

# Investigation of Magnetic Modified Clay Nano-adsorbents in Removing Micro-pollution from potable water

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**Abstract**—Natural clay nano-materials are relatively ideal adsorbents for its huge specific surface area and abundant pore structure, wide resources and low price. However, it is easy to form the suspension system after adsorption, which is difficult to separate and recycle. To surmount these deficiencies, new magnetic clay-based adsorbents are synthesized and investigated. By using single factor experiment, found out the impact of its adsorbing micro pollutants in drinking water. The mechanism of adsorption has also been studied.

In this paper, we chose Cr and As as the target micro pollutant, while halloysite and sepiolite adsorbents are chosen to be magnetized.

Magnetic modified carbonization halloysite nanocomposite ( $\text{Fe}_3\text{O}_4/\text{HNT}@C$ ) and iron oxides@sepiolite nanocomposites ( $\text{Fe}_2\text{O}_3/\text{SEP}$  and  $\gamma\text{-Fe}_2\text{O}_3/\text{SEP}@C$ ) exhibited selective and high efficient adsorption ability for Cr(IV) and As(III). Meanwhile, they have enough magnetic intensity to be recycled by using the external magnetic field.

In addition, the adsorption is strongly dependent upon solution pH value.

**Keywords**—Magnetic modified, clay nano-adsorbents, heavy metal pollution.

## I. INTRODUCTION

**W**ATER is one of the basic conditions to the survival of all life on the earth. However, with the development of economy, industry and human being's daily life makes the water pollution worse and worse.

Slightly polluted source water contains kinds of pollutants, divided into organic pollutants and inorganic pollutants. And people found out that heavy metals, which belong to inorganic pollutants, are harmful to human health, and are difficult to remove by conventional water treatment method. Therefore, it is urgent that the study of micro-pollution removal methods and techniques in the water.

The main methods for water pollution are adsorption, ion exchange, membrane separation technology and biological technology and so on. But adsorption becomes the first choice for its low cost, high efficiency and easy operation. However, the adsorbents people have already had are useful for high concentration water pollution of industry, so many researchers try to figure out the problem for low concentration pollution in the potable water.

There are many scholars studying magnetic nano-adsorbents [1] and they reached some certain conclusions. However, they just demonstrated the feasibility of separation by using the external magnetic field and most of them studied on manufactured nanomaterials [2]. In this paper, the magnetic halloysite-based and sepiolite-base nanocomposites were investigated and found exhibit selective and high efficient adsorption ability for Cr(IV) and As(III) ions, which seldom be studied before.

This paper shows the research achievement of new magnetic modified clay nano-adsorbents, meant to get theory and technology about adsorption and separation, aimed at reliable scientific basis for potable water purification.

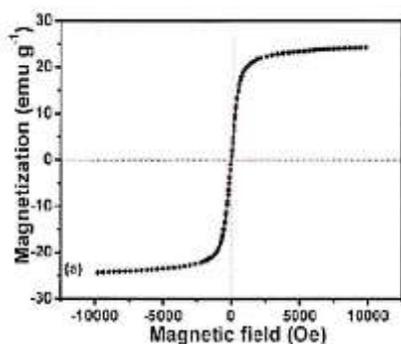
## II. INVESTIGATION OF MAGNETIC HALLOYSITE-BASED NANOCOMPOSITES

Magnetic modified clay composite materials have high surface potential, large specific surface area, and superparamagnetism properties. A new kind of carbonization halloysite ( $\text{HNT}@C$ ) adsorbent was synthesized with a one-step hydrothermal carbonization process by using halloysite and glucose.  $\text{Fe}_3\text{O}_4/\text{HNT}@C$  was prepared via solvothermal reaction by using  $\text{HNT}@C$  and  $\text{FeCl}_3$  as reactant. The  $\text{Fe}_3\text{O}_4/\text{HNT}@C$  nanocomposite possesses high reduction and immobilization capability for Cr(VI)

