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Cadmium(II) adsorption using functional mesoporous silica and activated carbon

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ABSTRACT

The role of surface functionality on silica and carbonaceous materials for adsorption of cadmium(II) was examined using various mesoporous silica and activated carbon. Silica surfaces were principally functionalized by mono-amino- and mercapto-groups, while carboxylic group was introduced to the activated carbons by oxidation. Functional groups on silica surface were formed using grafting and co-condensation techniques in their preparation. Mono-amino group was found more effective than di- and tri-amino groups for cadmium(II) adsorption on the grafted silica. Mono-amino groups prepared by co-condensation adsorbed cadmium(II) as much as 0.25 mmol/g compared to mercapto- and carboxyl-groups which adsorbed around 0.12 mmol/g, whereas Langmuir adsorption affinities were as strong as 50–60 L/mmol for all of the three functions. The working pH range was wider for mercapto- and carboxyl-functions than for amino-group. Basic site could be an adsorption center for amino-functional groups while ion exchange sites were found to work for the mercapto- and carboxyl-functions to adsorb cadmium(II) from aqueous phase. Based on the experimental results, surface functional groups rather than structure of silica and carbon seemed to play a decisive role for cadmium(II) adsorption.

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1. Introduction

Adsorption is one of the promising techniques for water purification [1–4]. For organic pollutants carbonaceous materials have been widely applied as adsorbents, because of the hydrophobic surface which is suitable for adsorption of trace amount of non-ionic organic compounds [5–7]. However adsorptive removal of ionic pollutants such as dyes of large molecule and heavy metal ions has not been well developed for silica and carbonaceous materials [8–10]. Accommodation of large molecule dye will require large pore radius, while that of heavy metal ions seems to require specific functional groups on the surface of adsorbents rather than large pore structure [11–13]. Mercury, cadmium, lead, chromium, nickel, cobalt, copper, zinc ions, etc. are considered as pollutant heavy metals in aqueous system. The famous Minamata and Itai-itai diseases are caused by methyl mercury and cadmium ions in aqueous phase, respectively [14,15]. Cadmium(II) is found to be one

of the most difficult heavy metals to be removed from water when adsorption is applied [16,17]. Numerous adsorbents have been examined to apply for the cadmium removal [18,19]. Some of them are efficient only at high cadmium concentrations and at high pH regions [20–24], while others are adsorb well at lower concentrations and even in acidic conditions [25]. Oxygen functional groups on carbonaceous materials are most widely studied as attractive adsorbents for cationic heavy metal adsorption [26,27]. Nitrogen functional groups are also candidates bringing increased attractive force in adsorption of heavy metal ions [28]. Bois et al. examined the nitrogen- and sulfur-functionalized silica for adsorption of copper, nickel, cobalt and cadmium cations in aqueous solutions and observed that mercaptopropyl functions exhibited a higher loading capacity for the cadmium than other cations [29]. Although many other materials suitable for removal of heavy metals can be found as adsorbents, in this study we focused on examining these heteroatomic elements of nitrogen, oxygen and sulfur on the surface of the adsorbents to elucidate the role of the functional groups. Carboxyl and mercapto groups are adopted as typical oxygen and sulfur functions on activated carbons and silica materials, respectively. Cyano, imidazole and amino groups are introduced to the silica materials as nitrogen functionalities, because these groups can be introduced through either grafting or co-condensation and easily be identified later.

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2. Experimental

2.1. Materials

The mesoporous silica materials were prepared using TEOS as source of silica and Tergitol 15-S12, Triton X-100, Igepal CA-720 and CO-720 as structure directing surfactants for MSU type mesoporous silica. Dodecylamine (DDA) surfactant was used in case of HMS synthesis. Sulfur and nitrogen functional groups were introduced to the silica materials using (3-mercaptopropyl)trimethoxysilane, (3-cyanopropyl)triethoxysilane, (3-aminopropyl)triethoxysilane, 1-(3-(triethoxysilyl)propyl)-1H-imidazole, (3-aminopropyl)trimethoxysilane, bis[3-(triethoxysilyl)propyl]amine, N-[3-(trimethoxysilyl)propyl]ethylenediamine, bis[3-(trimethoxysilyl)propyl]ethylene diamine and N1-(3-trimethoxysilylpropyl) diethylenetriamine through grafting and co-condensation techniques [30]. All chemicals used in the study were reagent grade.

