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SOLID PHASE EXTRACTION BASED ON Mn_3O_4-TIO_2 NANOCOMPOSITE FOR THE DETERMINATION OF MOLYBDENUM IN WATER SAMPLES

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Abstract. The Mn_3O_4-TiO_2 nanocomposite was applied as a new solid phase adsorbent for preconcentration of Molybdenum before determination by an UV-Vis spectrophotometer. The solid-phase extraction conditions as pH, the mass of sorbent, contact time, stirring speed, and the elution condition were investigated. Under optimized conditions, the adsorption capacity of adsorbent was 20.69 mg/g, and the elution condition was 0.2M NaOH solution. Molybdenum ions were determined based on its catalytic effect on the oxidation of 1-amino-2- naphthol-4-sulfonic acid (ANSA) with H_2O_2. The linear calibration graph was in the range of 0.2–2.5 µg/L ($r^2 = 0.995$) with a detection limit of 0.0502 µg/L. The relative standard deviation for five measurements of 2 µg/L of Mo (VI) was 3,37%. The method was applied to the determination of Molybdenum in water samples.

Keywords: Solid-phase extraction, Mn_3O_4-TiO_2 nanocomposite; Molybdenum; UV-Vis spectrophotometry

1. INTRODUCTION

Molybdenum (Mo) has been long known as a key micronutrient for plants, animals and microorganisms [1,2]. Mo containing enzymes hold important positions both in the biogeochemical redox cycles of carbon, nitrogen, and sulfur on earth [3] and in the metabolism of every individual organism [4]. Molybdenum exists very abundant in waters, soils and plants. Over the last few years, the Molybdenum compounds were used in many fields of industry as catalysis, lubrication, refractories, smoke suppressants, pigments, paints, fertilizer, and other allied industries. However, one thing is certain that the increased consumption of chemical grade Mo-products will lead to the increasing of seriously affection on living organisms and environment by these products [5]. Therefore, the development of method for the removal and determination of Mo becomes an important issue, especially in the field of the water environment. Many methods were published as inductively coupled plasma mass spectrometry (ICP–MS) [6, 7], inductively coupled plasma optical emission spectrometry ICP-OES [8], UV-Vis spectrometer [9, 10], etc. These methods have been used for the determination of Mo in a variety of samples. Therefore, it is usually necessary to carry out a separation and preconcentration step before the analysis. Some methods for separation and preconcentration of trace metal ions have been developed, including ion-exchange [11, 12], liquid-liquid extraction [13, 14], cloud point extraction ([15, 16], and solid-phase extraction (SPE) ([17, 18]. Compared with another method, SPE technique becomes more popular because of the fast, high enrichment factor, economic advantages and the ability of combination with different detection techniques. Some adsorbents have been used for the preconcentration of Mo ([19, 20, 21]. Among adsorbents, nano TiO_2 was often used for heavy metal removal from aqueous solutions because of its unique physical and chemical properties such as non-toxicity, large surface area, and a good adsorption capacity [22, 23]. Moreover, nano TiO_2 was modified to get higher adsorption capacity of heavy metal. Many works have been focused on the removal of Pb, Cd, Cu,...[24-28] instead of Mo. Hence, it is essential to find a fast and efficient adsorbent based on TiO_2 nanocomposite for removing Mo from water. In this study, Mn_3O_4-TiO_2 nanocomposite was synthesized and investigated for Mo extraction. Mo ions were determined based on its catalytic effect on the oxidation of 1-amino-2- naphthol-4-sulfonic acid (ANSA) with H_2O_2. The procedure was applied for the determination of Mo (VI) ions in water samples.

2. EXPERIMENTAL

2.1. Materials and reagents

All chemicals were of analytical grade reagents. Titanium dioxide Degussa P25 (TiO_2 P25) with a purity of 99.9% was supplied by Evonik Degussa (Germany). Manganese (II) chloride tetrahydrate ($MnCl_2.4H_2O$) was purchased from Shanghai Ruizheng Chemical Technology Co., Ltd. (China). The MoO_4^{-2} stock solution (1000 µg/L) was prepared with deionized water using ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$). Experimental solutions for adsorption and analysis were freshly prepared by diluting MoO_4^{-2} stock solution with distilled water.

