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Performance, synthesis and removal of vanadium on ferruginous manganese composite material

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Through the processes of precipitation，filtration, drying and calcination, Fe-Mn compounds were synthesized artificially. The performance of these processes is accessed. By using X-ray fluorescence, testing the specific surface area, analyzing the X-ray diffraction, infrared spectroscopy, scanning electron microscopy testing technology to characterize this material, in order to investigate its mechanism of arsenate adsorption and the factors that influence. The results of the experiment showed that when the initial concentration of vanadium was 50mg/L, 0.1g of ferruginous manganese composite material was used, the reaction time reached 2 hours. The best absorption efficiency was obtained at the temperature 30°C and pH value of 4. Adsorption of ferruginous and manganese complexes of vanadium (V) are in accord with the Langmuir adsorption model (R^2=0.9682), the kinetic data are consistent with the two order kinetic models (R^2=0.9999), the maximum adsorption capacity is 14.16mg/g.

Key words: Fe-Mn compounds; Vanadium (V); influencing factors; adsorption mechanism; kinetics

INTRODUCTION

Vanadium is one of the main trace elements in fossil fuels, the vanadium compounds are usually toxic and their toxicity is enhanced by the increase vanadium content. Vanadium compounds have the highest toxicity. The vanadium smelt factory and vanadium alloy plant produce the chemical dust and aerosols which cause the high concentration of vanadium pollution in the neighboring area. The oil refineries, fuel and coal fired plants and chemical plants, also cause high toxicity and vanadium pollution of the water body. In the process of vanadium industry development the high concentration of vanadium industrial waste water has the characteristics of large and harmful emissions, heavy-toxicity, not easy to biodegrade. Therefore, finding an effective treatment to the vanadium containing wastewater and restoring the vanadium (V) polluted soil has become one of the most important research subject in the field of environmental science and technology.

Currently, the research on the treatment methods of industrial wastewater containing vanadium (V) at home and abroad mainly include chemical precipitates (including iron precipitation, lime neutralization precipitation and SO2 precipitation), the ion exchange method and the adsorption method. The adsorption method is renewable and widely used. The previous reports in the literature on vanadium adsorbents, such as natural mineral water talc [5], manganese acid leaching residues [6], modified iron-chips [7], modified ferrous ion zeolite [8], that have the good adsorption capacity of vanadium (V) ions. At the same time, the pilot study of the experiment [2] proved that natural iron manganese ore has the adsorption capacity of vanadium (Ⅴ) up to 522μg·g-1 and the contrast experiment resulted that the proportion of different iron ore and ferro-manganese has a great influence on the removal of vanadium (V). Due to the above study, this experiment will compound the oxide iron that has a high surface charge, large specific surface area and strong adsorption ability for many inorganic contaminants [9] with manganese that has a strong oxidation ability. In the experiment, an effort to obtain more efficient vanadium (V) adsorption materials as well as the absorption performance and the functional mechanism of the oxide ferro-manganese compound surface on the absorption of vanadium (V).

Introduction to the experiment

The main reagents and equipment

The equipment used in the experiments is comprised of ASAP 2020M an automatic specific surface area and porosity analyzer (American Micromeritics), an Axios advanced X-ray fluorescence spectrometer (Netherland PANaLyticaL B.V), D/MAX-RB a target X-ray diffractometer (Japan RIGAKU), JSM-5610LV a scanning electron microscope (JEOL), UV-1100 an ultraviolet and visible spectrophotometer (Shanghai MAPADA) and others.

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The main reagents used in this experiment were NaVO3, carbamide, BPHA, FeSO4•7H2O, MnSO4•H2O, with a high purity, the water was deionized.

Introduction of the experimental methods

The preparation of ferruginous manganese composite material

To prepare the compound a series of different concentrations of Fe/Mn solutions, through the mixture of FeSO4•7H2O and MnSO4•H2O in water and drop the precipitation saturated solution respectively in the series solutions. In the process of dropping, the stirring of solution need be done until it no longer produces new precipitation, the solution be put standing, and pour out the supernatant liquid. Following suction and filtering the lower metal oxide hydrate precipitate in the solution and after repeatedly washing the precipitate with deionized water, until the adding of BaCl2 no longer produces a white precipitate in the filtrate. The metal oxide is dried under 105°C for 2 hours at a constant weight then put in a muffle furnace and calcinated for 2 hours under 450°C. After cooling, grinding and sieving with a 100 ~ 190 mesh, it is stored for further use.