All syntheses were done at room temperature. Each surfactant was completely dissolved in de-ionized water by magnetic stirring and tetraethyl orthosilicate (TEOS) was added to the stirred solution with the molar ratio of TEOS/surf. = 8 [31]. Appropriate amounts of 2 M HCl yielded a clear solution about 1 h after TEOS addition. Sodium fluoride was added to the solution (NaF/TEOS = 4 mol% [31–33]) to promote catalyzed condensation. Nucleation of silica particles, almost 10 min after catalyst addition, resulted in a milky solution which consequently formed white sediments at the bottom of beaker. The silica material was filtered and dried at 80 °C and then named MSU-1 and MSU-2 depending on the types of surfactant [31,34]. HMS silica was synthesized by dissolving TEOS in a solution of dodecylamine (DDA) in de-ionized water and ethanol at neutral pH with the molar ratio of 1TEOS:0.35DDA:3.9EtOH:13H₂O, which after stirring for 18 h was filtered and dried [35]. Grafting of functional silanes was carried out in boiling anhydrous toluene in a refluxed condition for 24 h. Mercapto- and amino-functional HMS were prepared through co-condensation, wherein a gradual increase in the molar ratio mercapto-/amino-functional silane (1:9, 8:2, 7:3, 6:4 and 5:5) was considered.

In case of MSU-2 synthesis, 11 g Igepal CA-720 and 25 g TEOS were dissolved in stirring 500 mL de-ionized water and 2.5 mL of 2 M HCl(aq.) which ultimately gave a clear solution. The resultant pH of the solution was around 2. At this point, 0.2 g of NaF was added to the solution to catalyze nucleation and subsequent precipitation of solid silica particles at the bottom of the beaker, and then the precipitate was filtered and dried at 80 °C and later washed with boiling ethanol in Soxhlet apparatus for 24 h to extract the surfactant and obtain mesoporous MSU-2 silica. In preparing mono-amino grafted MSU-2, 1.0 g of mesoporous silica and 0.3 g (3-aminopropyl)triethoxysilane were added to a flask in which 25 mL anhydrous toluene was added to be boiled in a reflux for 24 h and then solution was filtered and washed with ethanol and dried.

On the other hand, in case of mono-amino grafted HMS using co-condensation technique, considering a molar ratio of TEOS:–NH₂ = 7:3, 1.8 g of DDA, 2.9 g TEOS and 2.6 g (3-aminopropyl)triethoxysilane were sequentially added to a stirred solution containing 6.4 mL de-ionized water and 8.4 mL ethanol (EtOH) to form silica materials. After 18 h stirring, white silica sediment was filtered and dried to yield mono-amino functionalized HMS.

Activated carbon (AC) purchased from Kureha Co., Ltd., Japan, was washed repeatedly with hot water to remove the contaminants. The AC, so obtained, was oxidized in ammonium peroxydisulfate aqueous solution at room temperature for 1 week to introduce carboxylic functional group and washed with hot de-ionized water until the solution pH reached a constant value [36].

2.2. Adsorption experiments

Cadmium(II) solution was prepared from a reagent grade cadmium(II) nitrate salt to meet the concentration 4.45 mmol/L (500 mg/L) as a stock solution. The solution was diluted by de-ionized water to obtain desired solution for adsorption experiments. Silica and carbon adsorbents were dried at 80 °C for 1 h prior to the measurement of sample weight. Twenty mg of adsorbent powder was dosed in 10 mL cadmium(II) solution and agitated for 24 and 48 h for silica and AC adsorbents, respectively, until the equilibrium state was reached corresponding to a preliminary test. The equilibrium solution was pipetted out and diluted with 0.1 M nitric acid because the calibration line was also obtained using cadmium(II) ions in nitric acid solution. After the dilution with the nitric acid to less than 1.0 mg/L, the prepared solution was analyzed using atomic absorption spectroscopy (PerkinElmer Model AAnalyst 400) to determine cadmium concentration in the aqueous phase. Adsorption capacities in mmol/g were calculated by the difference between initial and equilibrium concentrations. Influence of pH on adsorption was also examined by adjusting initial solution pH using nitric acid and sodium hydroxide solutions.

2.3. Structure and surface study of adsorbents

Using Micromeritics ASAP 2010 analyzer, nitrogen adsorption and desorption isotherms were obtained for silica, and specific surface areas and pore distributions were calculated. BET method was used to figure out the specific surface area in m²/g. Total pore volume in mL/g was calculated from the total volume of nitrogen adsorbed. Mesopore volume in mL/g was determined by the Subtracting Pore Effect (SPE) method from α_s -plots using nitrogen adsorption and desorption isotherms for standard silica and carbon black as well as those for the samples [37,38]. The standard silica and the carbon black materials were essentially non porous with small specific surface areas of 36 m²/g and 30 m²/g, respectively [39–42]. Prepared particles were also observed by scanning electron microscope (SEM, JEOL JSM-6510).