2.2. Preparation of Mn_3O_4-TiO_2 nanocomposite

The Mn_3O_4-TiO_2 nanocomposite was prepared by the co-precipitation method [29]. In a typical procedure, 1.0 g of $MnCl_2·4H_2O$ was mixed with 50 mL of deionized water in a flask to wholly dissolved. The aqueous solution of 1.0 g TiO_2 was mixed with manganese (II) chloride tetrahydrate solution. The ammonia solution was gradually dropped into the mixture, until the pH value reached 10. The reaction was prolonged for 12 hours at 60°C with stirring speed of 300 rpm. The obtained Mn_3O_4-TiO_2 nanocomposite was washed with a 1:1 mixture of distilled water and ethanol, and then filtrated with 0.22 µm membrane. Finally, the product was dried at room temperature and further calcined at 400°C for 5 hours.

2.3. Characterization

Phase composition and structure of the Mn_3O_4-TiO_2 nanocomposite were detected by X-ray powder diffraction on a Bruker D2 Phaser diffractometer with CuKa radiation. Morphology of the samples was examined using a FE-SEM S4800 Hitachi scanning electron microscope with an accelerating voltage of 10.0 kV. The elemental analysis was carried out on an energy-dispersive X-ray (EDX) Micro Analyzer H-7593 (Horiba, Japan).

2.4. Solid-phase extraction and determination procedure

In the first step, 50.0 mg of the Mn_3O_4-TiO_2 nanocomposite was put into 100.0 mL of 25.0 µg/L Mo solution. Then, the pH of the solution was adjusted to 3.5, and the solution was stirred with a magnetic stirrer for 1 hour to facilitate the adsorption of the Mo ions onto the nanocomposite. After that, the adsorbent was separated via centrifugation. In the next step, the adsorbed Mo ions were eluted from the Mn_3O_4-TiO_2 nanocomposite adsorbent with 20 mL of 0.2 M NaOH solution by ultrasonication for 1 hour. Finally, the adsorbent was removed by centrifugation and the supernatant was collected for the determination of Mo (VI) by UV-Vis spectrophotometry.

The determination of Mo (VI) was studied based on its catalytic effect on the oxidation of 1-amino-2-naphthol-4-sulfonic acid (ANSA) with H_2O_2. The reaction increased the spectrophotometric absorbance of the oxidized product of ANSA at 465 nm after 30 min of mixing the reagents [10]. The reaction conditions as pH, ANSA concentration, H_2O_2 concentration, and temperature were optimized in sequent for Mo (VI) determination. The 5 mg/L solution of diethylenetriaminepentaacetic acid (DTPA), 5 mg/L solution of NaF, and 5 mg of NaN_3 were added to confer high selectivity for the proposed method. Following the recommended procedure, Mo (VI) could be determined with a linear calibration based on $\Delta A=A_1-A_0$ and Mo (VI) concentration (in which A_1 with the catalytic effect of Mo (VI), A_0 without the catalytic effect of Mo (VI)).

The application of method implemented to the determination of Mo (VI) in tap, ground, and river water samples that were collected from locations in Ho Chi Minh City, then filtered through 0.22 µm membranes and adjust to pH ≤3.5 before use. The acidified samples were stored at 4°C until the day of analysis [30]. Before the analysis step, the water samples were heated up to room temperature. The adsorption, desorption and determination of Mo (VI) ions in water samples were carried out following the above procedures.

3. RESULTS AND DISCUSSION

3.1. Characterization of Mn_3O_4-TiO_2 nanocomposite

The SEM images of Mn_3O_4-TiO_2 nanocomposite are presented in Fig. 1a. As shown in Fig. 1a, TiO_2 nanoparticles consist of uniform near-spherical grains with a diameter of 50 nm [31]. The SEM images of Mn_3O_4-TiO_2 nanocomposite, as shown in Fig. 1b with a scale bar of 1µm indicated that Mn_3O_4 grains of bigger sizes about 100 nm were mixed with TiO_2 nanoparticles. The elemental composition analysis (Fig. 1c) indicated that the synthesized Mn_3O_4-TiO_2 nanocomposite contained the main elements of composite components, such as Ti, O, Mn. Further, the EDX mapping analysis also shows the uniform distribution of each element on the surface of the composite (Fig. 1d), indicating the successful synthesis of Mn_3O_4-TiO_2 composite.

