



Novel alkyimidazolium/vanadium pentoxide intercalation compounds with excellent adsorption performance for methylene blue

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ABSTRACT

Novel alkyimidazolium-intercalated V_2O_5 compounds were synthesized by a redox reaction between iodide ion and V_2O_5 . The X-ray photoelectron spectroscopy and the diffuse reflectance UV–vis spectrometry experiments reveal that the vanadium in the intercalated V_2O_5 products was partially reduced by an iodide ion and the resultant iodine can be removed in the final products. The transmission electron microscope observation and X-ray diffraction analysis testify that the prepared alkyimidazolium/ V_2O_5 intercalation compounds have typical lamellar structure with different d_{100} interlayer spacing values and the special straw-like nanofiber morphology with the length of 0.5–10 μm . Systematic investigation indicates that new intercalation compounds possess the extraordinary adsorption performance for methylene blue in an aqueous solution.

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1. Introduction

The intercalation compounds are attracting more attention, because of their novel functional properties and potential applications in various fields [1–4]. Vanadium pentoxide is a suitable host material for an intercalation chemistry, due to its unique redox activity and layered structure [1,5,6]. Many novel functional materials have been prepared by the insertion of various atomic and molecular species into the layered framework of V_2O_5 , such as surfactants [7], polymers [8–11], dyes [12–14], coordination complexes [15,16] and other organic molecules [17]. These V_2O_5 intercalation materials have received significant interest due to their special microstructures and potential applications in photochemistry, electrochemistry and catalysis [1,7–16].

Using ionic liquids (ILs) as the solvent or reactant, various nanostructured materials with different morphologies have been synthesized by self-assembling or solvent thermal methods [18–20]. Immobilizing ionic liquids on the layered host materials to improve their functional properties are attracting much attention, for example, Zhou et al. [21] reported the synthesis of the lamellar silica using 1-hexadecyl-3-methylimidazolium chloride as template materials. Wang et al. [22] prepared 1-alkyl-3-methylimidazolium chloride ionic liquid–zirconium phosphates intercalation materials in an aqueous solution of ILs. A novel ionic liquid–kaolinite intercalation materials were also obtained by the intercalation in the interlamellar spaces of the clay mineral kaolinite with ionic liquids based on imidazolium derivatives [23]. Recently, the intercalated compounds

of vanadium pentoxide-IL ($C_2\text{mimBF}_4$, $C_4\text{mimSO}_3\text{CF}_3$ and $C_8\text{mimBF}_4$) were synthesized using VOCl_3 as precursor together with imidazolium-based ILs as solvent and structure-directing agent [24]. However, there are few reports about the synthesis of ionic liquid intercalated metal oxides materials with semiconducting properties [24]. In the present work, the imidazolium-based ionic liquid with I^- anion was used in the preparation of alkyimidazolium-intercalated V_2O_5 compound. A simple oxidation–reduction reaction of I^- and V_2O_5 host materials resulted in the formation of novel alkyimidazolium (the cation of an ionic liquid) intercalated V_2O_5 compounds (see Scheme 1). The prepared materials exhibit the typical layered structure and special straw-like nanofiber morphology and possess an interesting functional property for ultra-fast removal of methylene blue from an aqueous solution by adsorption.

2. Experimental

2.1. Reagents

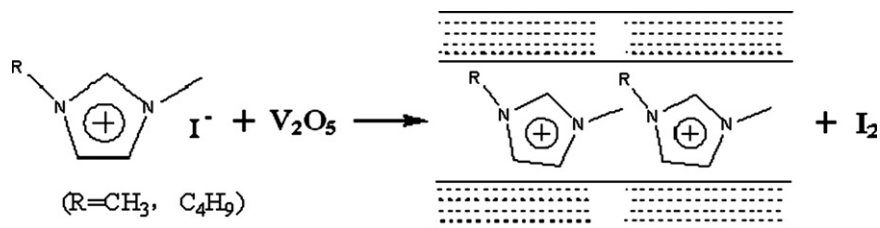
All the chemicals used (1-iodo-butane, iodomethane, ammonium metavanadate, acetone, dichloromethane and N-methylimidazole) are analytic purity and purchased from China National Medicines Corporation. The N-methylimidazole was further purification by distillation before use.

