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Layered double hydroxide/eggshell membrane: An inorganic biocomposite membrane as an efficient adsorbent for Cr(VI) removal

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ABSTRACT

Hexavalent chromium, Cr(VI), is carcinogenic and mutagenic to the living organisms, and hence more hazardous than other heavy metals. The choice of Cr(VI) removal adsorbents has always been a hot issue in environmental protection. Here we report a novel inorganic biocomposite membrane, layered double hydroxide/eggshell membrane (LDH/ESM) as adsorbent for Cr(VI) removal, in which ESM serves as the substrate and template to immobilize the LDH formed by an *in situ* hydrothermal crystallization method. X-ray diffraction (XRD) and scanning electron microscope (SEM) images showed that MgAl–CO_3^{2-}–LDH grown on the fibers of ESM, and the final LDH/ESM composite membrane both maintained the network structure of the ESM substrate. After being treated with an NaCl/HCl mixed solution, the interlayer CO_3^{2-} anions in the LDH portion of the composite membrane were exchanged for Cl^-. The ESM, MgAl–CO_3^{2-}–LDH/ESM and MgAl–Cl^-–LDH/ESM composite membrane were evaluated as adsorbent to remove Cr(VI), respectively, and the effect of the pH values on the adsorption was mainly investigated. It showed that the MgAl–Cl^-–LDH/ESM composite membrane had a higher adsorption capacity than ESM and MgAl–CO_3^{2-}–LDH/ESM—even when the pH value of the Cr(VI) solution was not further adjusted by addition of acid, which is of practical significance in a wastewater treatment plant. The adsorption isotherm of the MgAl–Cl^-–LDH/ESM composite membrane showed a good fit with the Langmuir isotherm model.

1. Introduction

Hexavalent chromium, Cr(VI), is widely presented in wastewaters from electroplating and metal finishing processes, pigment manufacture, tannery facilities, and chromium mining operations [1]. Effluents of Cr(VI) occurs as highly soluble and toxic chromate anions ($HCrO_4^-$ or $Cr_2O_7^{2-}$), which are carcinogenic and mutagenic to the living organisms, and hence more hazardous than other heavy metals [2,3]. Therefore, it is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. Because of the stricter environmental regulations, a cost effective technology for the treatment of Cr(VI) contaminated wastewater is highly desired by the industries.

Sorption is one of the most common methods for the removal of Cr(VI) from wastewaters, and the adsorbents are mainly concerned on inorganic materials as activated carbon [4–6], zeolites [7], iron [8,9] and oxides [10,11], and biomaterials as bacteria [12], weed [13], tea and coffee dust [14], seaweed [15,16] and agricultural biowastes [17]. In this manuscript, we aimed to fabricate a inorganic-bio composite material as adsorbent for Cr(VI) removal, and layered double hydroxides (LDHs) and eggshell membrane (ESM) were chosen as the materials, respectively.

LDHs are a class of anionic clays whose structure is based on brucite-like layers in which some of the divalent cations in the layers have been replaced by trivalent ions giving positively charged sheets [18,19]. The layer charge is balanced by intercalation of anions in the hydrated interlayer galleries. LDHs can be represented by the general formula $(M^{II}_{1-x}M^{III}_{x}(OH)_2)^{x+}(A^{n-})_{x/n}\bullet yH_2O$. The identities of the divalent and trivalent cations (M^{II} and M^{III}, respectively) and the interlayer anion (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials [20]. This flexibility in composition allows LDHs with a wide variety of properties to be prepared and is one of their most attractive features [21]. In view of their ion exchange ability, LDHs have been widely used as adsorbents for removal of oxyanions [22], arsenate [23], selenite [24], pesticide [25] and so on. For the Cr(VI) removal, Goswamee et al. [26] investigated the effect of the host cations of LDHs on the removal of Cr(VI), and it showed that adsorption was higher in the Mg–Al LDHs than in Ni–Al and Zn–Cr LDHs. Carriazo et al. [27] made a comparative study between the chloride and calcined carbonate LDHs as adsorbents for Cr(VI), and the results show that chloride LDHs are better adsorbents than calcined car-

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bonate LDHs. There were also several other reports [28–30] for Cr(VI) removal by using LDHs as adsorbents which demonstrates the applicability of LDHs in this field.