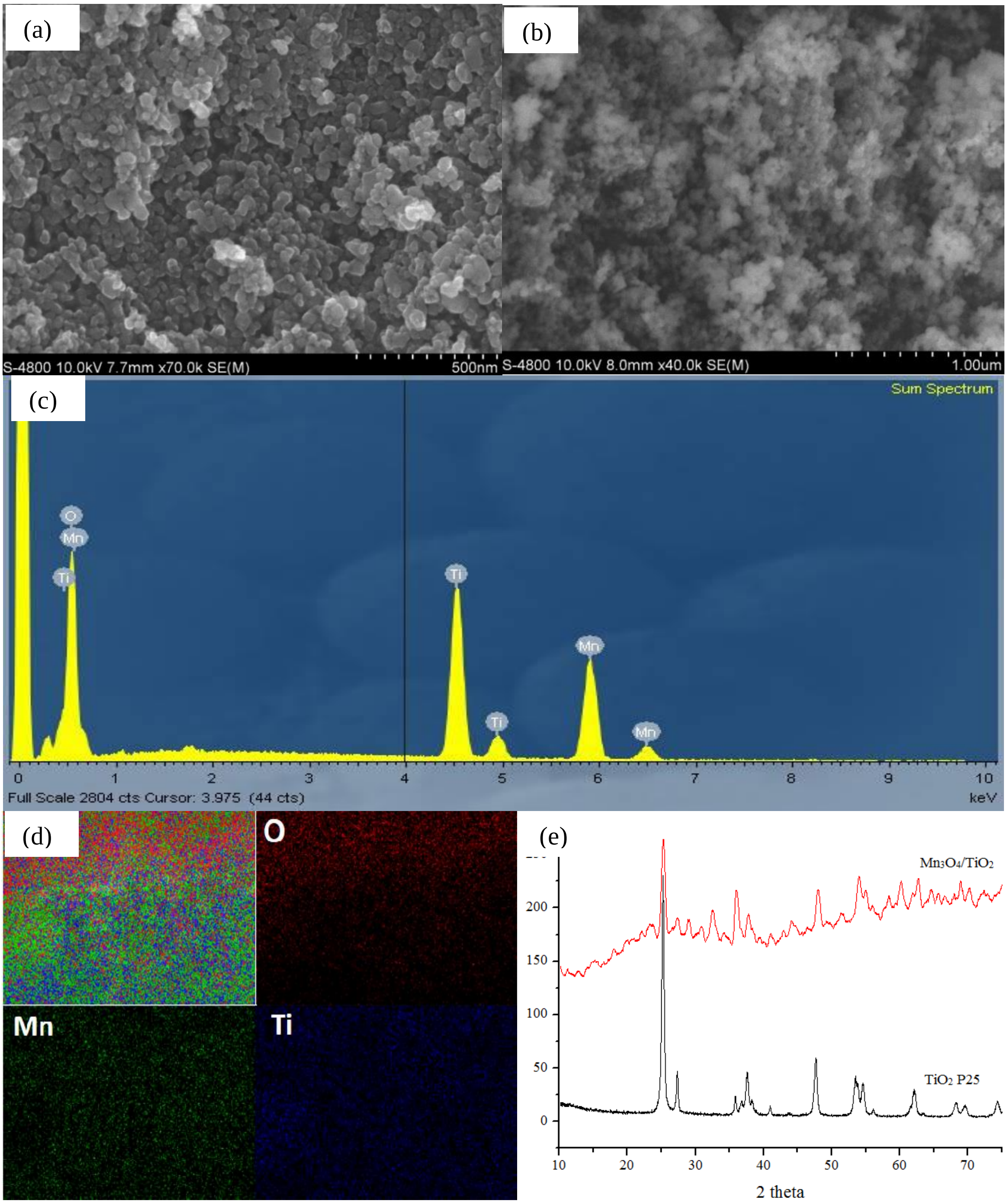

Figure 1. a) SEM images of TiO_2; b) Mn_3O_4-TiO_2; c) EDX spectrum; d) Elemental mapping results; e) X-ray diffraction spectrums of Mn_3O_4-TiO_2.