2.2. Synthesis

The V_2O_5 powders were prepared by heating ammonium metavanadate at 823 K for 4 h in air. The heating rate was 1 K/min from

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Scheme 1. The synthesis of alkylimidazolium/V₂O₅ intercalation compound.

298 to 823 K. 1-methyl-3-methylimidazolium iodide ([Mmim]I) and 1-butyl-3-methylimidazolium iodide ([Bmim]I) ionic liquids were synthesized according to the reported method [25]. The mechanism of the intercalation reaction is the direct redox reaction of the reducing agents I⁻ in the intercalation reagents ([Mmim]I and [Bmim]I) and V(V) of the host crystals (V₂O₅), which has been reported in literatures [12,13]. In a typical synthesis of 1-methyl-3-methylimidazolium/V₂O₅ compounds (denoted as [Mmim]/V₂O₅), a solution containing 2 g [Mmim]I and 10 g deionized water was mixed with 3 g V₂O₅ powders ($nV_2O_5:n[Mmim]I=1.9$), and then heated at 393 K for 8 h in a sealed autoclave (25 ml). After that, the resulted mixtures were washed with deionized water and acetone for several times, and the separated products were finally dried in air at 353 K for 4 h. 1-Butyl-3-methylimidazolium intercalated V₂O₅ compound (denoted as [Bmim]/V₂O₅) was prepared by the same synthesis method, using 2.0 g [Bmim]I and 2.6 g V₂O₅.

2.3. Adsorption experiments

The adsorption performance of the intercalated V₂O₅ materials for different dyes (methylene blue, methyl orange and rhodamine B) in an aqueous solution was investigated at room temperature. In a typical experiment, intercalated materials of 0.01 g were added into 500 ml aqueous solution of methylene blue at the concentration of 10 mg/l. After a preselected time of decolorization, the samples were collected by centrifugating, and the residual dyes concentration in the experimental solution (mg/l) was analyzed using an ultraviolet–visible spectrophotometer (UV1102, TECH-COMP) at a λ_{max} of 662 nm and determined, using the standard curve method. For comparison, the adsorption performance of activated carbons and V₂O₅ for methylene blue was also investigated, using the same method and experimental conditions.

2.4. Characterization

The X-ray diffraction (XRD) patterns of all samples were collected in θ – 2θ mode using a Bruker Corporation D8-Advanced diffractometer (Cu K α radiation; $\lambda=0.154$ nm), and the XRD samples run as powders transmission electron microscopy (TEM) was measured with JEM-2010 electron microscope operated at 200 kV. Infrared spectra (FT-IR) were recorded on a Nexus-870 Fourier-transform spectrophotometer from KBr pellets with a measuring range 400–4000 cm⁻¹. The elemental analysis for C, H and N was carried out on Vario EL III elemental analyzer. The UV–vis diffuse reflectance spectra were measured with a JASCO UV550 UV–vis adsorption spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed on the instrument of PHI 5000C ESCA system using C_{1s} (284.6 eV) as a reference to correct the binding energy. Thermogravimetric analysis (TGA) was performed on Perkin Elmer Diamond thermogravimetric analyzer in air from room temperature to 973 K, with a heating rate of 10 K/min.