Recently, extensive research on the choice of adsorbents has centered on biomaterials as mentioned above. These so-called biosorbents are considered the cheapest, most abundant, and environmentally friendly option [31]. ESM, which is stable in aqueous and alcoholic media, consists of the outer shell membrane, inner shell membrane, and limiting membrane surrounding the egg white [32], and are mainly composed of biological molecules and highly cross-linked protein fibers that are arranged so as to form a semi-permeable membrane [33]. Therefore, the ESM possesses an intricate lattice network of stable and water-insoluble fibers and has high surface area, resulting in various applications as immobilization supports [34–36], biotemplates [37–39], and adsorbents [40].

Here we aimed to prepare an LDH/ESM inorganic biocomposite membrane by an *in situ* hydrothermal crystallization method in which the ESM was not only served as the substrate but also as the structure template of the composite membrane. The composite membrane was investigated as adsorbents for Cr(VI) removal. The initial pH values of the Cr solution and the anions between the layers of LDHs were mainly concerned in adsorption. From another point of view, it would also provide an effective way to prepare LDH-based functional materials with complicated structures by making use of the biomaterials as templates.

2. Materials and methods

2.1. Materials

$Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_{3.}{\cdot}9H_2O$, and $CO(NH_2)_2$, $K_2Cr_2O_7$, HCl, NaCl, acetone, 1,5-diphenylcarbazide, HNO_3, H_2SO_4, and H_3PO_5 were all analytical grade and purchased from Beijing Yili Fine Chemical Reagent Co. and used without further purification. Deionized water was used in all the experimental processes.

2.2. Preparation of LDH/composite membrane

Separation of eggshell membranes: Fresh eggs from a local supermarket in Beijing were gently broken and emptied via the blunt end and the eggshells then washed with water. The inner shell membrane and the limiting membrane were manually removed and the remaining eggshells were rinsed in 1 M HCl to dissolve the residual eggshell (i.e. $CaCO_3$), leaving the organic outer shell membrane. After washing thoroughly with water, the outer shell membrane was used as the ESM template for the LDH coating.

Preparation of MgAl–CO_3^{2-}–LDH/ESM composite membrane: $Mg(NO_3)_2{\cdot}6H_2O$ (1.71 g), $Al(NO_3)_3{\cdot}9H_2O$ (1.25 g) and urea (5.60 g) were dissolved in deionized water to form a clear solution with a total volume of 100 mL. The ESM was placed vertically in a Teflon-lined stainless steel autoclave containing the resulting solution, and the apparatus placed in a conventional oven at 90 °C for 3 days. After completion of the growth of the LDH, the composite membrane was taken out of the autoclave, thoroughly rinsed with deionized water, and then dried at room temperature.

Preparation of MgAl–Cl^-–LDH/ESM composite membrane by ion exchange: The anion exchange process was carried out by treating the as-prepared MgAl–CO_3^{2-}–LDH/ESM composite membrane with a salt/acid mixed solution as reported [41]. Typically, 1.0 g of the composite membrane sample was dispersed into 500 mL of an aqueous solution containing 0.5 M NaCl and 1.65 mM HCl under a flow of N_2, and then the system was kept at ambient temperature for 12 h with continuous stirring. The exchanged product was isolated, thoroughly rinsed with deionized water and then dried at room temperature under vacuum.

