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Amino-functionalized multi-layer core-shell mesoporous organosilica nanospheres for Cr(VI) removal

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Abstract: Developing low-cost and highly efficient adsorbents for the removal of toxic heavy metal ions has been the subject of intensive research with the increasingly stringent water pollution control standards. In this paper, three types of amino-functionalized multi-layer core-shell mesoporous organosilica nanospheres (MCMONs) have been synthesized using an indirect co-condensation method for Cr(VI) removal applications. Results show that amino groups have been successfully immobilized on the nanospheres and these amino-functionalized MCMONs exhibit unique organic-inorganic multi-layer core-shell structures. When used as adsorbent for Cr(VI) removal, our N-(3-trimethoxysilylpropyl)diethylenetriamine functionalized MCMONs exhibits an maximum adsorption capacity of 279.92 mg/g at initial Cr(VI) concentration of 150 mg/L. This is about 20% greater than the highest Cr(VI) adsorption capacity previously reported for other core-shell silica-based adsorbents, demonstrating the great potential of our MCMONs in Cr(VI) removal applications.

Keywords: multi-layer, core-shell, amino-functionalization, mesoporous organosilica, Cr(VI) removal

1. Introduction

The fast-paced economic development and industrial production have led to various environmental problems and water pollution is considered as one of the most challenging issues. Heavy metals, in particular, hexavalent chromium Cr(VI), is one of the most prominent water pollutants. Being a manufacturing byproduct of various large scale industrial processes (e.g., electroplating, metallurgy, tanning, paints, dyes and fertilizer production etc), Cr(VI) is highly mobile, water-soluble and carcinogenic ^[1-3] and has posed a severe threat to the ecological environment as well as human health ^[4-6]. Unfortunately, not many industries have taken proper measures in toxic waste treatment before its release into the environment. For China's electroplating industry alone, there is on average 4000 million tons of Cr-polluted water produced every year ^[7], leading to a severe challenge in meeting the anti-pollution guidelines recommended by the World Health Organization (0.05 ppm) ^[8]. To address the problems of increasing ecological toxic burden and its subsequent impact on the public health, effective solutions for Cr(VI) removal are urgently needed.

To date, various technologies, such as precipitation ^[9], ion exchange ^[10-11], electrodepositing ^[12], membrane separation ^[13], etc., have been proposed for Cr(VI) removal. However, most of these involves high cost, high manufacturing energy consumption, and production of secondary pollutants. In contrast, the adsorption method is proven to be simple, efficient and cost-effective for heavy metal ions removal ^[14-20]. Various adsorbents, such as activated carbon ^[21-22], polymers ^[23-26], biosorbents ^[27], and mesoporous silica-based materials ^[18, 28-30] have been proposed

and studied extensively. Among these, mesoporous silica-based materials are considered as one of the most promising candidates for heavy metal removal applications due to their non-toxicity, ease of surface functionalization, and high adsorption efficiency ^[31-35].

The high concentration of silanol (Si-OH) groups on the surface of mesoporous silica-based materials can enable incorporation of various active groups (e.g., amino) with strong heavy metal chelating capability ^[36-37]. On the other hand, development of organoalkoxysilanes on mesoporous silica can enable immobilization of various functional groups which may further enhance the adsorption capacity and selectivity for heavy metal ions. As a result, much research effort has been directed towards the fabrication of amino-functionalized mesoporous silica-based adsorbents for the removal of Cr(VI) ^[38-42]. Unfortunately, most of the existing functionalized mesoporous silica-based adsorbents still demonstrate insufficient adsorption capacity, limiting their practical applications.

Recently, core-shell structured mesoporous silica-based materials consisting of magnetic nanoparticle cores have attracted increasing research interest ^[43-49]. For instance, Sun et al. ^[45] prepared Fe₃O₄-SiO₂-CTS-PEI which demonstrated a maximum Cr(VI) adsorption capacity of 236.4mg/g. S. Egodawatte et al. ^[46] synthesized Fe₃O₄@SiO₂@Kit-6-NH₂ nanoparticles by a post-grafting method, and the maximum Cr(VI) adsorption capacity was 185.2mg/g. However, despite the enhanced heavy metal ions adsorption capacity demonstrated by such systems, the easy agglomeration of magnetic nanoparticles may present challenges to their

synthesis and handling, and achieving further enhanced adsorption capacity still remains a challenge. It is therefore of interest to explore new avenues towards the synthesis and application of non-magnetic core-shell structured mesoporous silica-based materials for enhanced Cr(VI) adsorption performance.