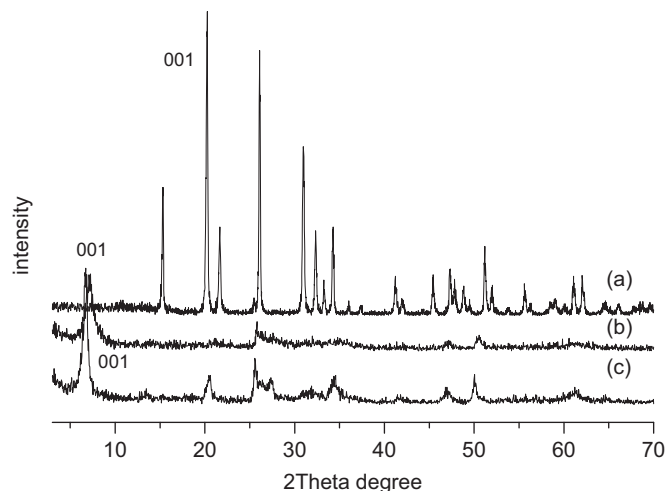


Fig. 1. XRD patterns of V₂O₅ (a), [Mmim]/V₂O₅ (b) and [Bmim]/V₂O₅ (c).

3. Results and discussion

3.1. The lamellar structure of alkylimidazolium/V₂O₅

The X-ray powder diffraction patterns of V₂O₅ host materials (Fig. 1a) are consistent with the data available in the No. 41-1426 diffraction file (JCPDS) for orthorhombic V₂O₅ [26]. The layered host lattices are in favor of immobilizing of guest molecules. A preliminary analysis of strong reflections in the X-ray powder diffraction pattern of the alkylimidazolium–V₂O₅ intercalation compounds is shown in Fig. 1b and c, which reveal that the alkylimidazolium–V₂O₅ intercalation compounds have new crystalline phases by comparison with the diffraction patterns of V₂O₅. The low intensity in these broad peaks suggests that these materials have lower crystallinity owing to the insertion of alkylimidazolium. Furthermore, a shift of the 001 reflection to lower 2θ values is observed in the XRD patterns of the intercalation compounds, which testifies an increase of the interlayer spacing after the insertion of ionic liquid cations into V₂O₅. The interlayer d_{001} -spacing increased with the increasing of the alkyl chain length, from 0.43 (V₂O₅) to 1.22 nm ([Mmim]/V₂O₅) and 1.32 nm ([Bmim]/V₂O₅).

3.2. TGA analysis and element composition of alkylimidazolium/V₂O₅

The TGA and DTA curves (Fig. 2) of [Mmim]/V₂O₅ reveal a total weight loss of 16.6 wt% in the temperature range 323–649 K and a total weight increase of about 0.6 wt% between 649 and 873 K. The weight loss should be ascribed to thermal decomposition of alkylimidazolium in air (about 16.0 wt%) and the O loss of V₂O₅ (about 0.6 wt%) in the reduction of V₂O₅, and a corresponding exothermic peak at 573 K in the DTA curve can be observed. The oxidation of partly reduced V₂O₅ in air is responsible for the total

weight increase and the corresponding exothermic peak is probably at 653 K. The exothermic phenomenon at 718 K is attributed to the crystallization of V_2O_5 in high temperature.

The element composition analysis (Table 1) shows that the C, H and N contents in $[Mmim]/V_2O_5$ material is 9.867, 1.572 and

4.681 wt%, respectively. It can be noted that the mole ratios of C, H and N in the intercalation compounds are the same to those of ionic liquid cations, suggesting that the structure of imidazolium-based cations was unchanged in the intercalation compounds. The total weight of C, H and N is 16.12 wt%, in well agreement with the loss of alkylimidazolium in TGA. Its molecular formula can be speculated as $(C_5H_9N_2)_{0.36}V_2O_5$. The molar ratio of alkylimidazolium in the intercalation compound is lower than the value in the added reactants. When $[Mmim]/V_2O_5$ in the molar ratio of 1:3.8 was used in the synthesis, the molecular formula of the resultant compound is $(C_5H_9N_2)_{0.25}V_2O_5$, which is in agreement with the reported results by Huang et al. [13] and approximate to the theoretical value. These results suggest that the stoichiometry of the intercalation compounds can be controlled only within the limit range. For $[Bmim]/V_2O_5$ intercalation compounds, the corresponding values were 13.260(C), 2.077(H) and 3.899 wt%(N). The inserted amount of the alkylimidazolium cations in the intercalation compounds decreases with the increasing length of an alkyl chain, probably because of their steric effect.