Introduction of the characterization experiment

The Fe-Mn compounds are experimentally characterized by using XRF, BET, XRD, FTIR and SEM.

Introduction of the static adsorption experiment

Using a sodium metavanadate simulated compound 500 mg/L of vanadium (V) contained in wastewater reserve liquid (in this paper, the vanadium in the solution is measured as V2O5). Accurately weigh a 0.1g adsorbent and put it in a 100mL conical flask, 30.00mL certain a concentration simulated V2O5 solution, reacting after 1 hour in the thermostat oscillator under 30°C, then subjected to a high speed centrifugal spin for 30 min, BPHA and the extraction spectrophotometric method are used to analyze the residual V2O5 concentrations in the supernatant.

Introduction to the adsorption and adsorption kinetics experiment

By changing the pH value (2.0~12.0) and temperature (25~50°C) for different water quality conditions of the vanadium solution the adsorptive characteristics of vanadium (V) by the Fe-Mn compound is explored. Weighing another 0.1g of adsorbent and putting it in a 100mL conical flask, with 30.00mL of the concentration of 50mg/l V2O5 solution is placed in a thermostat oscillator under 30°C, the samples were taken at different time intervals, the vanadium (V) concentrations were measured and calculate the adsorption quantity for different periods.

THE RESULTS AND ANALYSIS

The best Fe/Mn mole ratio in the preparation of composite material

The selection of precipitant

In the preparation of a series of solutions where the Fe/Mn mole ratios are 5:1, 3:1, 1:1, 1:3, 1:5, NaOH and Na2CO3 are used as the precipitants, to prepare the compound oxides, the removal efficiency of vanadium (V) is compared, the results are shown in figure1. When the Na2CO3 is used as the precipitant, the removal rate of vanadium (V) is obviously higher than the NaOH precipitant, the reason is that Na2CO3 reacts with iron, manganese and generates the carbonate precipitation, in the subsequent calcination process, the carbonate decomposition releases large amounts of CO2, and the porosity of the Fe-Mn compound is increased. Due to the higher porosity, a better removal will result for vanadium (V), therefore, when Na2CO3 is used as the precipitant the Fe-Mn composite compound removal of vanadium (V) is better than when NaOH is the precipitant. In the subsequent experiments, Na2CO3 will be used as the precipitant to prepare the Fe-Mn compound and the precipitation sequence of different precipitants can be analyzed.

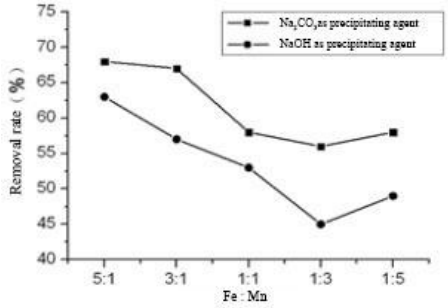


Fig.1. Comparison of the removal efficiency of the Fe-Mn compound when NaOH and Na2CO3 are used as precipitants.

Selection of the Fe/Mn mole ratio

Preparation of a series of solutions with Fe/Mn mole ratios (in this study refer to the mole ratio) are 12:1, 8:1, 5-1, 3:1, 1:1, 1:3, 1:5, 1:8, 1:12, the Na2CO3 is used as the precipitant to prepare the Fe-Mn compounds, by comparing the best Fe/Mn ratio for the removal efficiency of vanadium (V), the results are shown in figure 2.

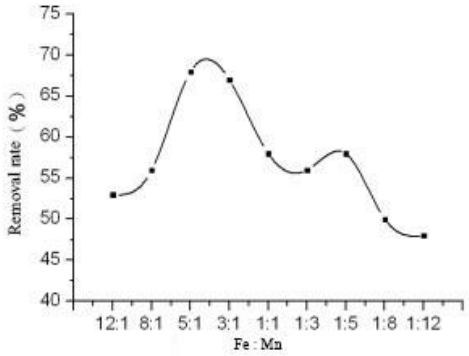


Fig. 2. Different Fe/Mn ratios (mole ratio) of Fe-Mn compounds with respect to the changes in the removal rate of vanadium (V).

As evident from figure 2 the removal efficiency increases quickly with the smaller ratio of Fe/Mn, when the Fe/Mn ratio was 5:1, the maximum removal rate reached 67.8%, and then showed a decrease trend. Therefore, the subsequent experiments will choose the 5:1 Fe/Mn ratio as the best ratio for the removal of vanadium (V).