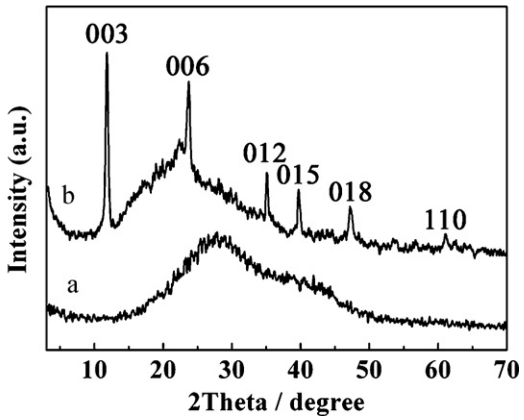

Fig. 1. XRD patterns of (a) ESM and (b) MgAl–CO_3^{2-}–LDH/ESM composite membranes.

2.3. Characterization

X-ray diffraction (XRD) patterns of samples were obtained on a Shimadzu XRD-6000 diffractometer, using Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV, 30 mA, a scanning rate of 10 °/min, a step size of 0.02 °/s, and a 2θ angle ranging from 3 to 70 °. The morphology of the films was investigated by using a scanning electron microscope (SEM, ZEISS supra 55). All samples were sputtered with gold. Elemental analyses for metal elements were performed with a Shimadzu ICPS-7500 inductively coupled plasma (ICP) spectrometer on solutions prepared by dissolving the samples in dilute HNO_3 (1:1). The composite membranes were weighed and then immersed in the HNO_3 for 24 h in order to completely dissolve the LDH.

2.4. Cr(VI) removal experiments

Cr(VI) solutions (100 mg/L) were freshly prepared using analytical grade $K_2Cr_2O_7$ dissolved in distilled water. Sorption kinetics were conducted in a continuously stirred solution in a plexiglass beaker at ambient temperature. For the binding studies, 0.25 g of adsorbent was exposed to 50 mL of Cr(VI) solution, and the pH of the solution was adjusted by 1 mol/L H_2SO_4 solution. The Cr(VI) concentration in the filtrate was subsequently determined using a colorimetric method [42]. Samples were analyzed by UV at 540 nm after complexation with 1,5-diphenylcarbazide. The amount of Cr(VI) adsorbed by the adsorbent and the percentage removal of Cr(VI) are calculated using the following Eqs. (A.1) and (A.2), respectively.

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{A.1}$$

$$\%\ \ \text{Removal of Cr(VI)} = \frac{C_0 - C_t}{C_0} \times 100 \tag{A.2}$$

where q_t (mg/g) is the adsorption loading of the composite membrane at time t, V the volume of solution (L), C_0 (mg/L) and C_t (mg/L) the initial concentrations of Cr(VI) and that at time t, and m the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of the MgAl–CO_3^{2-}–LDH/ESM composite membrane

The XRD patterns of the ESM and the as-prepared MgAl–CO_3^{2-}–LDH/ESM composite membrane are shown in Fig. 1. It can be seen that the ESM is almost amorphous. After the LDH film growth, the typical characteristic peaks of an LDH phase