The pH of the point of zero charge (pH_{pzc}) for the ACs before and after oxidation was determined using the pH drift method [43]. The functional oxygen groups on surface were determined using titration technique developed by Boehm [44]. The amounts of nitrogen and sulfur in HMS were measured using CHN analyzer (PerkinElmer 2400II) and X-ray fluorescence analyzer (XRF, Rigaku RIX2100), respectively. The nitrogen and sulfur species on HMS surfaces were estimated from the spectra of X-ray photoelectron spectroscopy (XPS, JEOL JPS-9010MX) using MgK α line and Fourier transform infrared spectroscopy (FT-IR, Shimadzu IRAffinity-1).

3. Results and discussion

3.1. Functionalized mesoporous silicas

Since the most widely applied functional groups are probably amino-functional groups [45], in this study mono-amino grafted silica was investigated for adsorption in 0.22 mmol/L (25 mg/L) cadmium(II) solution. Fig. 1 shows the cadmium(II) removal as a function of mesoporous silica type prepared from different surfactants. MSU-2 (prepared with Igepal CA-720 surfactant) followed by HMS resulted in highest removal of cadmium, however, some cadmium(II) adsorption still observed on bare silica surfaces. It was postulated that the amounts of silanol groups on the surface for MSU-2 (CA-720) and HMS might be greater than the other silica materials. Therefore, MSU-2 was selected for further inspection of types of functional groups for cadmium(II) removal. Fig. 2 displays the difference in adsorptive removal of cadmium(II) when the

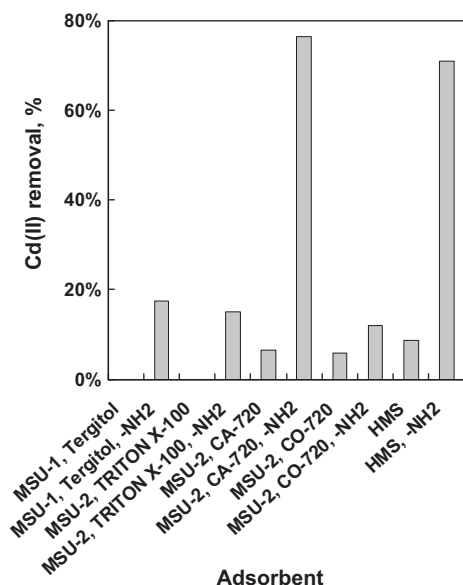


Fig. 1. Removal of cadmium(II) by various mesoporous silica materials and corresponding 3-aminopropyl grafted silica. ‘-NH₂’ denotes amino-functional groups, e.g. ‘MSU-2, Triton X-100, -NH₂’ represents MSU-2 prepared from the surfactant of Triton X-100 followed by grafting aminopropyl groups. Initial cadmium(II) concentration, solution volume and silica dosage are 25 mg/L (0.22 mmol/L), 10 mL and 20 mg, respectively.

surface functional group is varied. Mono-amino function exhibited the best result in the experiments even though similar amounts of functional compounds were used for grafting [45,46]. Bis functional groups were less effective adsorbents than corresponding non-Bis groups having the same number of amines. This might be caused by less degree of freedom of functional groups due to bridged binding of Bis onto the silica surface. Cyano-functional group did not adsorb any cadmium(II) ions while mercapto-function did to some extent.

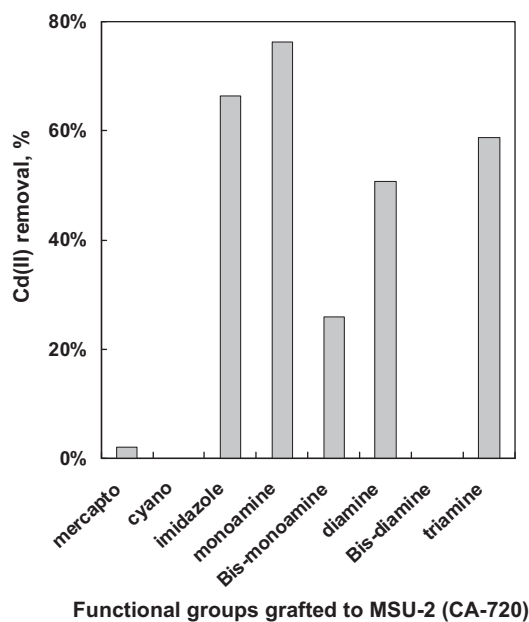


Fig. 2. Removal of cadmium(II) by various functional groups grafted to MSU-2 prepared using Igepal CA-720 surfactant. Initial cadmium(II) concentration, solution volume and silica dosage are 25 mg/L (0.22 mmol/L), 10 mL and 20 mg, respectively.