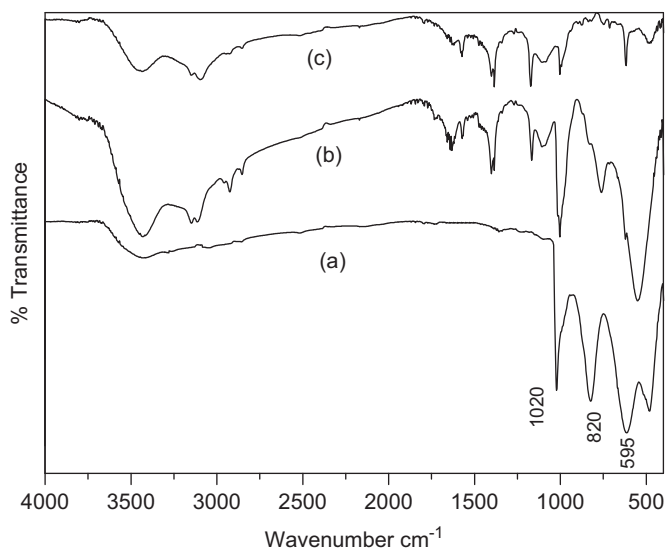


Fig. 2. TG (a) and DTA (b) curves of $[Mmim]/V_2O_5$.

Table 1

The element composition of alkylimidazolium/ V_2O_5 .

Compounds	N (wt%)	C (wt%)	H (wt%)	Molecular formula
$[Mmim]/V_2O_5$	4.681	9.867	1.572	$(C_5H_9N_2)_{0.36} \cdot V_2O_5$
$[Bmim]/V_2O_5$	3.899	13.260	2.077	$(C_8H_{15}N_2)_{0.31} \cdot V_2O_5$
$[Mmim]/V_2O_5 - 2^a$	3.272	6.984	0.189	$(C_5H_9N_2)_{0.25} \cdot V_2O_5$

^a In the synthesis, the molar ratio of $[Mmim]/V_2O_5$ is 1:3.8.

3.3. FT-IR, XPS and UV-vis spectra alkylimidazolium/ V_2O_5

The infrared spectra of the V_2O_5 , $[Mmim]/V_2O_5$ and $[Mmim]$ were also investigated (Fig. 3). In the spectrum of bulk V_2O_5 , the band at 1020 cm^{-1} has been ascribed to the V–O stretching of the vanadyl group (V=O), and the bands at 820 and 595 cm^{-1} are related to the vibrations associated with the vanadium–oxide bridges (V–O–V). The bands at 2800 – 3200 , 1400 , 1200 and 620 cm^{-1} ascribing to the C–H, C–N and N–H vibrations of 1-methyl-3-methylimidazolium were observed in the IR spectrum of $[Mmim]/V_2O_5$, which testifies 1-methyl-3-methylimidazolium was inserted into the interlayers of V_2O_5 . The band at 1000 cm^{-1} corresponding to the V=O vibration in the intercalated compounds displays an obvious shift towards the lower wavenumber, and the result suggests that 1-methyl-3-methylimidazolium is intercalated into the interlamellar region of layered vanadium–oxide, accompanying the reduction of V(V) [8]. The XPS results from the