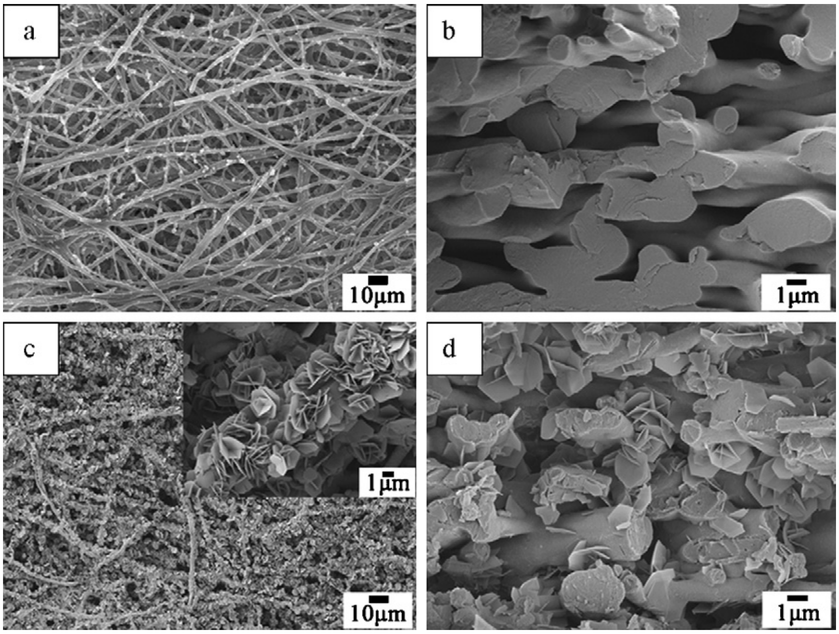

Fig. 2. Top view and cross-sectional views of (a and b) the ESM and (c and d) the MgAl–CO_3^{2-}–LDH/ESM composite membranes.

could be clearly observed, demonstrating the successful formation of the LDH film on the ESM. The two peaks below 25° can be assigned to the [0 0 3] and [0 0 6] reflections of an LDH phase with a basal spacing of 0.75 nm, which agrees well with the published values for MgAl–LDH with interlayer carbonate anions [43].

As mentioned above, the structure of the ESM is an intricate lattice network composed of highly cross-linked protein fibers. However, is the composite membrane able to maintain the network structure? SEM was used to characterize the morphology of the films and the images are shown in Fig. 2.

The hexagonal LDH crystals grown on the fiber of ESM can be clearly observed, and the whole hybrid membrane maintains the network structure. In addition, because the ESM is a semipermeable membrane, the LDH crystals can be formed throughout the whole membrane. LDH crystals with a size of about 1.5 μm are studded in the intricate lattice network of ESM, as the ESM contains an abundance of amine, amide and carboxylate surface functional groups [44], which may interact with the magnesium and aluminum precursor cations, anchoring them on the membrane fiber surface thus facilitating growth of the LDH coating. This mechanism is agreed with other reports about the preparation of $BaCrO_4$ [45], $CaCO_3$ [33] and Pd#PdO [46] nanoparticles by using ESM as template. This is the first time that an LDH has been directly incorporated in such a material by a simple one-step *in situ* hydrothermal crystallization process, and an LDH/ESM composite membrane was successfully obtained (see Fig. 3).

3.2. ESM and MgAl–CO_3^{2-}–LDH/ESM composite membrane as adsorbent

It is well known that the initial pH of a system is an important parameter in the adsorption of Cr(VI). Here, we firstly used ESM as adsorbent for Cr(VI) removal, and the effect of pH values was concerned. The initial pH value of the Cr(VI) solution is 5.1, and 0.1 mol/L H_2SO_4 solution was used to adjust it. We can clearly observe that the removal efficiency of Cr(VI) by ESM is seriously related to the pH value of the solution, the removal efficiency increases with the decrease of the pH value, which is in accordance with the published papers [12–17].

Compared with the adsorption behavior of ESM, the effect of the pH values on the CO_3^{2-}–LDH/ESM is much lower as Fig. 4 illustrates. In addition, the percentage of the Cr(VI) removal is not high in different pH values although the composite membrane containing LDH. It is not hard to come to that CO_3^{2-}–LDH is very stable in composition and the interlayer CO_3^{2-} anions are hard to be exchanged by other anions as $Cr_2O_7^{2-}$.

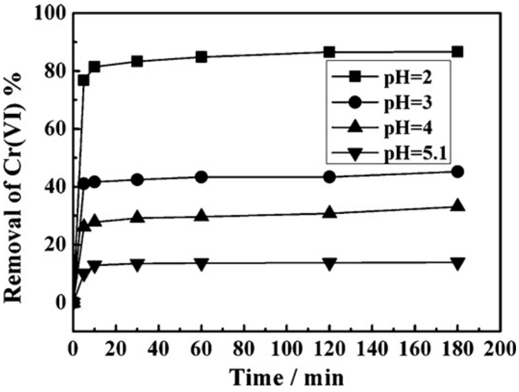

Fig. 3. Effect of pH values on Cr(VI) removal by ESM (initial Cr(VI) concentration: 100 mg/L, solid to liquid ratio (s/l): 5 g/L, temperature: 25 °C).