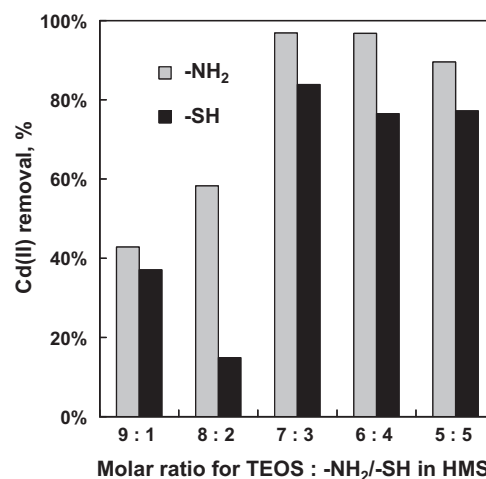


Fig. 3. Removal of cadmium(II) by amino- and mercapto-functionalized HMS prepared through co-condensation method against TEOS:-NH₂/-SH molar ratio in their preparation. Initial cadmium(II) concentration, solution volume and silica dosage are 25 mg/L (0.22 mmol/L), 10 mL and 20 mg, respectively.

3.2. Influence of TEOS:-NH₂/-SH ratio on cadmium removal

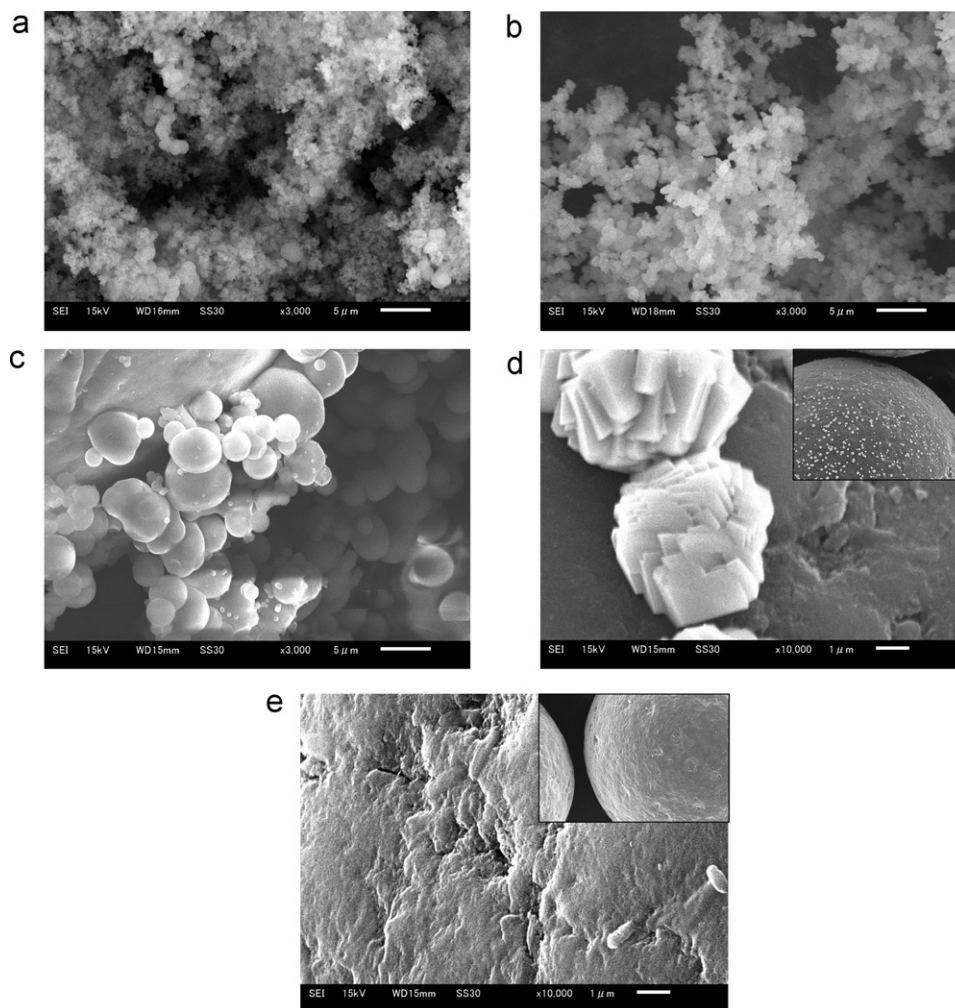
Fig. 3 represents the influence of TEOS:-NH₂ and TEOS:-SH molar ratios in the preparation of functionalized HMS through co-condensation on cadmium(II) removal. When the ratio was equal to or greater than 7:3 for both amino- and mercapto-functions, maximum removal was observed in 0.22 mmol/L (25 mg/L) cadmium(II) solution. A removal rate of as much as 80% could be achieved for mercapto-functionalized HMS in this case. However, for the mercapto-grafted MSU-2 only a few percent removals was observed (Fig. 2). This could be as a result of grafting more functional groups onto HMS pores. Bois et al. compared amino- and mercapto-functionalized HMS prepared by co-condensation to be used for adsorption of Cu²⁺, Ni²⁺, Co²⁺ and the anionic Cr(VI); according to their findings mercapto-group was superior to amino-function for cadmium(II) whereas the latter was more efficient for adsorption of other heavy metals ions [29].