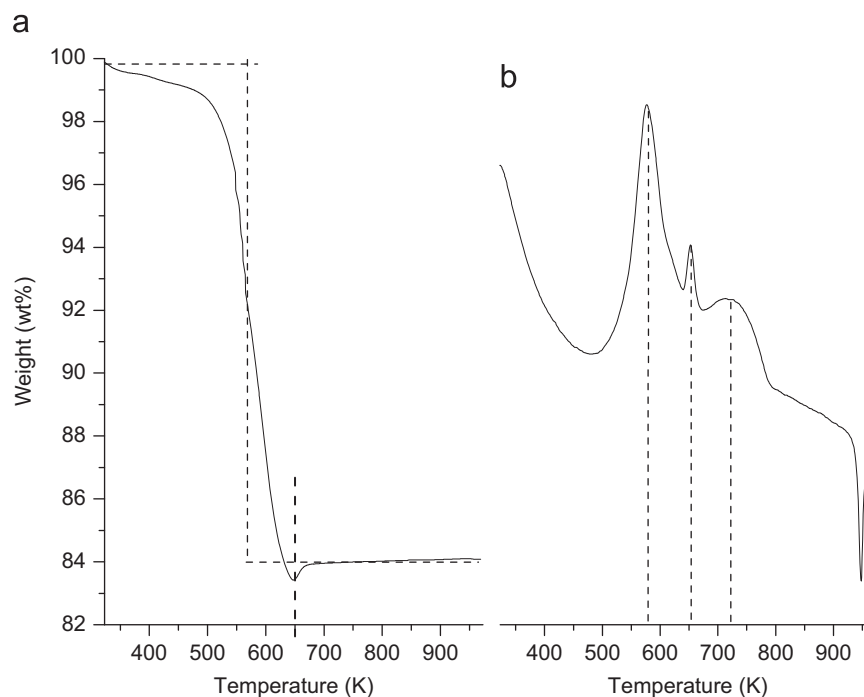


Fig. 3. FT-IR spectra of V_2O_5 (a), $[Mmim]/V_2O_5$ (b) and $[Mmim]$ (c).

$V2p_{3/2}$ core levels of the intercalation compounds are displayed in Fig. 4. The $V2p_{3/2}$ XPS signals in two intercalation compounds can be deconvoluted into individual spectral lines, as shown in Fig. 4. There are two peaks located at the binding energy of 516.8 and 514.4 eV in the $V2p_{3/2}$ spectra. A binding energy feature at 516.8 eV is apparent along with V^{5+} species and a low binding energy feature at 514.4 eV is attributed to V^{4+} . These phenomena confirmed the partly reduction of V(V) in these intercalation materials.

The UV–vis spectra of [Mmim]/I in aqueous solution and I_2 in CH_2Cl_2 solution (Fig. 5b and c) show that [Mmim]/I have two remarkable adsorption peaks at 290 and 350 nm and I_2 has a strong adsorption band between 400 and 600 nm. A little of [Mmim]/I existed in the aqueous phase in an autoclave at the end of the reaction, which can be confirmed by the corresponding UV–vis spectra (Fig. 5a) in contrast to the adsorption peaks of [Mmim]/I. It indicates that [Mmim]/I is not completely reacted with V_2O_5 , in agreement with the element analysis results. The corresponding CH_2Cl_2 extract from the reaction mixtures testified the production of a large amount of I_2 (Fig. 5d), which is resulted from the redox reaction of V_2O_5 and I^- in the heating process of reactants. In addition, there are no adsorption bands of I_2 in the diffuse reflectance UV–vis spectra (Fig. 6) of

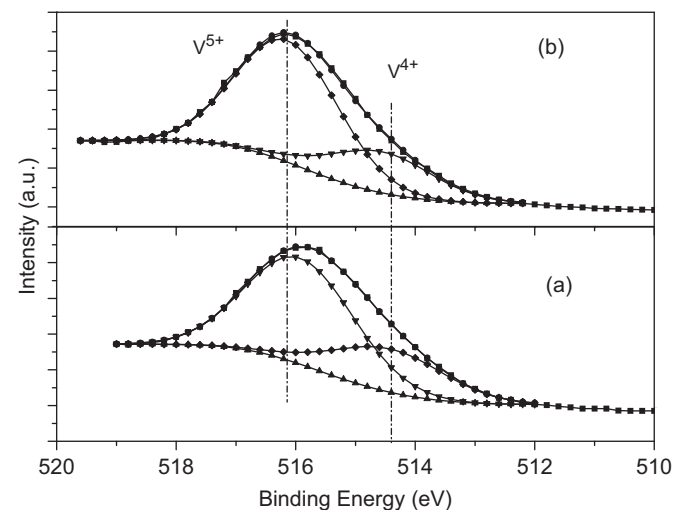


Fig. 4. Curve-fitting XPS spectra of $V2p_{3/2}$ in [Mmim]/ V_2O_5 (a) and [Bmim]/ V_2O_5 (b).