Fig. 1e shows XRD spectrum of TiO_2 nanoparticles and its synthesized Mn_3O_4-TiO_2 nanocomposite. As shown in Fig. 1e, the obtained XRD pattern of TiO_2 P25 revealed peaks at 2θ of 25.5, 41.6, 47.8, 55.8, and 62.1, which are assigned to TiO_2 present in the synthesized product. The XRD pattern also showed some additional peaks at 2θ of 29.1, 31.0, 32.5, 36.3, 38.2, 44.5, 50.9, 58.7, and 60.0, which indicated the presence of manganese oxide grown in the tetragonal form [29, 32, 33]. Totally, the characterization studies using morphology analysis, EDX, and XRD confirmed the successful synthesis of Mn_3O_4-TiO_2 nanocomposite, ready for Mo (VI) ion adsorption and determination.

3.2. Effect of parameters on the solid-phase extraction process

3.2.1. Effect of pH

It's well known that pH value has a critical role in adsorption of Mo (VI) ions. Therefore, a series of solutions with 25 µg/L of Mo (VI) as the initial concentration was adjusted to a pH range of 2 ÷ 7 by 0.1 M HCl or 0.1 M NH_4OH solutions.

As can be seen in Fig. 2a, the adsorption efficiency increases in the increase of pH from 2 to 4, almost reaches a maximum at pH = 3.5, and then decreases with the increasing pH. As we have known, the effect of pH on Mo (VI) adsorption depended apparently on the charge properties of both Mo (VI) and Mn_3O_4-TiO_2 nanocomposite in solution. Following [34], the distribution of Mo (VI) ions in solutions could be summarized as MoO_4^{2-}, $HMoO_4^-$, H_2MoO_4,$Mo_7O_{21}(OH)_3^{3-}$, $Mo_7O_{21}(OH)_2^{4-}$, $Mo_7O_{23}(OH)_5^-$, and $Mo_7O_{24}^{6-}$. Clearly that, almost species of Mo (VI) are anions except H_2MoO_4. It should also be noted that anions are preferably adsorbed at low pH [35]. Moreover, as reported in literature [8, 36], for Mo (VI) as molybdate, the two pK_a values were found out within a narrow pH interval around pH 4. It is explainable and could be rather attributed to the tendency of Mo (VI) adsorption in weak acidity medium. On the other hand, the surface of the Mn_3O_4-TiO_2 adsorbent subjected to protonation is also dependent on the pH solution. Following [37, 38] point of zero charges of TiO_2 is at pH between 5.6 and 6.4. At this point, positive charges of TiO_2 $(Ti(OH)_2)^+$ are formed predominately. However, following [39], Mn_3O_4 nanoparticles distributed a positively-charged surface at pH=3. In the aggregation form, it can be showed that the positively-charged surface of the Mn_3O_4-TiO_2 nanocomposite arises from the protonation process in weak acid solution. According to the experimental data, the adsorption efficiency of Mo (VI) on Mn_3O_4-TiO_2 adsorbent was reached maximum at pH =3.5, so pH = 3.5 was chosen for further studies.

3.2.2. Effect of the mass of sorbent

The dosage of Mn_3O_4-TiO_2 nanocomposite adsorbent is also an important factor on the quantitative adsorption of Mo (VI) ions in aqueous solution. The effect of amount of Mn_3O_4-TiO_2 adsorbent on the adsorption of Mo (VI) at optimal pH was examined in the range of 10 ÷ 200 mg. As can be seen in Fig. 2b, the quantitative recoveries were obtained in a range of 50 ÷ 200 mg of Mn_3O_4-TiO_2 adsorbent. Therefore, a dosage of 50.0 mg of adsorbent was chosen as optimal for further studies.