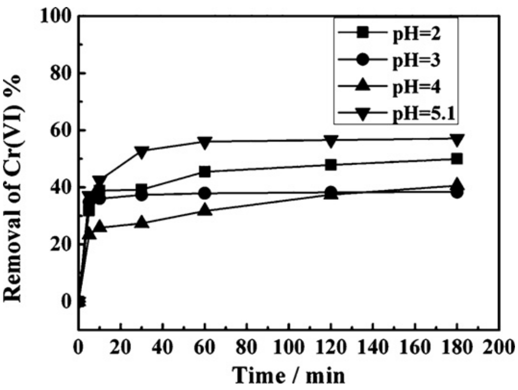

Fig. 4. Effect of pH values on Cr(VI) removal by CO_3^{2-}–LDH/ESM (initial Cr(VI) concentration: 100 mg/L, solid to liquid ratio (s/l): 5 g/L, temperature: 25 °C).

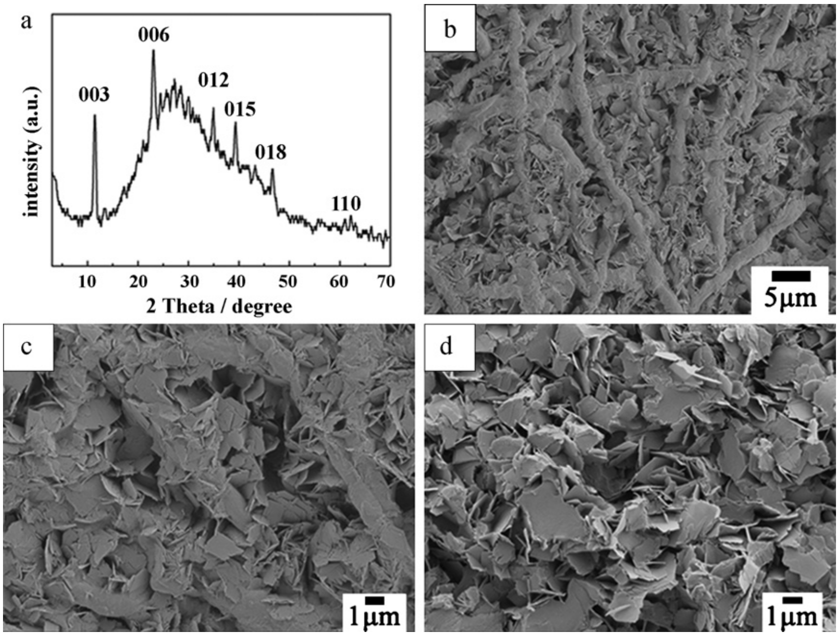

Fig. 5. (a) XRD pattern and SEM images of the MgAl–Cl^-–LDH/ESM composite membrane after anion exchange ((b and c) top view and (d) cross-sectional view).

3.3. Characterization of the MgAl–Cl^-–LDH/ESM composite membrane

In order to improve the adsorption ability of the LDH in the composite membrane, we tried to obtain Cl–LDH/ESM composite membrane by using an anion exchange treatment. The as-prepared hybrid LDH/ESM film was treated with a mixed solution of NaCl/HCl to exchange the CO_3^{2-}–LDH to Cl^-–LDH. The XRD pattern of the treated hybrid (Fig. 5a) shows the typical peaks of an LDH phase. However, in this pattern, the basal reflection with a *d* value of 0.75 nm (0 0 3 reflection) for the CO_3^{2-} form has completely disappeared, and a new series of intense basal reflections at lower 2θ angles appeared instead, corresponding to a basal spacing of 0.77 nm. This interlayer expansion is consistent with that reported in previous work [47,48], suggesting that the decarbonation was successful and that a crystalline Cl^-–LDH product had been formed. The SEM images (Fig. 5 b–d) show that the Cl^-–LDH/ESM composite membrane exhibits almost the same morphology and crystallite size as that of the CO_3^{2-}–LDH/ESM precursor.