The influence of water quality on Fe-Mn compound removal performance for vanadium

The influence of the pH value on the removal performance of vanadium

Under the same reaction conditions, the initial pH value of the vanadium solution is changed in turn to explore the adsorption effects, the results are shown in figure 3. It can be seen from the figure 3 that in the pH value range of 2.0 ~ 12.0, the removal rate of the Fe-Mn compound of vanadium (V) first increases with the increase of the pH then decreases. Under the acidic reacting conditions the adsorption efficiency of vanadium (V) is higher, when the pH value reaches around 4.0, the best adsorption efficiency is achieved, the reason is that the colloid of the Fe-Mn compound is positively charged; when the experiment deals with the adsorption of positive and negative charges the pH value is close to 2, vanadium exists as VO2+, where the positive charge is not conducive to adsorption. When the pH value is between 3.8 ~ 3.8, the vanadium acid radical ion is V10O286-, HV10O285− when the removal rate achieves a maximum [1]. The reason is that the acidic condition can enhance the protonation effect of the manganese ore surface, thus increasing the positive charge on the manganese ore surface[10] and plenty of H+ will dissolve the ore into some metal, making it appear more porous increasing the specific surface area, thereby increasing the removal efficiency of vanadium (V) [11]. The adsorption efficiency obviously decreases with the increasing pH value, the reason is that the vanadium anion is under an alkaline environment and for the OH there is a competition for adsorption sites on the surface of the manganese ore. Therefore, the best pH value for vanadium (V) adsorption of the Fe-Mn compound is 4.0.

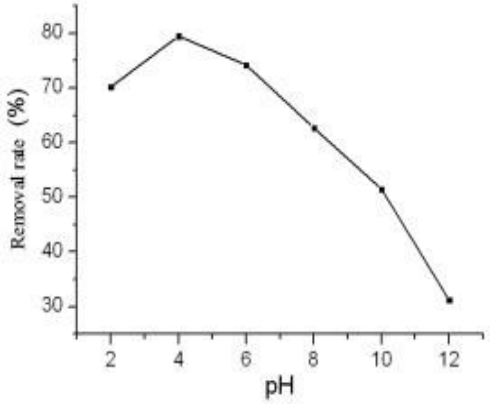


Fig. 3. The influence of the change in pH value on the removal performance of vanadium (V).

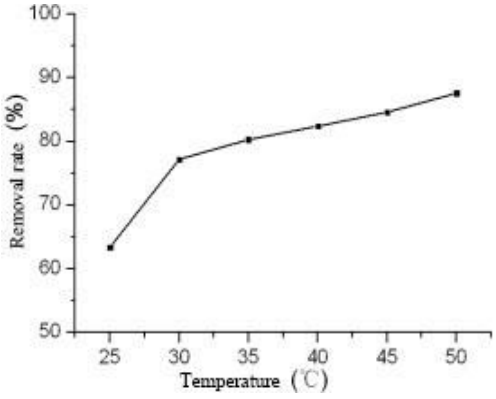


Fig. 4. The influence of the change reaction temperature on the removal performance of vanadium (V)

The influence of the reaction temperature on the removal performance of vanadium (V)

The characterization and functional mechanism of the Fe-Mn compound

The analysis of the Fe-Mn compound's composition

The composition of the adsorbent is the key factor that decides the adsorption performance of the material. In this study, the best Fe-Mn mole ratio of three mixture preparations are chosen as the adsorbents and the adsorbents are processed by grinding, drying and calcination, so the preparation of the adsorbent will not only contain iron, manganese ions, but could still contain a variety of other elements. In order to fully and accurately research the removal mechanism of compounds of the vanadium (V), XRF technology is used to obtain the composition elements of the Fe-Mn compound is shown in table 1. From table 1, it can be seen that there are 10 kinds of elements for Fe-

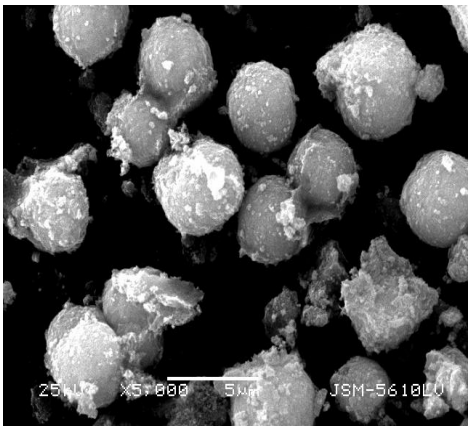
Mn compounds and according to the calculation the mole ratio is 5.04:1. In addition to iron and manganese oxide together with the Fe-Mn compound, due to cleaning that produce only residues of sodium oxide content that are more than 1%, the rest of the elemental contents are negligible. The removal efficiency in elimination of other elements' rather than vanadium (V) is high.