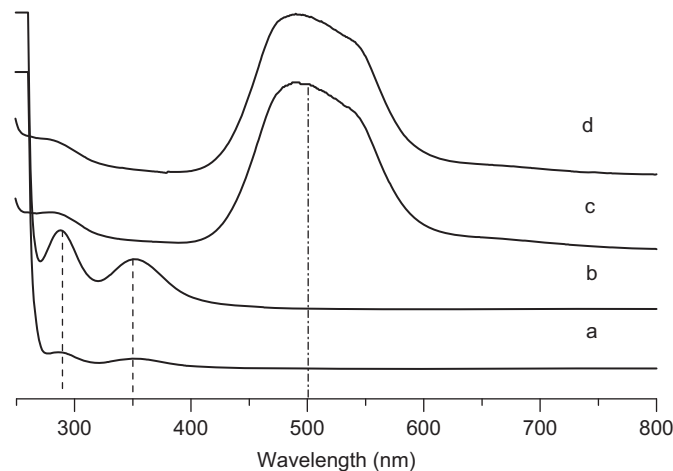


Fig. 5. The UV–vis spectra of the water extract from solid mixtures after reaction (a), 0.1 M [Mmim]/I solution (b), 5×10^{-4} M CH_2Cl_2 solution of I_2 (c) and the CH_2Cl_2 extract from solid mixtures after reaction (d).

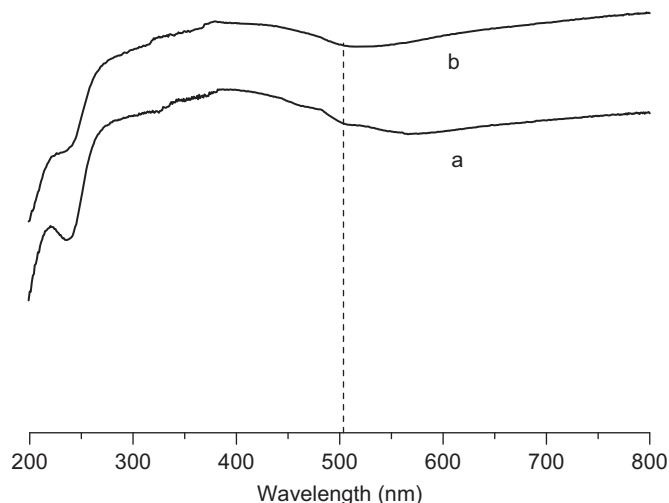


Fig. 6. The diffuse reflectance UV–vis spectra of [Mmim]/ V_2O_5 and [Bmim]/ V_2O_5 .

[Mmim]/ V_2O_5 and [Bmim]/ V_2O_5 , suggesting that I_2 was removed in the final intercalated compounds (Fig. 6).

3.4. Morphology of alkylimidazolium/ V_2O_5

TEM images (Fig. 7) of the [Mmim]/ V_2O_5 materials reveal its interconnected nanofiber morphology. These special straw-like fibers have width of 20–50 nm, and length of 0.5–10 μm . The lamellar structure of 1-methyl-3-methylimidazolium intercalation vanadate can obviously be observed in the HRTEM image of [Mmim]/ V_2O_5 (Fig. 6b). The size of two dark fringes was about 1.2 nm, in agreement with the result evaluated by the $d(001)$ reflection in the broad X-ray diffraction pattern.