We hypothesize that by increasing the amino group density on the mesoporous silica surface, a greater adsorption capacity can be achieved. In this work, amino-functionalized mesoporous organosilica nanospheres with multi-layer core-shell structures (MCMONs) were synthesized deploying an indirect co-condensation method. Three types of adsorbents have been produced, where both the core and shell structures consist of amino-functionalized organosilica (amino-organosilanes containing one, two, or three amino groups were deployed, respectively). The Cr(VI) removal efficiency of these novel amino-functionalized MCMONs has been investigated and the regeneration of these materials was assessed.

2. Experimental

2.1 Chemicals

Tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), concentrated ammonia aqueous solution (25~28wt%) and anhydrous ethanol were purchased from Chengdu Jinshan Chemical Reagent Co., Ltd., China. 1,2-Bis(triethoxysilyl)ethane (BTSE, 96%) and 3-aminopropyltriethoxysilane (1N silanes, 99%) were supplied by Shanghai Aladdin Co. Ltd., China. N-(3-Triethoxysilylpropyl)ethylenediamine (2N silanes, 98%) was supplied by Xiya Reagent Co. Ltd., China.

N-(3-trimethoxysilylpropyl)diethylenetriamine (3N silanes, 95%) was supplied by Shanghai Yuanye Bio-Technology Co. Ltd., China. The chemical structures of the amino-organosilanes used in this study are shown in Figure 1.

Figure 1 The chemical structures of three types of amino-organosilanes used in this study

2.2 Materials Synthesis

Amino-functionalized mesoporous organosilica cores were prepared using a sol-gel method. More specifically, CTAB (0.96 g) was dissolved in a mixture of ethanol (180 mL), water (450 mL), and concentrated ammonia aqueous solution (6.0 mL) under 60 °C and stirred for 1 h. A mixture of silane precursors (TEOS and BTSE) was then added and the obtained mixture followed by stirring under 60 °C for 12 h. The mixture was then divided into three equal portions, to which different amino-organosilanes, namely, 1N silanes (0.4 mL), 2N silanes (0.3 mL) and 3N silanes (0.25 mL), were added respectively to achieve different surface functionalization. The resultant three mixtures were stirred under 60 °C for another 12 h, and white reaction products can be obtained. These as-prepared materials were then used as the inner core and template for the assembly of the mesoporous

organosilica shell and the subsequent amino-functionalization.

To obtain the amino-functionalized mesoporous organosilica shell structure, a mixture of TEOS (0.25 mL) and BTSE (0.25 mL) was first added to the three mixtures obtained earlier, stirred under 60 °C for 12 h. 1N silanes (0.4 mL), 2N silanes (0.3 mL) and 3N silanes (0.25 mL) were then added into the three resulting mixtures, respectively, followed by stirring under 60 °C for another 12 h, and the precipitates were collected by centrifugation and washed with ethanol. The products were re-dispersed in water and transferred to Teflon-lined stainless-steel autoclaves under 120 °C for 5 h. Upon cooling to room temperature, the products were collected through centrifugation. Finally, the CTAB templates were removed from all samples in a solution containing ethanol (194 mL) and concentrated HCl (6 mL, 37%) at 60 °C for 6 h, and the process was repeated three times. The final extracts were washed with ethanol several times and dried in a vacuum oven. The resultant products were multi-layer core-shell structured mesoporous organosilica nanospheres functionalized with 1N silanes, 2N silanes and 3N silanes, respectively, (namely, 1N-MCMONss, 2N-MCMONs, and 3N-MCMONs).