Table 1. The weight percentage of each oxide in the Fe-Mn compound.

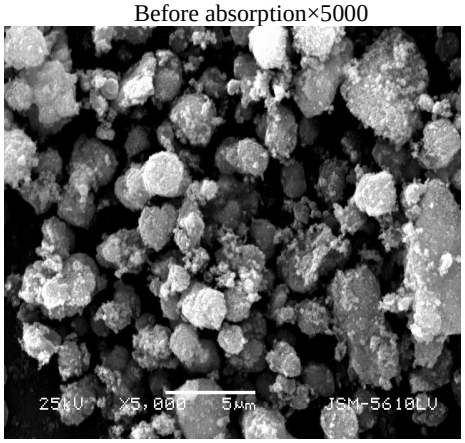
Name	Percentage（%）
Na2O	2.76
MgO	0.06
Al2O3	0.02
SiO2	0.05
P2O5	0.01
SO3	0.74
CaO	0.10
MnO	7.53
Fe2O3	85.47
Cl	0.02
Initial weight	3.14

The analysis by SEM and BET

The methods of SEM and BET are used to analyze and measure the surface topography and specific surface area of the Fe-Mn compound. Presented in Figure 5 is a photo taken by a scanning electron microscopy that shows the morphology at an Fe/Mn ratio of 5:1. The Fe-Mn composite material before and after the removal of vanadium (V) are observed. It can be seen from figure 5 that the most of particles of the Fe-Mn compound are uneven in size although some are spherical, these particles adhere to each other and form a network structure, this natural phenomenon reflects the inherent adsorption properties of the Fe-Mn compound. The vanadium (V) ions are absorbed by water surface particles, with the help of a mesh structure bridge connection, the vanadium (V) ions form a large film that separates and removes the water. In the photo of after absorption that the space between spherical particles are significantly reduced, and large amounts of vanadium particles is absorbed by the surface of spherical particles. This photo further illustrates the reasons why the Fe-Mn compound has a good removal performance. Meanwhile, in the method of nitrogen adsorption - stripping characteristics are used to measure the specific surface area of the Fe-Mn compound that is 69.2m2/g. The result shows that the Fe-Mn compound particles have a large specific surface area and high a surface free energy, which increases the chances that the particles react with the vanadium in the water and has a strong ability to remove the vanadium in the waste water.



Before absorption×5000



After absorption×500

Fig. 5. The SEM pictures before and after the Fe-Mn compound adsorbs vanadium (V)

The analysis by XRD

The XRD technology is used to analyze the phase compositions of the Fe-Mn compound before and after adsorption of vanadium (V). It can be seen from figure 6 that before adsorption the composition of the Fe-Mn compound, appears similar to the magnetite and Mn2O3 characteristics of the diffraction peak, the main phase compositions are Fe3O4 (JCPDS 01-1111) and Mn2O3 (JCPDS 02-0902). There are some serious wide and diffuse peaks in the Fe-Mn compound XRD figure showing that the Fe-Mn compound is not crystalline but porous, most of the Fe-Mn compound is amorphous in form. Compared with the XRD figures presenting the material before and after adsorption, it can be argued that the graphics have large changes before and after adsorption. The material presented in figure 7 after the reaction appears similar to the V2O3, Fe2O3 and Mn2O3 characteristics of the diffraction peak in the Fe-Mn

compound, the main phase compositions are V2O3(JCPDS 01-1293), Fe2O3(JCPDS 03-0800), O3(JCPDS 02-0902). These show that the chemical reaction occurs in the process of surface adsorption, partial vanadium acid radical ions are generate V2O3 and Fe3O4 is oxidized to Fe2O3.

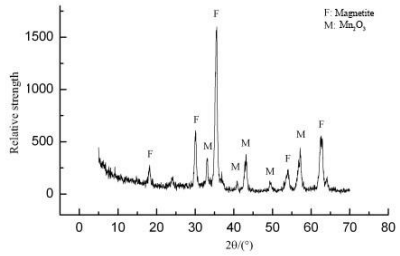


Fig. 6 The XRD figure before the Fe-Mn compound adsorbs vanadium (V).