3.3. Adsorption isotherms for cadmium(II) ions

Adsorption on amino- and mercapto-functionalized HMS prepared by co-condensation method was studied for obtaining adsorption isotherms to inspect the detailed adsorption characteristics. Carboxylic functional group on activated carbon was comparatively examined to clarify the adsorption mechanism. HMS and AC with no functional groups were also investigated as references. Physical and chemical properties of these adsorbents are tabulated in Table 1. In Fig. 4 are shown images of scanning electron microscope (SEM) for non-functionalized, amino- and mercapto-functionalized HMS and non-functionalized and carboxyl-functionalized AC. All SEM images were obtained after cadmium(II) equilibrium adsorption tests using the initial concentration of 0.89 mmol/L. Some particles were observed for HMS silicas whereas only rough surfaces could be observed for AC. In spite of the small amount of cadmium(II) adsorption as represented latter in this section, the platy crystals of cadmium hydroxide could be clearly observed for non-functionalized AC by the surface precipitation of cadmium(II). This is due to the basic character of the carbon surface resulted from the π -electrons of graphene layers. On the contrary, no such crystals were observed for other adsorbents revealing that the adsorption would occur at the specific sites on the surface of the adsorbents. No significant change of adsorbent surfaces was observed before and after

Table 1
Physical and chemical properties of adsorbents of HMS silica and activated carbon.

Material	HMS From TEOS and dodecylamine	HMS-NH ₂ (TEOS:–NH ₂ = 7:3) With co- condensation	HMS-SH (TEOS:–SH = 7:3) With co- condensation	AC Supplied by Kureha Co., Ltd.	AC-COOH Oxidized by ammonium persulfate (NH ₄) ₂ S ₂ O ₈
Elemental analysis, mmol/g	–	2.44 (nitrogen) ^a	0.45 (sulfur) ^b	–	1.39 (–COOH) ^c
BET specific S.A., m ² /g	1330	17	550	1320	1220
Total pore volume, mL/g	0.62	0.017	0.29	0.62	0.58
Meso-pore, mL/g by SPE method from α -s plots	0.1	0.01	0.03	0.08	0.05

^a CHN Analyzer (PerkinElmer 2400II).^b X-ray fluorescence analyzer (Rigaku RIX2100).^c Boehm titration, amount of carboxyl groups on activated carbon.**Fig. 4.** SEM images for (a) non-functionalized, (b) amino-, (c) mercapto-functionalized mesoporous silica (HMS), and (d) non-functionalized and (e) carboxyl-functionalized activated carbon (AC) after equilibrium adsorption of cadmium(II) with the initial concentration of 0.89 mmol/L.

cadmium(II) adsorption except in case of non-functionalized AC as shown in Fig. 4(d). For silica materials unfunctionalized HMS had the largest specific surface area, pore volume and mesopore volume. Introduction of amino-functional groups resulted in drastic decline in surface area and pore volume whereas they were not to the extent that was used in case of mercapto-functional groups. Nitrogen and sulfur contents were 2.44 and 0.45 mmol/g for amino- and mercapto-functionalized HMS by elemental analysis, respectively, as displayed in Table 1. The surface concentration of carboxyl group was 1.39 mmol/g or mequiv./g on AC surface. Fig. 5 represents XPS spectra for N_{1s} signal of amino-function and S_{2p} signal of mercapto-function. Amino- and mercapto-functions were

considered to be successfully introduced to the HMS silica pore surfaces judging from the binding energy at the peaks of the spectra. N_{1s} signal of amino-group would appear between 399.5 and 399.9 eV in binding energy [47] and S_{2p} signal would be between 162 and 163 eV [48,49]. FT-IR spectra in Fig. 6 just confirmed the XPS results showing the absorption peaks at 1560 cm⁻¹ for HMS-NH₂ and 2580 cm⁻¹ for HMS-SH that could be assigned to the mono-amino- and mercapto-functions, respectively [50–52]. These properties combined with the adsorption results revealed that surface functionality rather than pore structure of silica materials possibly played a more decisive role in cadmium(II) adsorption.