1N silanes functionalized mesoporous organosilica nanospheres (1N-MONs) inner cores and pure core-shell mesoporous organosilica nanospheres (pure MCMONs) without any amino-functionalization were also prepared and used as references for comparison. The detailed synthesis process has been described by the schematic in Figure 2.

Figure 2 The synthesis process and Cr removal mechanisms of amino-functionalized MCMONs

2.3 Characterization methods

The morphologies and dispersion of the nanospheres were characterized by scanning electron microscopy (SEM, JSM-7500F, JEOL, Japan). The detailed materials surface/interface structures were further investigated using transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, FEI, America) under an acceleration voltage of 200 kV. The mesoporous silica structure was studied by low angle X-ray diffraction (XRD, EMPYREAN, PANalytical B.V., Holland) with Cu K α radiation (0.15406 nm) in the range $2\theta = 0.5^{\circ} \sim 10^{\circ}$ with steps of 0.02° . Fourier transform infrared spectroscopy (FT-IR) was carried out using a Thermo Electron Corporation Nicolet 6700 pattern FT-IR spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos Analytical Ltd., UK) with Al K α X-ray source was used to provide information on the materials surface chemical

composition. A nitrogen adsorption experiment was performed at 77 K on a Micromeritics ASAP 2460 system, the specific surface area and pore size distribution were analyzed by Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods, respectively. The total pore volume of the samples was calculated at $P/P_0 = 0.99$.

2.4 Cr(VI) adsorption

Cr (VI) adsorption experiments were carried out under room temperature (25 °C) for all adsorbents. On reaction with 1,5-diphenylcarbazide, Cr(VI) can form a purple 1,5-diphenylcarbazide-Cr(VI) complex, which gives a characteristic adsorption intensity at wavelength of 540 nm under UV-vis analysis. The Cr(VI) containing solutions before and after the adsorption tests (supernatant separated from centrifugation) were analyzed using a UV-vis spectrometer (UV-1000, AOE instrument, China) and the adsorption intensity can be correlated to the Cr(VI) concentration. The effects of different adsorption time, solution pH and initial Cr(VI) concentration have been investigated. The adsorbent dose used is 0.2 g L⁻¹ unless otherwise stated.

The Cr(VI) removal efficiency (R%) of the adsorbent was calculated using Equation. (1):

$$R\% = \left(\frac{C_0 - C_e}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C_e are the initial and final Cr(VI) concentrations, respectively.

The equilibrium adsorption capacity q_e (mg g⁻¹) can be associated to the Cr(VI)

adsorbed onto adsorbents, Equation (2):

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (2)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium Cr(VI) concentrations, respectively, V (L) is the volume of Cr(VI) solution, and m (g) is the mass of the adsorbent.

3. Results and discussion

3.1 Materials characterization

The morphologies and structures of 1N-MCMONs, 2N-MCMONs and 3N-MCMONs have been characterized using SEM and TEM, see Figure 3. All three samples display uniform spherical shape with an average diameter of ~ 500 nm, 500 nm and 420 nm, respectively. In contrast to 1N-MCMONs (Figure 3a), both 2N-MCMONs and 3N-MCMONs (Figure 3b, c) exhibit much rougher surface, which may favor Cr(VI) adsorption.

All samples show core-shell structures (Figure 3d-i), where both the cores and shells consist of amino-functionalized mesoporous organosilica. The diameter of cores and thickness of shells are about 406 and 52 nm for 1N-MCMONs, 383 and 50 nm for 2N-MCMONs, and 345 and 41 nm for 3N-MCMONs, respectively. Under hydrothermal reaction, the degree of cross-linking of the organosilica framework is higher on outer surface than on the inner surface, hence nucleation centers can be found at the core-shell interface during the shell formation process for the re-organization of the mesoporous organosilica frameworks ^[50]. As a result, a separation at the interface of the core and shell can be expected, see Figure 3 (g-i).