### A. Magnetic Analysis

To study  $\text{Fe}_3\text{O}_4/\text{HNT}@C$  sample magnetic, we use superconducting quantum interference device (SQUID) characterization methods to research. Using the samples, we did magnetism performance analysis at room temperature. From fig. 1, the saturation magnetization of  $\text{Fe}_3\text{O}_4/\text{HNT}@C$  was found to be 24.5 emu/g. It is also demonstrated that  $\text{Fe}_3\text{O}_4/\text{HNT}@C$  has enough magnetic intensity to be recycled in the magnetic field force.

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Fig. 1 Magnetizing curve of  $\text{Fe}_3\text{O}_4/\text{HNT}@C$ 

### B. Influence Factor Of The Adsorption

#### 1) Test solution pH value

Before studying the effect of pH value on adsorption, the electrical charge on the surface of the material were analyzed first. According to the fig. 2, in the range of PH 2 to 9 HNT@C is negatively charged. In addition, at a higher pH, more negative surface charges. It's more advantageous to combine with heavy metal ions in solution. But there will be a certain degree of electrostatic repulsion to anion.

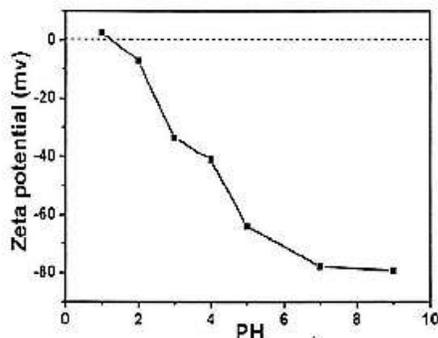


Fig. 2 HNT@C zeta potential diagram

PH value is not only influence the electric charges on the surface of the adsorbent, also influence the form of metal ions in the solution. At pH values of 2-6, Cr(VI) mainly exists in  $\text{CrO}_4^{2-}$  and a small amount of  $\text{Cr}_2\text{O}_7^{2-}$ . Meanwhile, with the increase of pH, the concentration of  $\text{CrO}_4^{2-}$  ions increase.

From fig. 3, we can find when the pH value is 2, adsorption effect is best. The cause of it is that with the value of the solution pH increasing, the negative charge density on the surface of the adsorbent is increased. It hinders the anion adsorption, so that the adsorption capacity decreases rapidly. Compared with HNT@C,  $\text{Fe}_3\text{O}_4$  loaded on the surface of HNT@C do not affect the adsorption of sorbent under various pH conditions.

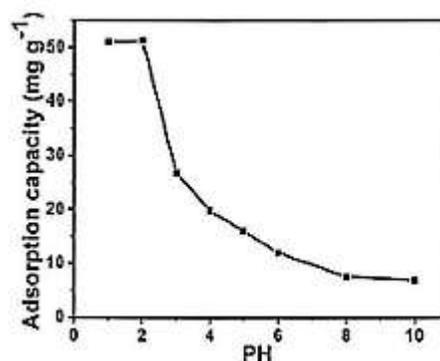
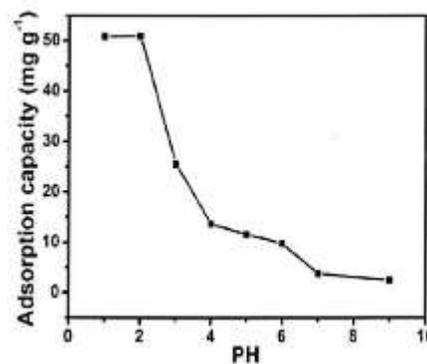


Fig. 3 (a) Effect of pH on the adsorption properties of HNT@C

Fig. 3 (b) Effect of pH on the adsorption properties of  $\text{Fe}_3\text{O}_4/\text{HNT}@C$ 

#### 2) Concentration of glucose and the initial concentration of the solution

HNT@C-1, HNT@C, and HNT@C-3 is synthesized in the case of clay and glucose mass ratios in 1:2, 1:5, and 1:8, respectively. Figure(4) shows the adsorption of Cr(VI) on halloysite(HNT), Carbon microsphere (Pure C), HNT@C-1, HNT@C, and HNT@C-3 at different initial concentrations of the solution.