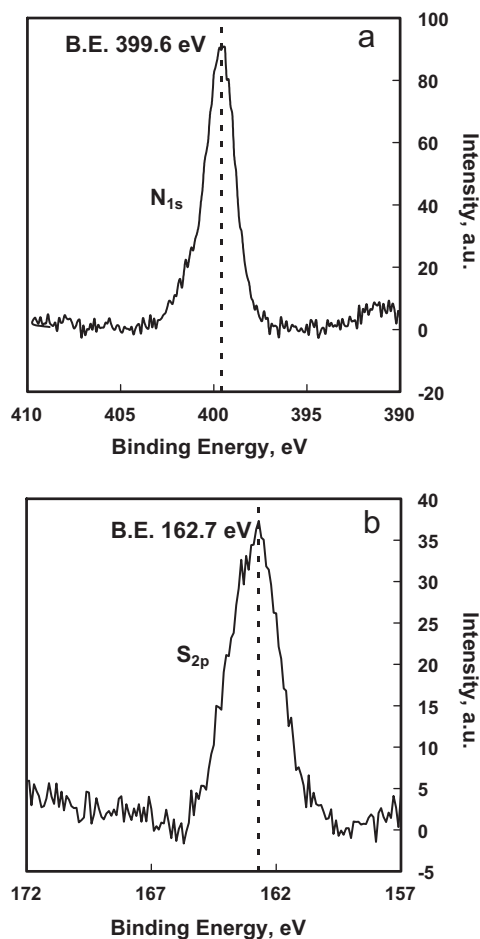


Fig. 5. XPS (ESCA) spectra of (a) N_{1s} for amino-functionalized HMS and (b) S_{2p} for mercapto-functionalized HMS.

A slight decrease in specific surface area and pore volume was also observed for activated carbon (AC) [27,53]. Fig. 7(a) shows the adsorption isotherms of HMS-NH₂, HMS-SH and AC-COOH as well as non-functionalized HMS and AC and Fig. 7(b) presents changes in equilibrium pH related to Fig. 7(a) for the functionalized adsorbents. Table 2 displays the adsorption affinities b and capacities Q_{max} of the functionalized adsorbents assuming Lang-

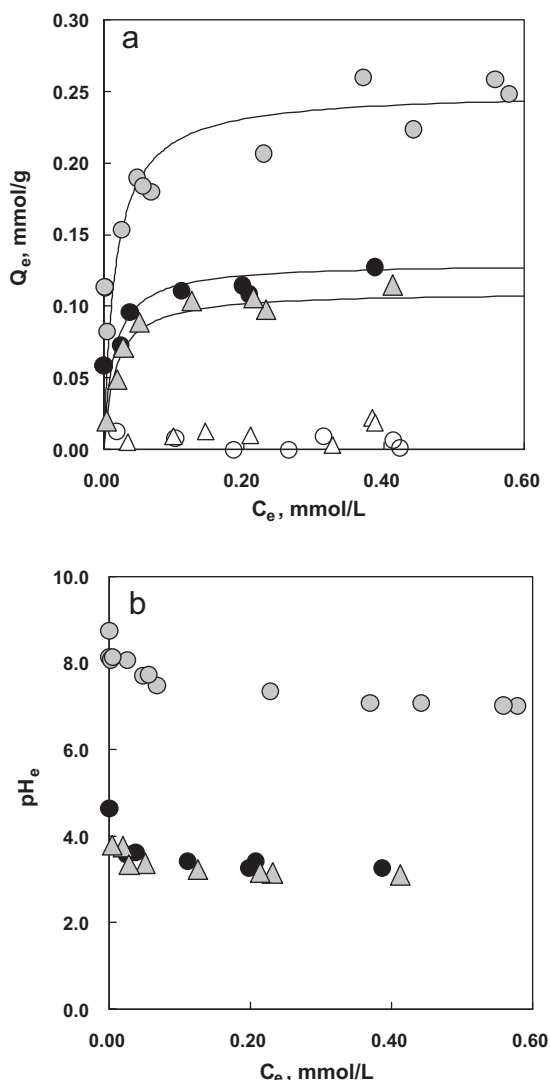


Fig. 7. Isotherms (a) for adsorption of cadmium(II) to functionalized mesoporous silica (HMS) and activated carbon (AC) and corresponding equilibrium pH (b). Gray, black and white circles indicate amino-, mercapto-functionalized HMS and non-functionalized HMS and gray and white triangles are carboxyl-functionalized AC and unoxidized AC, respectively. Solid lines show prediction using the Langmuir parameters in Table 2. Initial cadmium(II) concentration, solution volume and adsorbent dosage are 0–125 mg/L (1.11 mmol/L), 10 mL and 20 mg, respectively.