Figure 3 SEM images of (a) 1N-MCMONs, (b) 2N-MCMONs and (c) 3N-MCMONs; TEM images of (d, g, h) 1N-MCMONs, (e, i) 2N-MCMONs and (f) 3N-MCMONs

Low angle XRD patterns for all adsorbents were examined to confirm the presence of mesoporous structure, see Figure 4. A distinct peak at $2\theta=0.83^\circ$ seen for pure MCMONs, 2N-MCMONs and 3N-MCMONs provide indication on the presence of ordered mesostructure. These visible peaks on 2N-MCMONs and 3N-MCMONs suggest that mesoporous structures were mostly retained after the introduction of 2N silanes or 3N silanes ^[51]. In contrast, 1N-MCMONs display a broader and weaker diffraction peak at $2\theta=0.83^\circ$, suggesting 1N silanes did not favor the mesoporous structure ^[52].

Figure 4 X-ray diffraction patterns of pure MCMONs, 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Figure 5 shows the FT-IR spectra of pure MCMONs and amino-functionalized MCMONs. The adsorption peaks at ~ 450 , 783 and 1056 cm^{-1} can be assigned to the siloxane (Si-O-Si) group, and the stretching peak of C-H around 2927 cm^{-1} is present in all MCMONs. The presence of C-N stretching vibration ($1200\text{-}1000\text{ cm}^{-1}$ [53]) cannot be manifested due to the overlapping vibration of Si-O-Si at around 1056 cm^{-1} and Si-CH₂-R in the range of $1250\text{-}1200\text{ cm}^{-1}$ [54]. The broad spectral peak at about 3434 cm^{-1} normally corresponds to water molecules adsorbed or hydrogen-bonded to the organic-inorganic framework [55]. However, widening of the peak in this region has been observed for all of the amino-functionalized MCMONs (Figure 5b-d), suggesting the potential emergence of new NH₂ peaks in the range of $3400\text{-}3250\text{ cm}^{-1}$ [56]. The peak around 1657 cm^{-1} in pure MCMONs can be assigned to the surface Si-OH stretching. When compared with pure MCMONs, amino-functionalized MCMONs (Figure 5b-d) show a lower peak intensity and a blue shift in this region, which may attribute to the presence of N-H groups ($1650\text{-}1500\text{ cm}^{-1}$) [56].

Figure 5 FT-IR spectra of (a) pure MCMONs, (b) 1N-MCMONs, (c) 2N-MCMONs and (d) 3N-MCMONs

The N_2 adsorption–desorption isotherms of pure MCMONs, 1N-MCMONs, 2N-MCMONs and 3N-MCMONs are shown in Figure 6. The incorporation of different organosilanes has led to significant change in the shape of the isotherms. According to the International Union of Pure and Applied Chemistry classification (IUPAC), the N_2 sorption isotherms of pure MCMONs, 2N-MCMONs and 3N-MCMONs are type-IV isotherms with hysteresis, typical for mesoporous materials ^[57-58]. The missing capillary condensation step in the isotherm of 1N-MCMONs indicates a type-I isotherm, which can be related to the presence of micropores ^[52]. This can be attributed to the adverse effect of 1N silanes on the formation of a mesoporous structure as previously discussed. In addition, the points corresponding to capillary condensation (red arrows) for 2N-MCMONs and 3N-MCMONs both shifted towards higher P/P_0 values as compared with pure MCMONs. This is consistent with the increase in the average pore size caused by the introduction of the silane coupling agent ^[29], see Figure 6(b).

Figure 6 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of pure MCMONs, 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

The BET surface area and total pore volume are listed in Table 1. It is worth noting that comparing to pure MCMONs, the specific surface area of the functionalized MCMONs decreased significantly, however, there was not much variation in their total pore volume, suggesting that the amino groups immobilized on the MCMONs surface has minor influence on the pore volume.