The composition and mass loading percentage of the LDHs in the composite membrane were measured by ICP and the results are shown in Table 1. The Mg/Al molar ratios in the LDHs in the final composite membranes are similar to that in the initial synthesis mixtures.

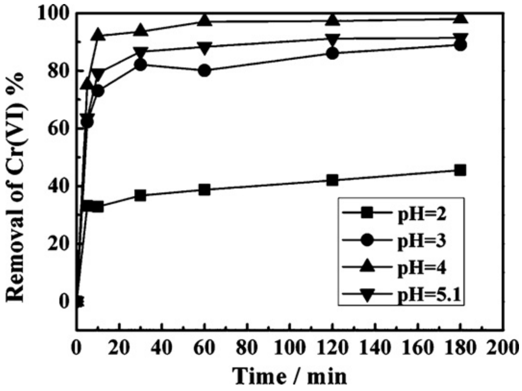

Fig. 6. Effect of pH values on Cr(VI) removal by Cl-LDH/ESM (Initial Cr(VI) concentration: 100 mg/L, solid to liquid ratio (s/l): 5 g/L, temperature: 25 °C).

3.4. MgAl–Cl^-–LDH/ESM composite membrane as adsorbent

The final Cl^-–LDH/ESM composite membrane was used as an adsorbent to remove Cr(VI) from wastewater, and the result is shown in Fig. 6. We could clearly observe that the removal percentage of Cr(VI) was evidently improved by using the Cl^-–LDH/ESM composite membrane as adsorbent. Cr(VI) uptake initially increased with contact time, and then slowed down as fewer active surface sites remained available on the composite membrane. After stirring for about 30 min, the Cr(VI) loading became almost constant, indicating attainment of equilibrium. Besides, the pH value also has effect on the removal efficiency. Be different from ESM, the removal efficiency of the Cl^-–LDH/ESM is much lower when the pH value is 2. We proposed that the LDH will mildly dissolve when the pH value is low to 2, and the adsorbed Cr(VI) would be released to the solution over again. On contrast, LDHs is relatively stable when the pH values are above 3. When the pH value is 3, the Cr(VI) removal rised to 89.0%, and when the pH value is between 4 and 5.1, the removal efficiency could be above 90%. It is worthy to mention that most of these adsorbents can achieve a high adsorption capacity only when the wastewater has extremely low pH values, which means that subsequent neutralization is needed before the treated wastewater can be discharged. Here, the Cl^-–LDH/ESM composite membrane we obtained shows

Table 1
Elemental analysis of the composite membrane by ICP.

Sample	Chemical composition	Mg/Al ratio	Mass loading of LDH (wt.%)
MgAl–CO_3^{2-}–LDH/ESM	$Mg_{0.70}Al_{0.30}(OH)_2(CO_3)_{0.15}\cdot 0.68H_2O$	2.33	19.3
MgAl–Cl^-–LDH/ESM	$Mg_{0.67}Al_{0.33}(OH)_2Cl_{0.33}\cdot 0.63H_2O$	2.05	14.4

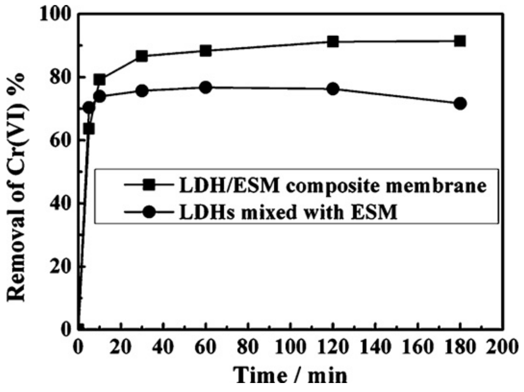

Fig. 7. Kinetics of Cr(VI) removal by an MgAl–Cl⁻–LDH/ESM composite membrane and a physical mixture of 85.6 wt.% ESM and 14.4 wt.% LDH for comparison (initial Cr(VI) concentration: 100 mg/L, pH value: 5.1, solid to liquid ratio (s/l): 5 g/L).