3.2.3. Effect of contact time and stirring speed

Contact time and stirring speed also play a crucial role in the adsorption of Mo (VI) ions onto the Mn_3O_4-TiO_2 nanocomposite adsorbent. The period of contact time (30 ÷ 180) min and stirring speed (100 ÷ 400) rpm were studied for the absorption rate of Mo (VI) ions by the adsorbent. Fig. 2c shows that the adsorption capacity of Mo (VI) ions was about 95.6% for 30 min and reached a maximum of 100% after 60 min.

The effect of stirring speed on adsorption capacity of Mo (VI) ions onto Mn_3O_4-TiO_2 nanocomposite adsorbent is presented in Fig. 2d. It's been found that the adsorption capacity of Mo (VI) ions reached the maximum at the stirring speed of 300 rpm. Therefore, a contact time of 60 min and a stirring speed of 300 rpm were selected for further studies.

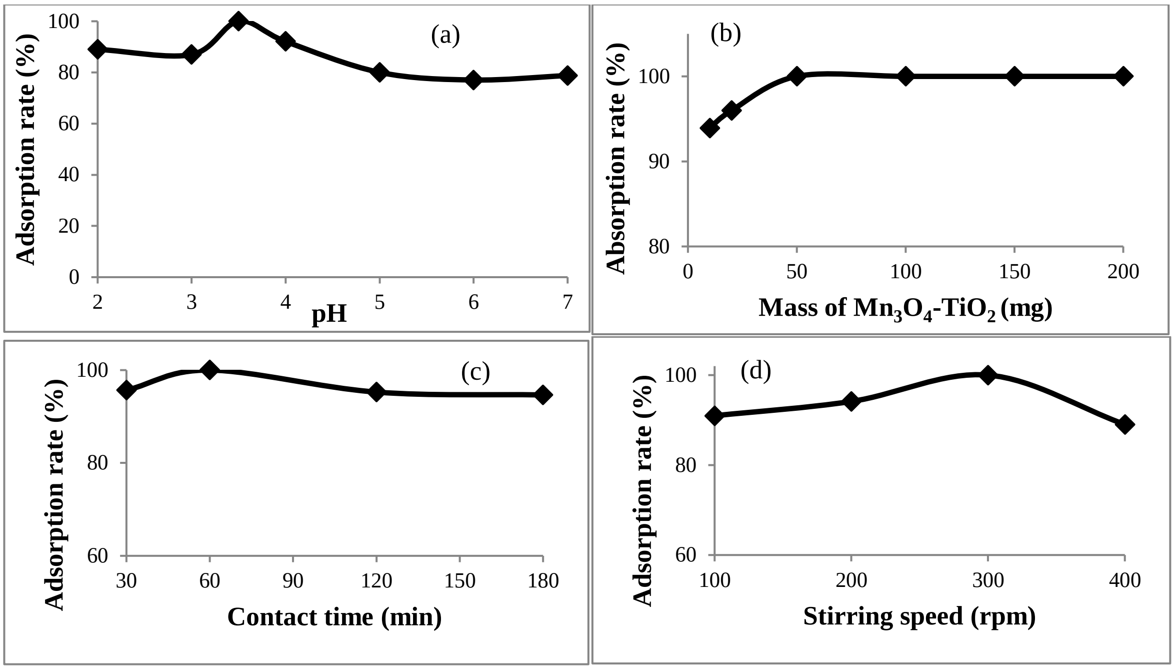

Figure 2. Effect of (a) pH; (b) mass of sorbent; (c) contact time; (d) stirring speed on adsorption rate of Mo (VI). Conditions: Mo (VI): 25 µg/L, sample volume: 100 mL, room temperature.

3.2.4. Elution study

The elution study was carried out at room temperature using four different concentrations of NaOH solutions (0.05 M, 0.1 M, 0.2 M, 0.4 M). Every 50.0 mg Mn_3O_4-TiO_2 were first reacted with 25 µg/L Mo (VI) solution at pH = 3.5 within 60 min at the stirring speed of 300 rpm. Subsequently, the adsorbents were washed with distilled water to remove excess salts, and NaOH solutions were added into adsorbent samples to initiate the elution process. The suspensions were ultrasonicated for 1 hour, and the adsorbents were then centrifuged to separate from the solutions. The elution efficiency was calculated from the amount of Mo (VI) released into the solutions [8]. The result as Fig. 3a displayed about 70 ÷ 96% Mo (VI) elution rate under investigated NaOH concentrations. It indicated that OH^- ions can replace Mo (VI) as molybdate anions from the adsorbent sites on Mn_3O_4-TiO_2 nanocomposite adsorbent [40]. The elution rate had the highest efficiency when 0.2 M NaOH concentration solution was used, thus, the concentration of 0.2 M of NaOH solution was selected for further studies.