Table 1. Specific surface area and total pore volume of pure MCMONs, 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Sample	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore size (nm)
Pure MCMONs	925.11	0.52	2.26
1N-MCMONs	446.11	0.68	1.93
2N-MCMONs	232.6	0.48	7.39
3N-MCMONs	124.57	0.50	11.13

3.2 Parameters influencing the Cr(VI) adsorption

3.2.1 Different types of adsorbents

The Cr(VI) removal rate of 1N-MONs, pure MCMONs and 1N-MCMONs, were selected for cross comparison. Adsorption experiments were conducted under room

temperature using 100 mL solution containing 20 mg L⁻¹ Cr(VI) under pH 3, 0.2 g L⁻¹ adsorbents was used and the contact time was 60 min. The results obtained are shown in Figure 7, the Cr(VI) removal rate of 1N-MCMONs (94.05%) was at least three times higher than that of pure MCMONs (31.54%) and 1N-MONs (27.17%). The high Cr(VI) removal rate demonstrated that the surface of the 1N-MCMONs had high density of active sites. Considering the high specific surface area of pure MCMONs, the greater adsorption efficiency of 1N-MCMONs can be attributed to combined effect of the mesoporous framework and the highly effective surface adsorption sites (amino groups), which result in formation of Cr-1N-MCMONs chelates ^[39]. Additionally, in comparison to 1N-MONs, 1N-MCMONs possess more open and accessible mesopore channels and the separation between the core and shell, all these can promote the penetration and transport of Cr(VI). Furthermore, the greater number of functional groups on the surface of 1N-MCMONs also enhance the adsorption of Cr(VI).

Figure 7 Cr(VI) removal rates for 1N-MONs, pure MCMONs and 1N-MCMONs

3.2.2 Effects of contact time

The effects of different contact time have been investigated using 100 mL 20 mg L⁻¹ pH 3 Cr(VI) containing solution. Figure 8 shows the effects of different contact time on the Cr(VI) removal rate for 1N-MCMONs, 2N-MCMONs and 3N-MCMONs. An abrupt increase of Cr(VI) removal rate can be found in the first 40 min, which is leveled off at ~ 60 min. There is because as the surface active sites on the adsorbents approaching saturation, the thermodynamic driving force for adsorption gradually declines ^[59]. The average removal rates for 1N-MCMONs, 2N-MCMONs and 3N-MCMONs are 93.88%, 95.16% and 96.39%, respectively. During the initial stage (< 40min), 1N-MCMONs and 2N-MCMONs exhibited higher Cr(VI) removal rates as compared to that of 3N-MCMONs. This is related to the larger specific surface areas seen for 1N-MCMONs and 2N-MCMONs (see Table 1) ^[60]. Interestingly, Cr(VI) removal rate of 3N-MCMONs exceeded those of 1N-MCMONs, 2N-MCMONs after 40 min, and the final Cr(VI) removal rate of the adsorbents was 3N-MCMONs > 2N-MCMONs > 1N-MCMONs. Higher N content (i.e. higher amino groups content) is seen for 3N-MCMONs and 2N-MCMONs (Table 2), indicating that higher number of amino groups (hence a greater number of adsorption sites) plays a dominant role in Cr(VI) removal at the later stage. As the system gradually reaches adsorption equilibrium, further increase of contact time (> 60 min) does not significantly change the removal rate, which may be due to reduced number of active sites and hence a much lower driving force for adsorption ^[58].

Figure 8 Effects of contact time on the adsorption of Cr(VI) for 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Table 2. Surface content of C, Si, and N in 1N-MCMONs, 2N-MCMONs and 3N-MCMONs evaluated by X-ray photoelectron spectrometry (XPS)

Samples	Surface atomic content (%)		
	C 1s	Si 2p	N 1s
1N-MCMONs	63.98	30.4	5.62
2N-MCMONs	61.3	28.6	10.1
3N-MCMONs	58.48	29.27	12.22

3.2.3 Effects of pH

The initial pH of solution can significantly affect the Cr(VI) adsorption of the amino-functionalized MCMONs, as the surrounding media affects their surface charge and the degree of ionization ^[61]. The Cr(VI) removal rates of 1N-MCMONs, 2N-MCMONs and 3N-MCMONs were measured under different pH (1-9) to determine the optimum Cr(VI) removal conditions. pH values of test solutions were adjusted using HCl or NaOH.