3.5. Adsorption performance of alkylimidazolium/ V_2O_5

The V_2O_5 and hybrid V_2O_5 materials are the widely studied and promising materials in catalysis and lithium-ion batteries [27,28]. However, their adsorption performances are rarely studied. Actually, the intercalation materials may be the effective adsorbents for dyes in wastewater owing to their special structures and components [29]. The adsorption performance of alkylimidazolium– V_2O_5 intercalation compounds for dyes in aqueous media has been investigated, and the results were shown in Fig. 8.

It can be seen that the [Mmim]/ V_2O_5 materials show the different adsorption performance for methylene blue, methyl orange and rhodamine B (Figs. 8 and 9). These intercalation compounds show lower adsorption ability for methyl orange and rhodamine B. However, the adsorption ratio for methylene blue reaches to 81 wt% within 5 min, and 5 mg methylene blue in 500 ml solution can be completely removed in 30 min, using 0.01 g [Mmim]/ V_2O_5 as the sorbent. Its adsorption amount and speed are higher than those of the reported adsorbents for methylene blue [30,31]. Moreover some photos at different steps in the whole adsorption procedure for methylene blue were recorded (Fig. 10). These images demonstrated that methylene blue dyes were fast absorbed on the surface of the intercalation compounds. The [Mmim]/ V_2O_5 materials were dyed and its volume in aqueous seems to become larger with the adsorption of methylene blue. The adsorption results of V_2O_5 , [Bmim]/ V_2O_5 and activated carbons were also obtained in the same experimental conditions (Fig. 9). The V_2O_5 exhibits very low adsorption amount for methylene blue. [Bmim]/ V_2O_5 exhibited the excellent adsorption performance for methylene blue and has 80 wt% adsorption ratio (the corresponding adsorbed amount is 400 mg/g) within 30 min. The adsorption ratio of activated carbons for methylene blue is 50 wt% within 30 min.

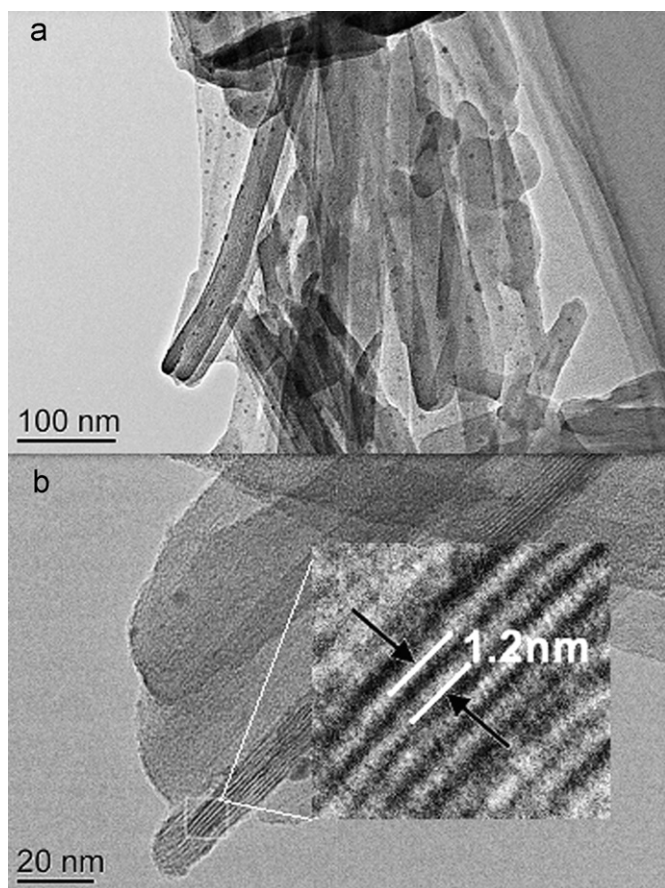


Fig. 7. TEM (a) and HRTEM (b) images of the [Mmim]/V₂O₅ materials.