3.3. Adsorption capacity

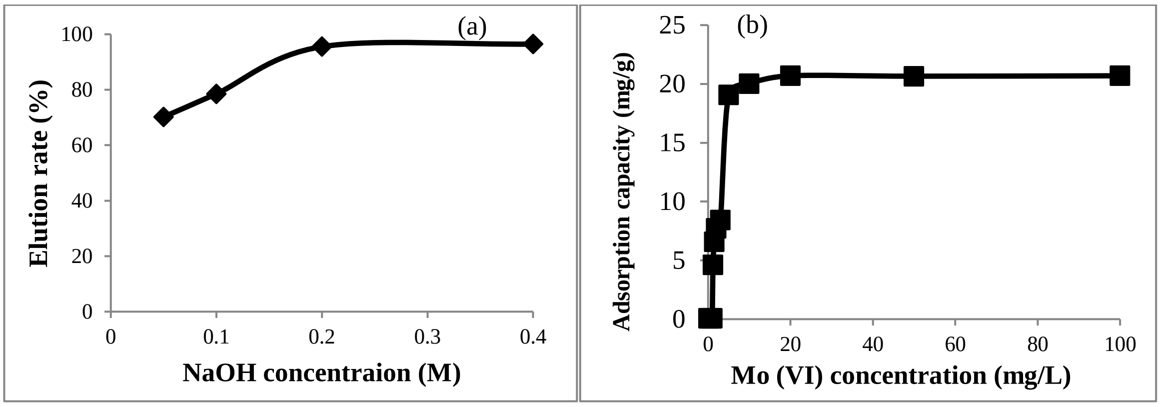

Figure 3. (a) Elution rate of Mo from Mn_3O_4-TiO_2 adsorbent; (b) Adsorption capacity of Mn_3O_4-TiO_2 nanocomposite adsorbent for Mo (VI);

The adsorption capacity is one of the important factors because it determines how much adsorbent is required to quantitative determination of the Mo (VI) ions from a given solution. For estimation of the Mo

(VI) ion adsorption capacity on Mn_3O_4-TiO_2 nanocomposite adsorbent, 100.0 mL Mo (VI) sample solutions with different concentrations (0 – 100.0 mg/L) were adjusted to pH 3.5 and individually mixed with 50.0 mg Mn_3O_4-TiO_2 adsorbent. These mixtures were stirred at 300 rpm for 1 hour at room temperature. The above described procedures of preconcentration, separation, and determination processes of Mo (VI) were applied. Fig. 3b shows the initial Mo (VI) concentration was increased untill the plateau value (adsorption capacity value) obtained. The result indicates that adsorption capacity of Mn_3O_4-TiO_2 nanocomposite adsorbent for Mo (VI) ions was experimentally found to be $\approx$ 20.69 mg/g.

3.4. Molybdenum determination

3.4.1. UV-Vis optimal spectrophotometry conditions

Optimal conditions for the determination of Mo have been done referring to [10] and resulted in Fig. 5. The Fig. 4 shows optimal conditions for Mo determination including: (a) pH = 5, (b) ANSA concentration = 4,8 mM, (c) H_2O_2 concentration = 20 mM and (d) temperature = 40^{o}C. The above results using $\Delta A = A_1 - A_0$ with the absorbance of the uncatalyzed reaction, A_0 and that of the reaction catalyzed by 2.0 µg/L Mo (VI), A_1.