It can be seen from Figure 9 that the Cr(VI) removal rates of 1N-MCMONs, 2N-MCMONs and 3N-MCMONs all increased drastically and reached maximum as pH increased from 1 to 3, after which the removal rates started to decline. Cr(VI) ions present themselves in different forms in aqueous solutions, depending on the

solution pH ^[62]. The major species at low pH (pH ~ 2) consist of H₂Cr₂O₇, and as the pH increases gradually (pH 2-6), negatively charged HCrO₄⁻ and Cr₂O₇²⁻ ions predominate and when pH >7, CrO₄²⁻ is predominant ^[63]. Owing to the greater amount of nonionic H₂CrO₄ at pH<3, adsorption is much lower at pH=1 ^[64]. At pH 3, amino groups on the functionalized MCMONs were protonated, forming positively charged sites (e.g. -NH₃⁺ or -NH₂⁺-), which interact strongly with the negatively charged HCrO₄⁻ (Equation 3), leading to a greater removal rate, see Equation (3).

With further increased pH, the degree of protonation of the amino groups decreases gradually due to the increasing OH⁻ concentration in the solution, resulting in a less efficient Cr(VI) removal rate ^[64]. It is noteworthy that the Cr(VI) removal rate for 1N-MCMONs dropped most significantly (from 94.40% to 55.28%) when pH increases from 3 to 9, whereas both 2N-MCMONs and 3N-MCMONs demonstrated reasonably stable Cr(VI) removal rates in pH 3-7. This can be attributed to the -NH- groups that present in 2N silanes and 3N silanes, which have stronger basicity in solution and are more easily protonated than -NH₂ under pH 3-7. As a result, 2N-MCMONs and 3N-MCMONs retained the relatively stronger absorption efficiency under pH 3-7.

Figure 9 Effects of pH on the Cr(VI) removal rate of 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

3.2.4 Effects of initial concentration

Based on the results from sections 3.2.2 and 3.2.3, a contact time 60 min and pH=3 were chosen as the optimal conditions, under which the effect of initial Cr(IV) concentration was investigated. As is shown in Figure 10, all adsorbents show a gradually decreasing Cr(VI) removal rate which is accompanied by an increasing adsorption capacity (q_e). Table 3 summarizes the Cr(VI) adsorption capacities of different core-shell silica-based adsorbents from the recent literature. It is worth noting that our 3N-MCMONs exhibits an maximum adsorption capacity ($q_{\max}$) of 279.92 mg/g at 150 mg/L initial Cr(VI) concentration, which is about 20% greater than the highest Cr(VI) adsorption capacity (236.4 mg/g ^[45]) reported so far for core-shell silica-based adsorbents.

Figure 10 The effects of initial Cr(VI) concentrations on the removal rate and adsorption capacity of (a) 1N-MCMONs, (b) 2N-MCMONs and (c) 3N-MCMONs

Table 3. Comparison of the Cr(VI) adsorption capacity of amino-functionalized MCMONs with other silica-based core-shell structured adsorbents

Adsorbent	$q_{\max}$ (mg g ⁻¹)	Reference
MnFe ₂ O ₄ @-SiO ₂ -CTAB	25.044	[41]
γ -Fe ₂ O ₃ /nSiO ₂ /mSiO ₂	53.06	[42]
Fe ₃ O ₄ -SiO ₂ -CTS-PEI	236.4	[43]
Fe ₃ O ₄ @SiO ₂ @Kit-6	185.2	[44]
A-M-S-MNPs	34.25	[45]
3N-MCMONs	279.92	This study

3.2.5 Adsorption kinetics

Two well established kinetic models (i) pseudo-first-order model (Equation 4) and (ii) pseudo-second-order model (Equation 5) ^[66] have been deployed to evaluate the adsorption kinetics of our experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) denote the adsorption rate constants, q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacity at time t (min) and at equilibrium, respectively.

Figure 11 shows the curve fitting of the experimental data to both models and the kinetic constants and correlation coefficients (R^2) are listed in Table 4. It can be seen that the Cr(VI) adsorption kinetics for all adsorbents can be best described by the pseudo-second-order kinetic model (with R^2 values greater than 0.999 for all datasets). This suggests that the process was controlled by the chemical adsorption

[67].