muir type mono-layer adsorption of cadmium(II). The adsorption affinity of b in Langmuir equation ranged 60–70 L/mmol revealing a strong adsorption of cadmium(II) on the surface. The results were supported by the fact that the desorption of cadmium(II) hardly occurred at similar pH region by adding de-ionized water though experimental results are not shown here. Adsorption of cadmium(II) took place at low concentration for both HMS and AC with heteroatom functional groups whereas no or a slight adsorption was obtained for the material in the absence of functional groups. Amino-group exhibited the highest adsorption capacities among all functional groups and the equilibrium pH was always above neutral, whereas the equilibrium pH in case

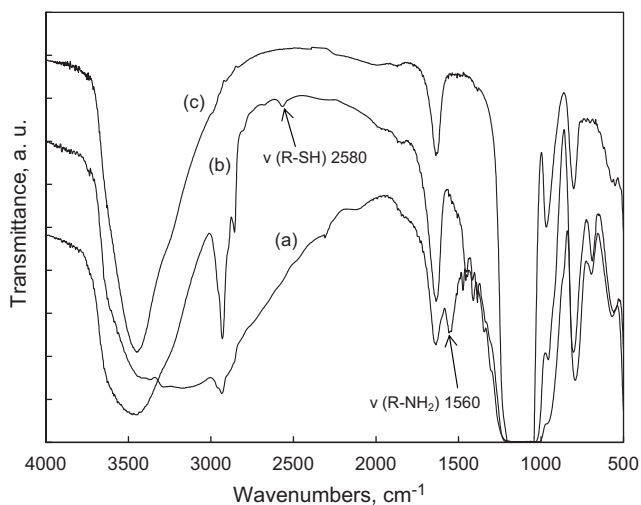


Fig. 6. FT-IR spectrum for (a) amino-, (b) mercapto-functionalized and (c) non-functionalized HMS.

Table 2
Langmuir parameters for Cd(II) adsorption onto silica and carbonaceous materials.

	HMS-NH ₂	HMS-SH	AC-COOH
b (adsorption affinity), L/mmol	60	70	60
Q_{max} (adsorption capacity), mmol/g	0.25	0.13	0.11

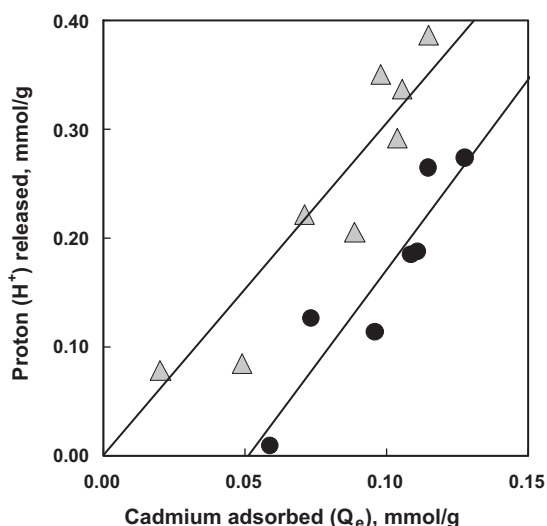


Fig. 8. Relationship between amounts of proton release from adsorbents and cadmium(II) adsorption to adsorbents using the results from Fig. 7. Gray triangle and black circle represent carboxyl-function on activated carbon (AC) and mercapto-group on mesoporous silica (HMS) prepared through co-condensation method.

of using mercapto- and carboxyl-functional groups ranged in the weak acidic region (pH 3–4). These results indicate that adsorption mechanism would be different between amino- and mercapto-/carboxyl-functional groups.