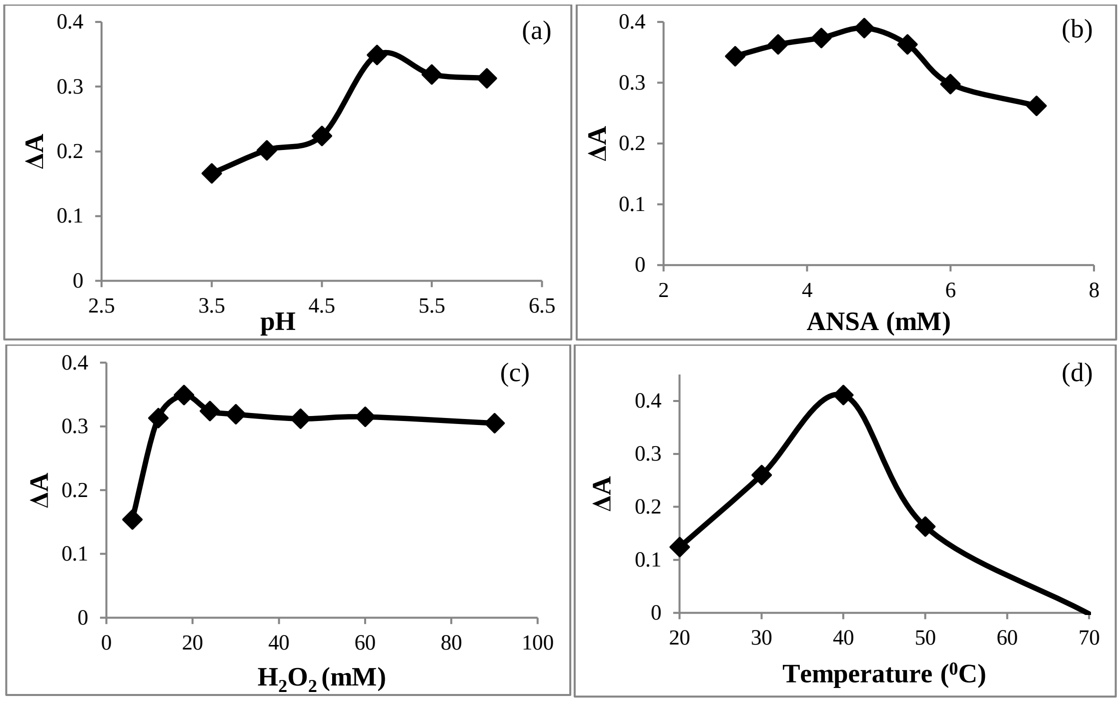

Figure 4. Optimal conditions for Mo determination: (a) pH; (b) ANSA concentration, (c) H_2O_2 concentration; (d) Temperature.

3.4.2. Calibration graph and detection limit

The calibration graph (Fig. 5) performed following the recommended procedure gave a linear relationship (r^2 = 0.995) between the ΔA and Mo (VI) concentration up to 2.5 µg/L. The detection limit, calculated as three times the standard deviation of the blank divided by the slope of the calibration curve was 0.0502 µg/L Mo (VI) concentration. The quantity limit, calculated as ten times the standard deviation of the blank divided by the slope of the calibration curve was 0.1676 µg/L Mo (VI) concentration, and the RSD% was 3,37% (n = 5).

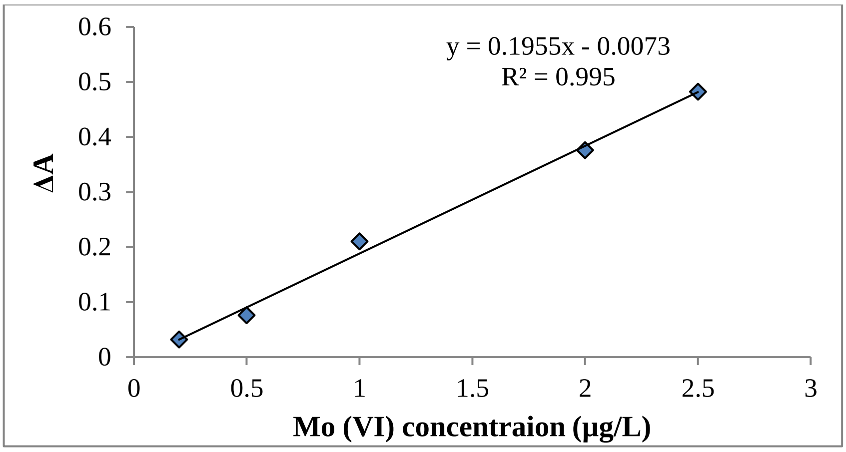

Figure 5. Calibration graph for Mo (VI) determination with above optimal conditions.