Figure 11 Curve fitting using (a) Pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model for the Cr(VI) adsorption on 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Table 4. Extrapolated parameters for the pseudo-first-order kinetic and pseudo-second-order kinetic models for the Cr(VI) adsorption on 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Samples	$q_{e, exp}$	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e, cal}$	k_1	R^2	$q_{e, cal}$	k_2	R^2
1N-MCMONs	119.81	6.67	0.01297	0.74833	120.48	0.01063	0.99996
2N-MCMONs	233.44	12.73	0.01534	0.69554	234.19	0.01109	0.99996
3N-MCMONs	279.91	106.51	0.04234	0.88533	291.54	0.00487	0.99916

3.2.6 Adsorption isotherm

The experimental data have been analyzed using two commonly used models, Langmuir (Equation 6) and Freundlich adsorption isotherms (Equation 7) models [68]. The Langmuir model assumes monolayer adsorption on the solid surface, while the Freundlich model is empirical in nature [39].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where C_e (mg L⁻¹) and q_e (mg g⁻¹) are the Cr(VI) concentration and the adsorption capacity at equilibrium, q_m (mg g⁻¹) the maximum adsorption capacity, K_L (L mg⁻¹) the Langmuir constant related to the adsorption energy, and K_F (L g⁻¹) and n the Freundlich constants characterizing adsorption capacity and intensity of adsorption.

Figure 12 shows the curve fitting of experimental data using the two proposed models. The R^2 values and corresponding constants extrapolated from the graphs are shown in Table 5. It can be seen that the Langmuir isotherm model shows a better data correlation and the calculated adsorption capacity (q_m) is consistent with our experimental data. The results imply that the adsorption process followed the Langmuir model where Cr(VI) was adsorbed onto functionalized MCMONs mostly via monolayer adsorption [45].

Figure 12 Langmuir isotherm model (a) and Freundlich isotherm model (b) for adsorption of Cr (VI) on 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Table 5. Parameters of Langmuir and Freundlich models for the adsorption of Cr(VI) on 1N-MCMONs, 2N-MCMONs and 3N-MCMONs

Samples	$q_{e, exp}$	Langmuir isotherm			Freundlich isotherm		
		$q_m(\text{mg/L})$	$K_L(\text{L/mg})$	R^2	K_F	n	R^2
1N-MCMONs	119.81	120.77	0.67	0.998	69.93	7.65	0.71219
2N-MCMONs	233.44	231.48	0.133	0.97668	79.5	4.47	0.93049
3N-MCMONs	279.91	283.29	0.156	0.96217	112.20	5.62	0.95345

On the other hand, the separation factor (R_L) can be calculated from the Langmuir parameter K_L [69], according to Equation (8).

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

where C_0 (mg L^{-1}) is the initial Cr(VI) concentration.

The value of R_L indicates whether the adsorption process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$) or unfavorable ($R_L < 0$). The R_L values for different adsorbents were listed in Table 6. It is clear that R_L values for Cr(VI) adsorption on 1N-DMOs, 2N-DMOs and 3N-DMOs fall between 0 and 1, suggesting that the adsorption of Cr(VI) on amino-functionalized MCMONs is favorable, particularly at lower Cr(VI) concentration.

Table 6. R_L values for Cr(VI) adsorption based on the Langmuir model

$C_0(\text{mg L}^{-1})$	R_L		
	1N-MCMONs	2N-MCMONs	3N-MCMONs
10	0.130	0.43	0.39
20	0.069	0.27	0.24
40	0.036	0.16	0.14
60	0.24	0.11	0.10
80	0.018	0.08	0.07
90	0.016		
100	0.015	0.07	0.06
120		0.06	0.05
150		0.05	0.04