3.4. Adsorption mechanism of cadmium(II)

Fig. 8 displays the proton release for the mercapto- and carboxyl-functional groups against the amount of cadmium(II) adsorbed. The amount of proton release was calculated by the difference of initial and equilibrium solution pH. For carboxyl functional groups three moles of proton were released when one mole of cadmium(II) was adsorbed. It was more than three for mercapto-groups, even though no proton was released until 0.5 mmol/g cadmium was adsorbed. The ion exchange mechanism has been widely proposed for carboxyl groups [53], which was also observed for cadmium(II) adsorption to mercapto-functionalized activated carbon [54]. On the contrary, no such ion exchange mechanism was observed for amino-functional groups. Higher equilibrium pH indicated that basic sites, originated from lone pair of nitrogen atoms in the amine group, could be involved in ligand formation with cadmium(II) as well as binding with protons [55,56]. Fig. 9 shows the influence of pH on cadmium(II) adsorption when the initial cadmium concentration was 25 mg/L (0.22 mmol/L). The adsorption of cadmium(II) was steeply declined when pH was decreased to less than 8. Based on the speciation diagram of cadmium(II) nitrate in aqueous solution, 90% of Cd^{2+} and 10% of $\text{Cd}(\text{NO}_3)^+$ fractions are maintained during the pH less than 8 [57]. Although surface precipitation as $\text{Cd}(\text{OH})_2$ might take place in part when cadmium(II) adsorption happens at pH above 8 as observed for non-functionalized AC (Fig. 4(d)), Cd^{2+} and $\text{Cd}(\text{NO}_3)^+$ would be the predominant species for cadmium(II) adsorption at pH below 8. The steep decline below this pH could be attributed to competitive adsorption of protons. For mercapto- and carboxyl-functional groups the decline of adsorption was observed at pH below 4.0 and 3.0, respectively. The points of decline in adsorption are according to pK_a , because pK_a values of thiols and carboxylic acids ranges 5–11 and 2–4, respectively. The point of zero charge (pH_{pzc}) of AC was decreased from 9.7 to 4.7 by the oxidation, also consistent with the decline of adsorption of cadmium(II) below pH 4, because the surface of AC would be positively charged when the solution pH is

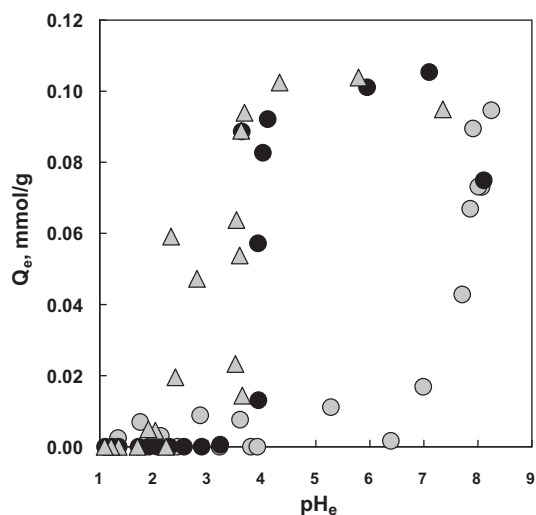


Fig. 9. Influence of equilibrium solution pH on cadmium(II) adsorption to three different functionalized materials. Gray and black circles, and gray triangle indicate amino-, mercapto-functionalized HMS and carboxyl-functionalized AC, respectively. Initial cadmium(II) concentration, solution volume and silica dosage are 25 mg/L (0.22 mmol/L), 10 mL and 20 mg, respectively.

less than pH_{pzc} leading to electrostatic repulsive force between the AC surface and cadmium(II) cations. Therefore, although maximum adsorption capacity can be observed for amino-functional groups, mercapto- and carboxyl-functional groups could be more effective to adsorb in a wider pH range where ion exchange with proton is expected during cadmium(II) adsorption.

4. Conclusions

Based on the discussed experimental results, the following gives a summary of the findings on adsorption of cadmium(II) adsorption onto amino-, mercapto- and carboxyl-functionalized silica and activated carbon:

- (1) MSU-2 (prepared with Igepal CA-720 surfactant) and HMS were considered suitable silica mesoporous materials with sufficient number of silanol groups available for grafting amino-functional groups on pore surfaces.
- (2) Mono-amino-functional groups performed superior in adsorption of cadmium(II) ion when compared to di- and tri-amino-, cyano- and mercapto- and even Bis-silanes.
- (3) In functionalized HMS materials prepared through co-condensation, the molar ratio TEOS: functional groups of 7:3 resulted in the highest adsorption capacity when employing amino- and mercapto-functional groups.
- (4) Amino-functionalized silica adsorbed greater amounts of cadmium(II) than what was adsorbed by either mercapto-functionalized silica or carboxyl-functionalized activated carbon. But the adsorption affinities of cadmium(II) calculated from Langmuir isotherms were similarly strong for all of the three functional groups.
- (5) Mercapto- and carboxyl-groups were found to behave as ion exchange sites for proton, whereas amino-functional group would serve as a basic site for cadmium(II) adsorption.
- (6) Amino-functional groups could well adsorb cadmium(II) at pH above 8, whereas mercapto- and carboxyl-groups would only be effective adsorption sites at a wider pH range.
- (7) Pore surface functionality was found to have a more decisive role in cadmium(II) adsorption rather than structural parameters for both silica and activated carbon.

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