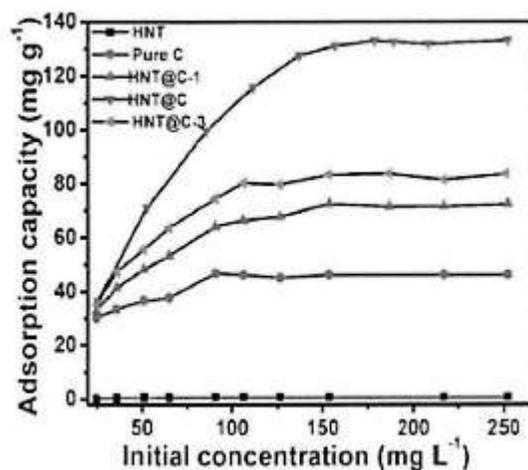


Fig. 4 Effect of concentration of glucose and the initial concentration of the solution

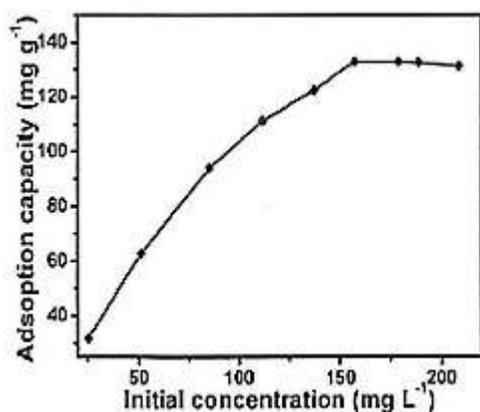


Fig. 5 Effect of concentration on the adsorption capacity of  $\text{Fe}_3\text{O}_4 / \text{HNT@C}$

It is the conclusion that the adsorption capacity of HNT is the smallest, for lacking active sites for the adsorption of heavy metals on the surface. They are formed by Si-O-Si bonds.. The adsorption capacity of pure C is also small. The reason for it is that the specific surface area of pure C is much smaller than HNT@C's.

These phenomena are explained that HNT displays nano-size effect in hydrothermal reaction, and turn to ideal clay nano-adsorbents. Meanwhile,  $\text{Fe}_3\text{O}_4$  loaded on the surface of  $\text{Fe}_3\text{O}_4 / \text{HNT@C}$  does not affect the adsorption of sorbent.

TABLE I  
THE MAXIMUM IMMOBILIZATION CAPACITY

Adsorbents	Maximum Adsorption
HNT	0.8147 mg/g
Pure C	46.35 mg/g
HNT@C-1	71.32 mg/g
HNT@C	132.5 mg/g
HNT@C-3	82.67 mg/g
$\text{Fe}_3\text{O}_4 / \text{HNT@C}$	132.8 mg/g

### C. The Mechanism Of Adsorption

In the previous experiment, HNT@C was always negatively charged. For the existence of the Cr(VI) as a form of anion, the electrostatic attraction has little effect on the adsorption process.

When the pH value was low, the surface of HNT@C can adsorb lots of anions formed by Cr(VI). With pH increasing, OH<sup>-</sup> retard the combination between Cr(VI) and adsorbents. Meanwhile, a part of Cr(VI) was reduced into Cr<sup>3+</sup> by surface oxygen-containing groups of HNT@C. And then, it can be adsorbed on surface of adsorbents via cation exchange capacity, complex effects, and electrostatic action.