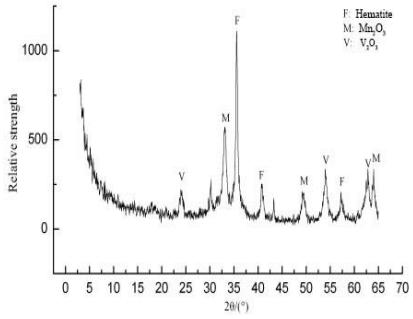


Fig. 7. The XRD figure after the Fe-Mn compound adsorbs vanadium (V).

The analysis by FTIR

In the study by an FTIR test to determine whether M-OH exist in the Fe-Mn compound, the FTIR figure of the process before and after adsorption is shown in figure 8.

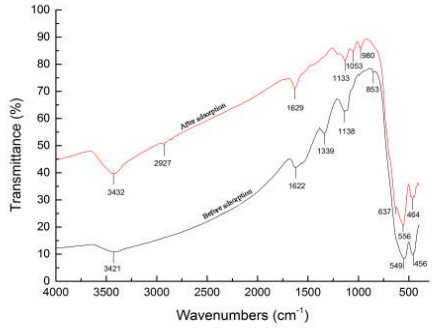


Fig. 8. The FTIR figure of the process before and after adsorption.

As shown in figure 8, the Fe-Mn compound there has the characteristic stretch vibration absorption peak of water and -OH (3421cm-1～3432cm-1) and -OH bending and vibration absorption peaks (1629cm-1-1622cm-1). The absorption peak and the corresponding hydrated MnO2 surface hydroxyl of the Mn-OH functional groups appear around 1138cm-1. The characteristic peaks appear at around 1200cm-1 both figures, which can explain the presence of Mn-OH. The absorption peak appearing at 1400cm-1 is caused by the MnO2 hydration component of the hydroxyl groups and water molecules. The stretching and vibration absorption peaks of the hydroxyl groups in Fe(OH)3 and water molecules appear at 3421cm-1 and 3432cm-1; the bending and vibration peaks of the hydroxyl groups in Fe(OH)3 and water molecules appear at 1622 cm-1, 1629 cm-1; the absorption peaks of α-FeOOH appear at 1162 cm-1 and 460 cm-1. Therefore, the iron compounds and hydroxyls play an important role in the process of the Fe-Mn compound removal of vanadium (V). It can result in adsorption of the Fe-Mn compound and removal of vanadium (V) and the complexation of the surface of material and hydroxyl of iron compounds. In figure 8, the vibration and absorption band at 980cm-1 is caused by the V=O bond in the partial vanadium acid radical and the absorption band at 547cm-1 corresponds to the vibration of the V-O-V bond in the aggregation of partial vanadium acid radicals[14].

The isotherm and kinetics of adsorption

The adsorption isotherm

Using the isothermal adsorption models of Langmuir and Freundlich and fitting the results show that the correlation of the former (R^2=0.9682) is bigger than the latter (R^2=0.9056), which shows that the removal of vanadium from the Fe-Mn compound is applicable in the Langmuir adsorption isothermal adsorption equation. The related model equation is shown below.

The Langmuir equation:

$$qe = 21.786\frac{1+0.513\rho_e}{0.513\rho_e}$$

The model of the Langmuir isothermal curves fit well and illustrate the adsorption process of vanadium by the Fe-Mn compound, when the concentration is low the adsorption rate is fast and the adsorption quantity of growth is slow with the increase in concentration while the adsorption is gradually in balance, which also illustrates the removal of vanadium (V) which is directly adsorbed.

The adsorption kinetics

Figure 9 shows the vanadium (V) adsorption kinetics process for the Fe-Mn compound. It can be seen that the adsorption rate of vanadium (V) by the Fe-Mn compound is very fast, the adsorption

capacity reached in 2-hours' is 13.19 mg/g, after 4-hours' the adsorption is gradually balanced.