3.3 Adsorption mechanism confirmed by the XPS analysis

XPS analysis was carried out to develop more insightful understanding of the detailed adsorption mechanisms. Since the adsorption mechanisms involved for all functionalized MCMONs are similar, only 3N-MCMONs have been selected for detailed investigation. It can be seen from Figure 13 (a) that the intensity of C-N decreased after adsorption of Cr(VI), implying that N has taken part in the adsorption reaction. A weak peak at 288.6 eV in the C 1s spectra has been assigned to C-O-Si species ^[52]. This peak, although unexpected, could probably due to the incomplete hydrolysis of TEOS ^[70]. In Figure 13 (b), the binding energies at 399.4 and 401.5 eV can be assigned to the C-N and protonated amino groups, respectively, suggesting part of the amino groups have undergone modification. The decrease and shift of the peak intensity after Cr(VI) adsorption can be attributed to the varying state of the amino groups during the adsorption process. Spectra corresponding to Cr 2p have been found in Figure 13 (c), where the peaks at 579.3 and 588.8 eV can be assigned

to Cr(VI), and the peaks at 577.5 and 586.7 eV correspond to Cr(III) [71-72]. The presence of Cr(III) suggests that the reduction of Cr(VI) has taken place during the adsorption process. Furthermore, the stronger 577.5 and 586.7 eV peaks indicate that most of the Cr(VI) ions have been reduced to Cr(III) by 3N-MCMONs.

Figure 13 XPS spectra of 3N-MCMONs before and after Cr (VI) adsorption: (a) C 1s, (b) N 1s and (c) Cr 2p

The above results suggest that the Cr(VI) removal by 3N-MCMONs takes place following the follow pathways: (i) Cr (VI) anions were first adsorbed onto the 3N-MCMONs surface via an electrostatic interaction between the Cr(VI) anions and the protonated amino groups; (ii) the adsorbed Cr(VI) was reduced to Cr(III) under acidic condition (Equation 9, Equation 10), the Cr(III) ions where then immobilized on the 3N-MCMONs surface by amino groups forming $\text{-NH}_2\text{Cr(III)}$ complexes (Equation 11).

3.4 Reusability of the adsorbent

In order to evaluate the reusability of our amino-functionalized MCMONs, the desorption of Cr(VI) from the adsorbents surface was performed using 3 mol L⁻¹ HCl solution (2 h stirring under room temperature). The desorption mechanism of the major Cr(VI) species (i.e. HCr₂O₇⁻) under acid condition can be described by Equation (12), where the formation of H₂Cr₂O₇ is more favorable to the electrostatic interaction between HCrO₇⁻ and -NH₃⁺ or -NH₂⁺.

Figure 14 shows that 1N-MCMONs retains high removal efficiency (89.65%) even after five adsorption–desorption cycles. The removal efficiency of 2N-MCMONs and 3N-MCMONs, on the other hand, decreases gradually as the number of experiment cycles increases, however both materials still exhibit a reasonably high Cr(VI) removal rate (> 75%) after the fifth cycle. The results suggest that our amino-functionalized MCMONs possess excellent recyclability suitable for practical applications.

Figure 14 Reusability of 1N-MCMONs, 2N-MCMONs and 3N-MCMONs to adsorb Cr(VI) for five cycles

4. Conclusions

In this study, three types of amino-functionalized mesoporous organosilica nanospheres with unique multi-layer core-shell structures have been synthesized using an indirect co-condensation using 1N, 2N or 3N silanes as surface modification agents. When used for Cr (VI) removal in aqueous solutions an optimal removal rate (~95%) can be achieved at pH=3. The adsorption capacity of all adsorbents increases with increasing initial Cr (VI) concentration, and 3N-MCMONs exhibited the maximum adsorption capacity (279.92 mg g⁻¹) at an 150 mg L⁻¹ initial Cr(VI) concentration. The reusability experiment suggested that our new adsorbents have high regeneration rate (~95% for 1N-MCMONs, and ~75% for 2N-MCMONs and 3N-MCMONs). The high adsorption efficiency can be ascribed to the strong electrostatic interaction between the positively charged amino groups on the surface of adsorbents and the negatively charged Cr(VI) species, and the subsequent reduction of Cr(VI) to Cr(III) in aqueous solutions. The adsorption kinetics and

adsorption isotherm for the new adsorbents are best described by the pseudo-second-order kinetic model and Langmuir isotherm model, respectively. This work suggests that our amino-functionalized multi-layer core-shell mesoporous organosilica nanospheres have a great potential for the removal of harmful Cr(VI) ions, hence can be used as highly effective adsorbents in future wastewater treatment and environmental control applications.

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Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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