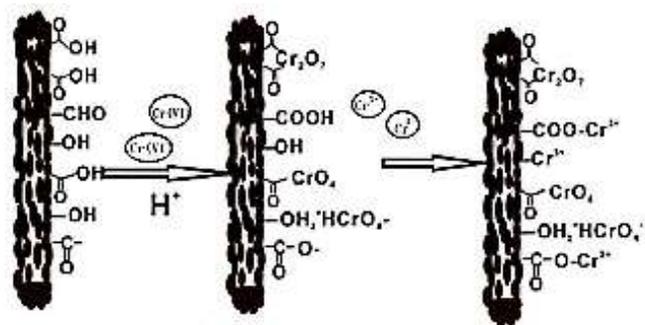


Fig. 6 Schematic diagram of adsorption process [3]

Then, we can draw a conclusion that the mechanism for the removal of Cr(VI) is the synergistic effect of surface complexation, redox reaction, and cation exchange. After adsorption, most of Cr(VI) are reduced to Cr(III), and immobilized on the surface of adsorbent. In other words,  $\text{Fe}_3\text{O}_4 / \text{HNT@C}$  can immobilize and detoxify Cr(VI) in the same time.

### III. INVESTIGATION OF MAGNETIC SEPIOLITE-BASED NANOCOMPOSITES

There are four different forms of iron oxide, namely,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\beta\text{-Fe}_2\text{O}_3$ ,  $\epsilon\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ . And their magnetism is not the same.  $\alpha\text{-Fe}_2\text{O}_3$  is antiferromagnetic;  $\beta\text{-Fe}_2\text{O}_3$  is paramagnetic; while  $\epsilon\text{-Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$  are ferromagnetism.

Surface carbonization of sepiolite (SEP@C) was synthesized from sepiolite, glucose, and iron acetylacetonate by hydrothermal reaction. Intermediate product  $\text{Fe}_3\text{O}_4 / \text{SHP@C}$  turned to  $\gamma\text{-Fe}_2\text{O}_3 / \text{SEP@C}$  under 250 °C calcinations and  $\text{Fe}_2\text{O}_3 / \text{SEP@C}$  turned to  $\text{Fe}_2\text{O}_3 / \text{SEP}$  (Mixed  $\alpha\text{-Fe}_2\text{O}_3 / \text{SEP}$  and  $\gamma\text{-Fe}_2\text{O}_3 / \text{SEP}$ ) with amorphous carbon lost under 500 °C calcination.

#### A. Magnetic Analysis

In order to study the magnetic properties of  $\text{Fe}_2\text{O}_3 / \text{SEP}$  and  $\gamma\text{-Fe}_2\text{O}_3 / \text{SEP@C}$  samples, we use superconducting quantum interference device (SQUID) characterization methods to research. The saturation magnetizations of  $\text{Fe}_2\text{O}_3 / \text{SEP}$  and  $\gamma\text{-Fe}_2\text{O}_3 / \text{SEP@C}$  are 29.53 emu/g and 31.95 emu/g respectively. The magnetization intensity of  $\text{Fe}_2\text{O}_3 / \text{SEP}$  slightly is lower than  $\gamma\text{-Fe}_2\text{O}_3 / \text{SEP@C}$ 's for a part of  $\gamma\text{-Fe}_2\text{O}_3$  changes into  $\alpha\text{-Fe}_2\text{O}_3$  after calcinating. After adsorption of As(III), both of them can be quickly gathered through the external magnetic field.