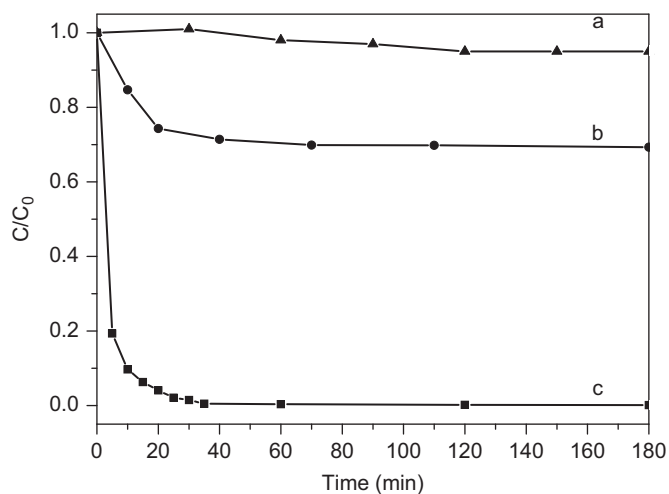


Fig. 8. The adsorption curves of [Mmim]/V₂O₅ for methyl orange (a), rhodamine B (b) and methyl blue (c).

The corresponding adsorption amount for methyl blue is 250 mg/g within 30 min and about 280 mg/g in 60 min. Its adsorption speed and amount for methyl blue are remarkably lower than those of the V₂O₅ intercalation materials.

4. Conclusions

In conclusion, these investigation results indicate that the adsorption ability of the laminal compound V₂O₅ can be obviously

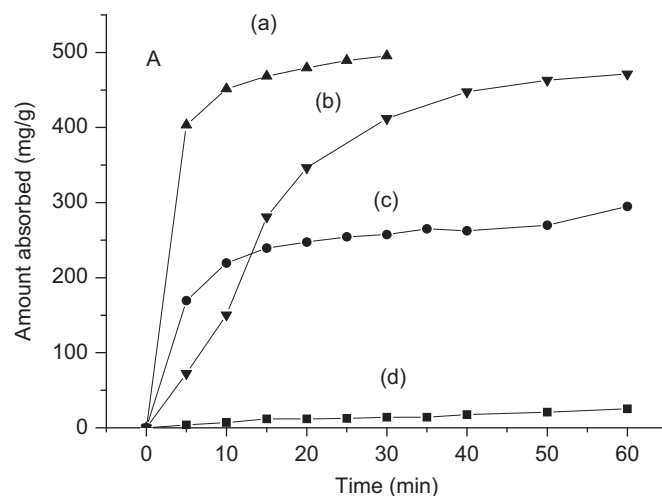


Fig. 9. Adsorption of methylene blue on different materials: [Mmim]/V₂O₅ (a), [Bmim]/V₂O₅ (b), activated carbons (c) and V₂O₅ (d).

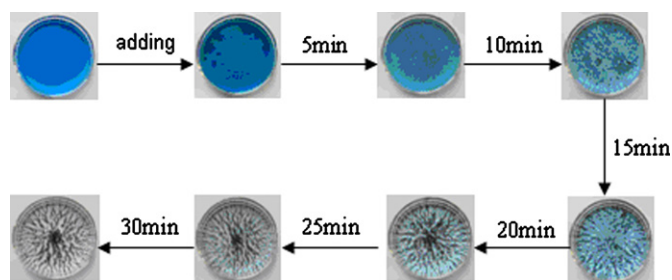


Fig. 10. The photos recorded at the different time for the adsorption of methylene blue on [Mmim]/V₂O₅.

upgraded by inserting alkylimidazolium into the interlayer of V₂O₅, which has been demonstrated by the extraordinary adsorption performance for methylene blue in aqueous media. However, these intercalation compounds also show lower adsorption ability for methyl orange and rhodamine B. It may offer an economical and simple adsorption treatment for the removal of methylene blue in wastewater from printing and dyeing industry.

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