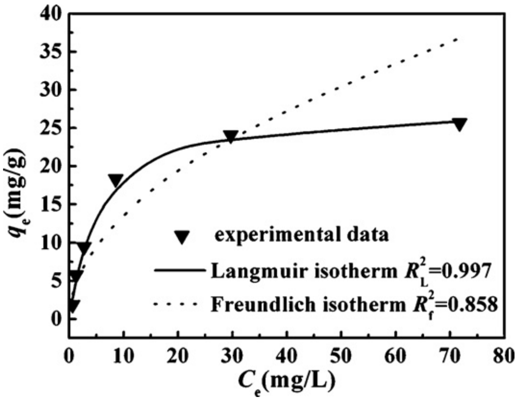

Fig. 8. Plot of equilibrium experimental data and calculated equilibrium data using the Langmuir isotherm model and the Freundlich isotherm model for the adsorption of Cr(VI) onto the MgAl–Cl⁻–LDH/ESM composite membrane.

high adsorption ability even when the initial pH value is at 5.1 without any further adjustment. We further investigated the adsorption behavior of the composite membrane fixing the pH value at 5.1.

For comparison, we also tested the removal efficiency of Cr(VI) using an adsorbent composed of a physical mixture of 85.6 wt.% ESM and 14.4 wt.% LDHs under identical conditions as shown in Fig. 7. The amount of LDH in the mixture was the same as the loading of LDH in the composite membrane. The adsorption behavior of the mixed adsorbent was similar to that of the composite membrane with a rapid initial uptake and a subsequent stable stage. However, the equilibrium removal of Cr(VI) by the mixed adsorbent was only about 76%, much lower than that for the composite membrane. We believe that, in case of the composite membrane, the ESM not only serves as an adsorbent in its own right but also as a support to uniformly disperse the LDH and increase the adsorption capacity of the latter, resulting in the superior performance of the composite membrane.

3.5. Adsorption isothermal study

Adsorption isotherms are important way of probing the mechanism of adsorption of Cr(VI) on the adsorbent surface. Equilibrium studies are useful in order to obtain the adsorption capacity of sorbents for Cr(VI) removal. In the present study, two general-purpose equilibrium models were used to fit the experimental data: (i) the Langmuir adsorption model [49] (Eq. (B.1)) and (ii) the Freundlich adsorption model [50] (Eq. (B.2)).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{B.1}$$

$$q_e = K_f C_e^{n_F} \tag{B.2}$$

In the Langmuir adsorption model, $q_{\max}$ (mg/g) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and b (L/mg) is the Langmuir constant. For a Langmuir type adsorption process, to determine if the adsorption is favorable or not, a dimensionless separation factor [51] is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{B.3}$$

If $R_L > 1$, the isotherm is unfavorable; when $R_L = 1$, the isotherm is linear; in the range $0 < R_L < 1$, the isotherm is favorable; when $R_L = 0$, the isotherm is irreversible.

In the Freundlich adsorption model, K_f ($\mathrm{mg}^{1-1/n}\,\mathrm{L}^{1/n}$/g) is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n_F is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as the Freundlich coefficient.