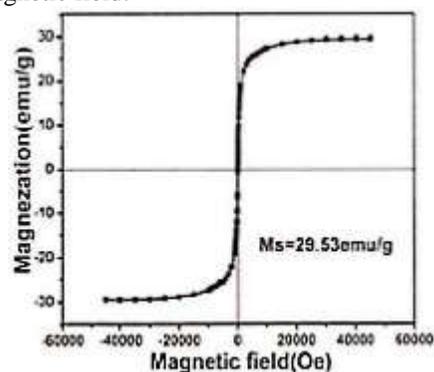


Fig. 7 (a) Magnetizing curve of  $\text{Fe}_2\text{O}_3 / \text{SEP}$

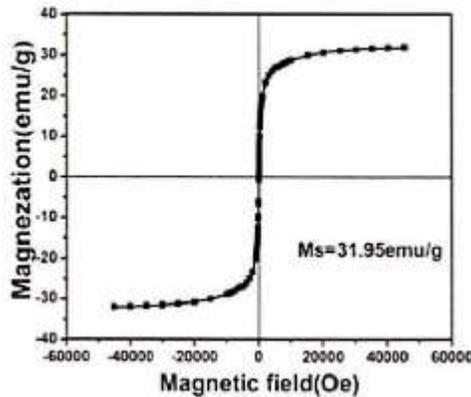


Fig. 7 (b) Magnetizing curve of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C

**B. Influence Factor Of The Adsorption**

**1) Test solution pH value**

Figure shows the effect of pH on the adsorption properties of As(III) and the change of pH value of the solution after the experiment (pH<sub>f</sub>).

When the solution is acidity, the adsorption capacity of Fe<sub>2</sub>O<sub>3</sub>/SEP increased with the increase of pH. And its adsorption capacity gradually decreased in alkaline solution. The maximum adsorption of As(III) could be reached under neutral conditions. Under acidic conditions, there are a large number of H<sup>+</sup>, As(III) and H<sup>+</sup> combine to form H<sub>3</sub>AsO<sub>3</sub>. However, the form of H<sub>3</sub>AsO<sub>3</sub> is not conducive to the combination of As(III) and active sites on the Fe<sub>2</sub>O<sub>3</sub>/SEP. In addition, there is a competitive adsorption between As(III) and OH<sup>-</sup> under alkaline conditions, which makes the adsorption capacity decrease.

According to the experiment, the maximum adsorption could be reached when the pH value is 7.

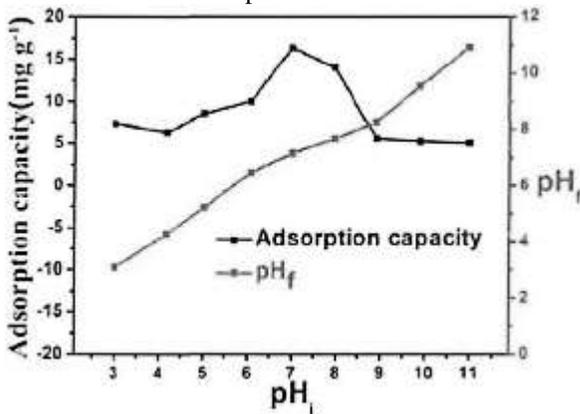


Fig. 8 Effect of concentration on the adsorption capacity of Fe<sub>2</sub>O<sub>3</sub>/SEP and pH value after reaction

The adsorption capacity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C has little change in the neutral and acid condition. When the initial solution is alkaline, pH value decreases after complete absorption, provided the evidence for reaction happened between OH<sup>-</sup> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C. There is a competitive adsorption between As(III) and OH<sup>-</sup>, which makes the adsorption capacity decrease.

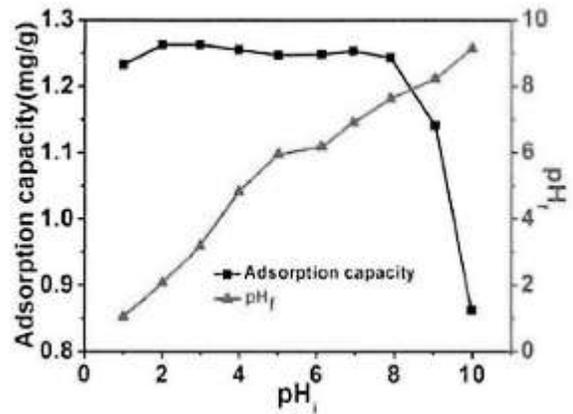


Fig. 9 Effect of concentration on the adsorption capacity of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C and pH value after reaction

**2) Concentration of glucose and the initial concentration of the solution**

Surface carbonization of sepiolite (SEP@C) was synthesized from sepiolite, glucose, and iron acetylacetonate.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C and Fe<sub>2</sub>O<sub>3</sub>/SEP are prepared through calcinations at different temperatures.

