}$, and $\text{Hg}^{2+}/\text{Fe}^{2+}$) in lake water. As shown in Table S7, all unknown samples were analyzed, and the classification accuracy was 90.90% (Fig. 6a and 6b). The value of R^2 of the corresponding curves of the true and predicted categories and the linear fitting curves is 0.6944 (Fig. 6c). The concentration accuracy for samples was 100% (Table S8), As shown in Fig. 6d, the 11 unknown samples were all distributed on the linear fitting curve between the true and predicted concentrations, with an R^2 value of 1.

4. Conclusion

In this study, we constructed a pH-regulated fluorescence sensor array by adjusting the pH environment of the solution and connecting CPC-CDs with metal indicators. Through chemical detection and data analysis, four types of heavy metals (Cr^{6+} , Fe^{2+} , Fe^{3+} , and Hg^{2+}) were identified and predicted. By building an SX-model to assist the fluorescence sensor array, the classification and concentrations of four single metal ions and binary mixtures of metal ions in deionized water and lake water can be effectively distinguished at a concentration of 1 μM . Based on the chelating effect of different metal ions, the best chelating metal indicator was selected comprehensively. A sensor array with sensitivity and selectivity was synthesized based on the ISR mode, which can be applied to complex media. The SX-model provides a unified prediction model, which is combined with a machine learning approach. Therefore, accurate identification and prediction can be achieved in both experimental and real samples. The fluorescent sensor array has great potential for rapid qualitative and quantitative analysis of various metal ions in the future.

Declarations

Acknowledgments

The writers gratefully acknowledge financial support the Xinjiang Uygur Autonomous Region Natural Science Foundation of China (No. 2019D01C068).

Author contributions

Yuying Liu: Conceptualization, Formal analysis, Writing - Original Draft. **Xiyuan Wang:** Writing - Review & Editing, Supervision, Project administration. **Jianjie Wei:** Methodology, Formal analysis. **Zijun Xu:** Conceptualization, Methodology, Writing - Original Draft, Writing. **Hao Liu:** Data Curation, **Tingting Yuan:** Writing - Review & Editing. **Qingdong Shi:** Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

(a) TEM (inset: size distribution of the CPC-CDs) and (b) HRTEM images of the CPC-CDs. (c) FT-IR spectra of CPC-CDs. (d) XPS survey scan of CPC-CDs.

Figure 2

Schematic diagram of fluorescence sensing based on the ISR analysis method.

Figure 3

Identification of four metal ions using the SX-model in deionized water (a) heat map of prediction results. (b) classified prediction confusion matrix heat map. (c) the linear fitting curve relationship between the true concentration and predicted concentration of unknown samples. (d) the linear fitting curve relationship between the true category and predicted category of unknown samples.

Figure 4

Identification of binary mixtures using the SX-model in deionized water. (a) heat map of prediction results. (b) classified prediction confusion matrix heat map. (c) linear fitting curve relationship between the true concentration and predicted concentration of unknown samples. (d) linear fitting curve relationship between the true category and predicted category of unknown samples.

Figure 5

Identification of the four metal ions using the SX-model in lake water. (a) heat map of prediction results. (b) the classified prediction confusion matrix heat map. (c) linear fitting curve relationship between the true concentration and predicted concentration of unknown samples. (d) linear fitting curve relationship between the true category and predicted category of unknown samples.

Figure 6

Identification of binary mixtures using the SX-model in lake water. (a) heat map of prediction results. (b) classified prediction confusion matrix heat map. (c) linear fitting curve relationship between the true concentration and predicted concentration of unknown samples. (d) linear fitting curve relationship between the true category and predicted category of unknown samples.

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