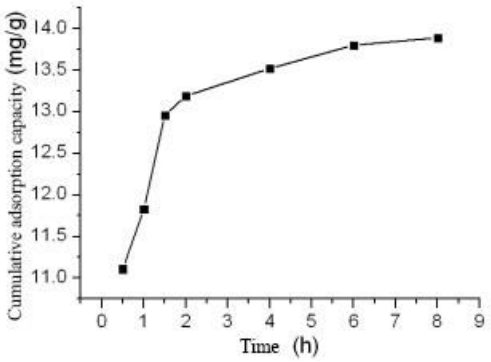


Fig.9. Curve of the adsorption rate of vanadium (V)

By using the kinetics adsorption model the specific fitting involved is shown in table 2, the adsorption model of the secondary kinetics (R^2=0.9999) has the greatest correlation and the Lagergren adsorption model of first order kinetics (R^2=0.9765) is greater than the fixed Elovich kinetics model (R^2=0.9066), so the adsorption kinetics of the Fe-Mn compound with vanadium is a better fit to the adsorption model of the secondary kinetics. Therefore, the adsorption process of vanadium (V) by the Fe-Mn compound is the chemical adsorption process. According to the calculation by this model, the maximum adsorption capacity of vanadium (V) by the Fe-Mn compound is 14.16 mg/g.

CONCLUSIONS

This paper presents a study on the removal performance of vanadium (V) through the co-precipitation preparation of the Fe-Mn compound; the conclusions obtained are as follows:

(1) The best conditions for preparation of the Fe-Mn compound are: the $FeSO_4 \cdot 7H_2O$ is chosen as the ferrous salt, the $MnSO_4 \cdot H_2O$ is chosen as the manganese salt and Na_2CO_3 is used as the precipitate agent, when the calcination temperature is 450°C and a Fe/Mn ratio of 5:1 the best removal ability of vanadium (V) is achieved.

(2) In this paper, the chosen removal agent has a good performance and the metal elements are distributed evenly in the Fe/Mn compound (the mole ratio Fe-Mn is 5:1), its specific surface area is 69.2m^2/g. Besides, the Fe-Mn compound particles attach to each other and form a mesh structure that arrange loosely, which has a good adsorption of the colloidal particles in the water that have a bridge connection and a trap function.

(3) Through the analysis of the controlling variables method the best water quality conditions are achieved: 0.1g of the Fe-Mn compound are used to process 50 mg/L of simulated wastewater that contain vanadium (V), oscillation under a constant temperature of 35°C for 120 min, when the pH value is 4.0 the highest removal efficiency of vanadium (V) is realized.

(4) The model of secondary kinetics and isothermal adsorption models of Langmuir can better fit the adsorption process of vanadium (V) respectively by using the Fe-Mn compound, in accordance with fitting the equation calculation of the Fe-Mn compound removal efficiency of vanadium (V), the maximum adsorption capacity is 14.16 mg/g.

The analysis of the mechanism of removal of vanadium (V) from the Fe-Mn compound contains the physical adsorption, electrical adsorption and co-precipitation, dependant on the pH value. The combination of multiple adsorption methods make the co-precipitation preparation of the Fe-Mn compound has a higher removal ability of vanadium (V).

Table 2. The fitting results of the stimulated kinetics data for the Fe-Mn compound adsorption of vanadium (V)

Lagergren first order kinetics	q_e /mg·g^{-1}	13.89	Secondary kinetics	q_e /mg·g^{-1}	14.16	Elovich Revised absorption kinetics	a	12.09
	k_1 /min^{-1}	-0.5321		k_2 /mg·g^{-1}min^{-1}	0.448		b	1.0007
	R^2	0.9765		R^2	0.9999		R^2	0.9066

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СВОЙСТВА, СИНТЕЗА И ОТСТРАНЯВАНЕ НА ВАНАДИЙ ОТ ФЕРО-МАНГАНОВИ КОМПОЗИТНИ МАТЕРИАЛИ

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(Резюме)

Изкуствено са синтезирани Fe-Mn-съединения чрез утаяване, филтруване, сушене и калциниране. Изследвани са свойствата им с помощта на рентгенова флуоресценция, инфрачервена спектроскопия, сканираща електронна микроскопия. Резултатите показват, когато началната концентрация на ванадия е 50 mg/L и са използвани 0.1 g от композитния материал реакционното време достига 2 часа. Най-добра абсорбция се постига при 30°C и pH 4. Адсорбцията на ванадий (V) върху композитите е в съгласие с изотермата на Лангмюир с висок коефициент на корелация (R^2=0.9682), а кинетичните данни се описват от кинетикана реакция от 2-ри порядък (R^2=0.9999). Максималният адсорбионен капацитет е 14.16mg/g.