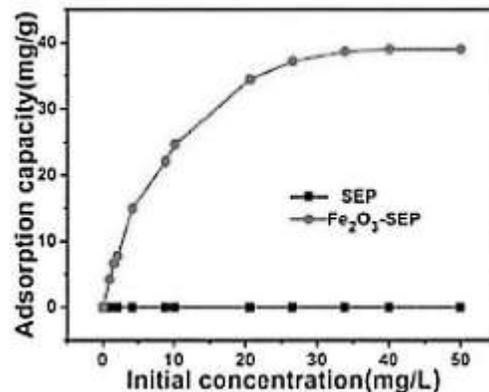


Figure.10 (a) Effect of the initial concentration of the solution on SEP and Fe<sub>2</sub>O<sub>3</sub>/SEP

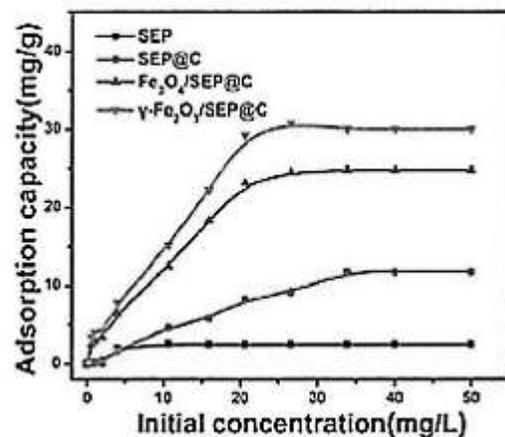


Figure.10 (b) Effect of the initial concentration of the solution on other adsorbents

TABLE II  
THE MAXIMUM IMMOBILIZATION CAPACITY

Adsorbents	Maximum Adsorption
SEP	2.54 mg/g
SEP@C	11.78 mg/g
Fe <sub>3</sub> O <sub>4</sub> /SEP@C	24.50 mg/g
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /SEP@C	30.78 mg/g
Fe <sub>2</sub> O <sub>3</sub> /SEP	38.62 mg/g

The experiment shows that the adsorption capacity of SEP is the smallest, for the outer surface of the strong electronegativity. It causes electrostatic repulsion among the particles. After SEP magnetized by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, the surface of adsorbents gains additional active sites by introducing a lot of functional groups. Meanwhile, the complexing reaction of Fe and the heavy metal ions form surface complexes.

### C. The Mechanism Of Adsorption

We use Fourier transform infrared spectrometer (FTIR Spectrometer) to test Fe<sub>2</sub>O<sub>3</sub>/SEP and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C before and after reaction. Fourier transform infrared spectrum (FTIR) of magnetic modified adsorbents after the reaction shows absorption peak at 783 cm<sup>-1</sup>, compared with that before adsorbing. It is As-O stretching vibration and these experimental results confirms that As(III) can be chemisorbed on magnetic modified sepiolite-based nanocomposites.