Fig. 8 shows that the Langmuir isotherm is a much better fit to the experimental data than the Freundlich isotherm on the basis of the correlation coefficients ($R_L^2 = 0.997$, $R_f^2 = 0.858$), confirming the monolayer adsorption of Cr(VI) onto the composite membrane surface. The Langmuir constant $q_{\max}$, which is a measure of the monolayer adsorption capacity of the composite membrane, was 27.9 mg/g. The Langmuir constant, b, which denotes adsorption energy, was found to be 0.176 L/mg. The dimensionless parameter, R_L, which is a measure of adsorption favorability was 0.0537 (i.e., $0 < R_L < 1$) suggesting that the adsorption of Cr(VI) on the composite membrane is favorable, as observed experimentally. In the experiments, we also studied the adsorption isotherms of the adsorbent composed of a physical mixture of 85.6 wt.% ESM and 14.4 wt.% LDHs under identical conditions. However, it seems that the adsorption behavior of the mixed adsorbent is much more complicated than the composite membrane. The correlated coefficient R_L^2 is only 0.761 which indicates that the Langmuir model is not the suitable model for describing the sorption behavior of the mixed adsorbents used here. The monolayer coverage was thus not obtained. On contrast, the Freundlich model is much more fitted to the experimental data than the Langmuir model, the correlated coefficient R_f^2 achieved 0.935, and the values of the K_f and n_F are 0.620 and 0.843, respectively.

In Table 2, the adsorption capacity of the MgAl–Cl⁻–LDH/ESM composite membrane is compared with the values for other adsorbents for the removal of Cr(VI) reported in the literature. The comparison indicates that the maximum adsorption capacity obtained with our composite membrane is higher compared than those obtained with many other low-cost adsorbents. It should be noted that all the other adsorbents are only effective after the pH is adjusted to low pH values (1.0–4.0) whereas our composite membrane was effective at the natural pH of the solution (5.1) without

Table 2
Summary of Cr(VI) adsorption capacities of various adsorbents.

Adsorbent	$q_{\max}$ (mg/g)	pH	Temperature (°C)	Reference
Coconut tree sawdust	3.46	3.0	25	[52]
Lignin	5.64	2.5	25	[53]
Activated carbon	15.47	4.0	25	[54]
Beech sawdust	16.13	1.0	25	[55]
Hazelnut shell	17.7	2.0	20	[56]
LDH/ESM	27.9	5.1	20	This work
Modified jacobsite	31.55	2.0	25	[57]
Neem leaves	62.97	2.0	30	[58]
Alligator weed	82.57	1.0	30	[13]

the necessity for addition of acid to lower the pH. This result is very encouraging as far as practical application in a wastewater treatment plant is concerned, because if the pH of the treated effluent is low, a further neutralization treatment would be necessary.

4. Conclusion

A novel inorganic biocomposite MgAl–CO_3^{2-}–LDH/ESM membrane has been obtained by using an *in situ* growth method. The LDH was immobilized on the surface of the ESM fibers, and the composite membrane maintained the network structure of the ESM precursor. Elemental analysis showed that the mass loading of the LDH in the composite membrane was about 19.3 wt.%. By treating the as-prepared CO_3^{2-}–LDH/ESM composite membrane with a salt/acid mixed solution, the interlayer carbonate anions in the LDH were exchanged by Cl^- and a MgAl–Cl^-–LDH/ESM composite membrane was obtained. The ESM, MgAl–CO_3^{2-}–LDH/ESM membrane and MgAl–Cl^-–LDH/ESM composite membrane was used as adsorbent for Cr(VI) removal respectively, and the effect of the pH value on the removal efficiency was mainly investigated. It resulted that the MgAl–Cl^-–LDH/ESM composite membrane could be an efficient adsorbent for the Cr(VI) removal even at pH values not requiring addition of acid. The removal efficiency was more that 90% and equilibrium was attained after only 30 min. The equilibrium data were tested with the Langmuir isotherm model and the Freundlich isotherm model. The data gave the best fit with the Langmuir isotherm model which confirms that there is monolayer adsorption of Cr(VI) on the composite membrane. The maximum adsorption capacity obtained with the Langmuir isotherm model was 27.9 mg/g, which is comparatively high in relation to that for other materials reported in the literature.

Acknowledgements

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