3.4.2. Determination of Mo (VI) in water samples

The preconcentration applicability of the Mn_3O_4-TiO_2 nanocomposite was further investigated with the determination of Mo (VI) in real water samples. The Duong Quang Ham river water sample, ground, and tap water samples, were filtered by 0.22 µm filter membranes, then spiked with Mo (VI) solution with 1 µg/L concentration and analyzed following the proposed method. As shown in Table 1, good recovery rates of 94.1–95% are achieved, indicating the preconcentration applicability of Mn_3O_4-TiO_2 nanocomposite adsorbent and the method in the analysis of Mo (VI) based on its catalytic effect on the oxidation of 1-amino-2- naphthol-4-sulfonic acid with H_2O_2 were reasonable for trace Mo (VI) analysis in water samples.

Table 1. Determination of Mo (VI) ion in water samples using the proposed methodology

Sample		Mo(VI) concentration (µg/L)				
		Proposed kinetic method				Reference SMEWW:3120
Number	Type	Added	Found±SD	RSD%	Recovery%	Found±SD
1	Duong Quang Ham River	-	3.020 ± 0.061	2.02		ND* (with LOD 10µg/L)
		1.0	3.961 ± 0.006	0.15	94.1	
2	Ground water	-	1.890 ± 0.060	3.17		
		1.0	2.835 ± 0.004	0.15	94.5	
3	Tap water	-	1.370 ± 0.037	2.70		
		1.0	2.320 ± 0.007	0.30	95.0	

*ND: Not detected

4. CONCLUSION

The proposed Mn_3O_4-TiO_2 nanocomposite was synthesized and successfully employed for the preconcentration and determination of molybdenum in water samples by UV-Vis. The optimal pH for the maximum adsorption was found to be 3.5 using 50.0 mg adsorbent in the contact time of 60 min with stirring speed of 300 rpm. The elution study resulted that Mo can be released from Mn_3O_4-TiO_2 nanocomposite adsorbent in OH^- solution. The proposed method has advantages of simple procedure in using a minimal amount of adsorbent, good accuracy, and gives a low detection limit. This study can be considered as a reasonable nonpolluting technique for the preconcentration and determination of trace molybdenum in water samples.

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XÁC ĐỊNH MOLYBDEN TRONG MẪU NƯỚC SỬ DỤNG KỸ THUẬT CHIẾT PHA RẮN VỚI VẬT LIỆU NANO Mn_3O_4-TiO_2

TRẦN THỊ THANH THÚY, ĐOÀN VĂN ĐẠT, NGUYỄN XUÂN HÙNG, TRƯƠNG THỊ UYÊN

Tóm tắt. Vật liệu nano Mn_3O_4-TiO_2 được tổng hợp và ứng dụng làm chất hấp phụ pha rắn để chiết Molybden trong mẫu. Các điều kiện tối ưu của kỹ thuật chiết pha rắn như pH, khối lượng chất hấp phụ, thời gian hấp phụ, tốc độ khuấy và điều kiện rửa giải được khảo sát. Với các điều kiện tối ưu, khả năng hấp phụ của vật liệu là 20.69 mg/g và nồng độ chất rửa giải NaOH là 0.2M. Molybden được xác định bằng phương pháp phổ hấp thu phân tử dựa vào sự xúc tác của Molybden cho phản ứng oxi hóa giữa 1-amino-2- naphthol-4-sulfonic acid và H_2O_2. Khoảng nồng độ Molybden tuyến tính trong khoảng 0.2–2.5 µg/L ($r^2 = 0.995$) với giới hạn phát hiện là 0.0502 µg/L. Độ lệch chuẩn trong 5 lần xác định là 3,37%. Phương pháp được áp dụng để xác định Molybden trong các mẫu nước.

Từ khóa. Chiết pha rắn, Mn_3O_4-TiO_2 ; Molybden; Phổ hấp thu phân tử.

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