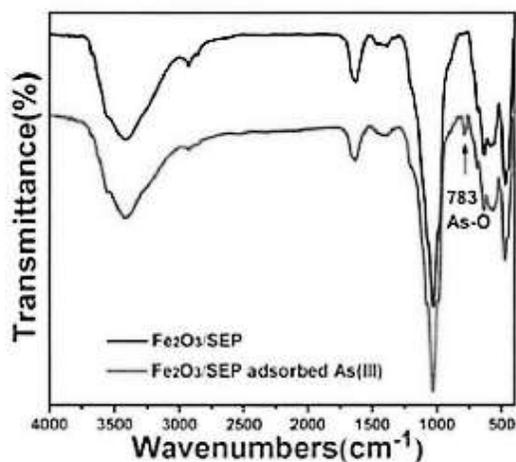


Fig. 11 (a) FTIR spectra of Fe<sub>2</sub>O<sub>3</sub>/SEP before and after reaction

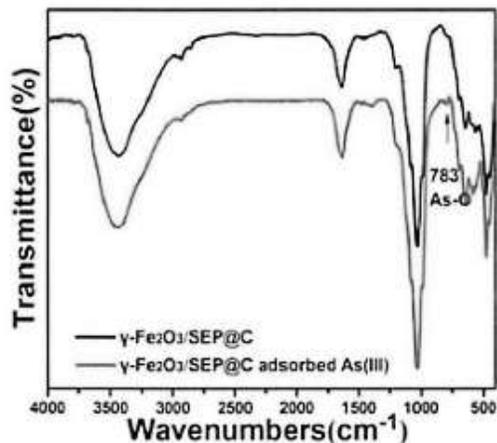


Fig. 11 (b) FTIR spectra of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C before and after reaction

The adsorption of these two magnetic modified adsorbent is the result of physical adsorption and chemical adsorption. The surface electrical properties are changed by these Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles on the surface of nano-adsorbent. They significantly increase the active adsorption point of the surface, which enhances the adsorption. Meanwhile, iron oxide reacts with arsenous acid radical through coordination complexes. So both Fe<sub>2</sub>O<sub>3</sub>/SEP and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C have strong selective adsorption ability to As(III).

### IV. CONCLUSION

Water pollution has become a serious global problem, and micro-pollution of potable water is closely related to all life on the earth. We try to find a nano-adsorbent which exhibited selective and high efficient adsorption ability for heavy metal ion with low cost. At the same time, it can overcome the shortcomings of clay nano-adsorbents, separating and recycling. In order to synthesize this new kind of clay nano-adsorbents, we took halloysite and sepiolite for research object and investigated effects of magnetic treatment on these clay nano-adsorbents.

The maximum adsorption capacity of Fe<sub>3</sub>O<sub>4</sub>/HNT@C is 132.8 mg/g, which shows high efficient adsorption ability. And the saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>/HNT@C was found to be 24.5 emu/g, meant the adsorbents could be separated in a short time by using external magnetic field. When the pH value is 2, adsorption effect of Fe<sub>3</sub>O<sub>4</sub>/HNT@C is best. Cr(VI) is adsorbed on surface of adsorbents via the cation exchange capacity, complex effects, and electrostatic action. After adsorption, most of Cr(VI) are reduced to Cr(III), and immobilized on the surface of adsorbent.

The saturation magnetization of Fe<sub>2</sub>O<sub>3</sub>/SEP and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C is 29.53 emu/g and 31.95 emu/g, respectively. The maximum adsorption capacities of Fe<sub>2</sub>O<sub>3</sub>/SEP and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C are 38.62 mg/g and 30.88 mg/g. Fe<sub>2</sub>O<sub>3</sub>/SEP is suitable for adsorption in neutral As(III) ion solution. When the environment is alkaline, the adsorption performance of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/SEP@C gets smothered. Besides, the removal of As(III) is the result of physical adsorption and chemical adsorption.

However, in this paper, we did not consider the influence on the coexistence anion.

This paper has provided a new direction for the further research of magnetic modified nano-adsorbents, and gets theory and technology about adsorption and separation, aimed at reliable scientific basis for potable water purification.

The results demonstrate that these magnetic modified clay nano-adsorbents are exceptionally promising candidate as low-cost, effective and environmentally friendly adsorbent for the removal of heavy metal ions from water. And I hope they can be applied in the purification of contaminated water and soil soon.

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