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Communication

## Highly efficient enrichment and adsorption of rare earth ions (yttrium(III)) by recyclable magnetic nitrogen functionalized mesoporous expanded perlite

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## ABSTRACT

A magnetic mesoporous expanded perlite-based ( $EP_{d-APTES}@Fe_3O_4$ ) composite was designed and synthesized as a novel adsorbent for enrichment of rare earth ions in aqueous solution. Effect of various factors including the pH of solution, contact time and adsorbent dosage on the adsorption behaviors of yttrium(III) by the  $EP_{d-APTES}@Fe_3O_4$  nano-material composites from aqueous solution was investigated. The maximum adsorption capacity of the as-prepared materials for yttrium(III) ions was 383.2 mg/g. Among the various isotherm models, the Freundlich isotherm model could well described for the adsorption of the rare earth ions at pH 5.5 and 298.15 K. The kinetic analysis indicated that the adsorption process followed the *pseudo*-second order kinetics model, and the rate-determining step might be chemical adsorption. Thermodynamic parameters declared that the adsorption process was endothermic. In addition, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and the quantum chemical calculation indicated that the yttrium(III) ions were captured on the  $EP_{d-APTES}@Fe_3O_4$  surface mainly by coordination with functional group of  $-NH_2$ . More importantly, the adsorption-desorption studies indicated that the  $EP_{d-APTES}@Fe_3O_4$  nano-material composites had a high stability and good recyclability.

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Rare earth elements (REEs), especially the heavy REEs, play irreplaceable roles in a wide range of advanced technological fields, such as high strength permanent magnets, superconductive material, chemical sensors, luminescent, lasers, hydrogen storage, fiber optics, computer hard disks, cell phones and cameras, due to their special diverse chemical, metallurgical, optical, electronic and catalytic properties [1–4]. The designation of “rare earth” refers to the 17 elements of “lanthanides” series in periodic table, which can be further divided into two groups according to the function of their atomic number. One is “cerium group” (light REE: La, Ce, Pr, Nd, Pm, Sm, Eu, Gd), and the other one is “yttrium group” (heavy REE: Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) [5,6]. Since the beginning of this century, the global consumption of REEs has increased significantly [6]. However, the global reserves of REEs are no more than 99 million tons which limits the use of REEs [7]. Among all

REE-based deposits, Bayan Obo deposit is the largest REE-containing deposit but it has high-grade carbonate and low-grade in heavy REEs. While the ion-adsorption type clay deposits in South China, in spite of small in scale and low in grade, dominate the heavy REEs market because of the low mining and processing costs and the high enrichment characteristics of heavy REEs in deposit [8]. To date, the traditional surface mining pool leach process and the *in-situ* leaching mining method are mainly employed to collect the heavy REEs in ion-adsorption type clay. Although most of the REEs in the ion adsorption clay could be collected by these two methods, they do harm to the surrounding environment and waste a substantial part of REEs [9]. It was reported that high concentration of rare earth ions (1–200 mg/L) were found both in downstream of the river and the wastewater of mining and refining factory [10]. Therefore, hundreds of tons of REEs will be lost every year if the wastewater is discharged directly without effective recovery. In addition, the content of REEs in the soil of rare earth mining area is much higher than that in other areas, which leads to the content of REEs in crops, fruits and

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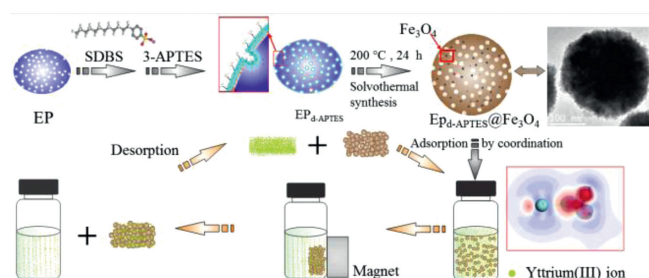
vegetables in the mining area exceeding the standard, and accumulating in the body through the food chain, and endangering the health by inhibiting the growth of pre-osteoblasts and poisoning the nervous system [11]. Due to the lack of economic, environmental protection and effective comprehensive recovery methods of low concentration rare earths, the discharge of rare earth wastewater not only causes mass of loss of rare earth resources, but also endangers human health [12]. Therefore, recovering and recycling the REEs in wastewater is thereby an urgent task that needs to be paid much attention.

Up to now, several methods and techniques, such as co-precipitation, filtration, solvent extraction, ion-exchange, liquid membrane and adsorption, have been used for purify, recovery, separation, pre-concentration and enrichment of REEs [2,9,13]. Among these methods, the adsorption by adsorbents including zeolite [14], clay [15], active carbon [16], bioresource materials [5,17], functionalized nano-composites [18–22] has received wide attention because of their simple fabrication process, high efficiency, reusability, low-cost and no secondary pollution. However, the maximum adsorption capacity of the most adsorbents is less than  $\sim 200$  mg/g [12]. Only a few adsorbents, such as granular grafted hydrogel composites, prawn carapace, sporopollenin/xylan-modified biohydrogel, neem sawdust and granular grafted hydrogel composites, can deliver the adsorption capacity of more than 200 mg/g [2]. Although remarkable progress has been made, the development of high-performance adsorbents with capacity of 350–400 mg/g is still a huge challenge, and the preparation of recyclable high-performance adsorbents is even harder.

Perlite is a glass mineral found in volcanic [23]. When the perlite ore is treated at 750–1700 °C, it expands 10–20 times of its original volume. After the physical transformation, it becomes granular materials with honey comb structure inside [24]. Expanded Perlite (EP) has many special properties including high porosity, light weight, high chemical and thermal stability, and exhibits abundance of silanol groups on the porous surfaces. The porous feature and abundant silanol groups on the surface of EP enable it to be easily functionalized through chemical grafting [25], which makes it a promising recyclable adsorbent for recovering the heavy REEs from mining and metallurgy wastewater [26–35].

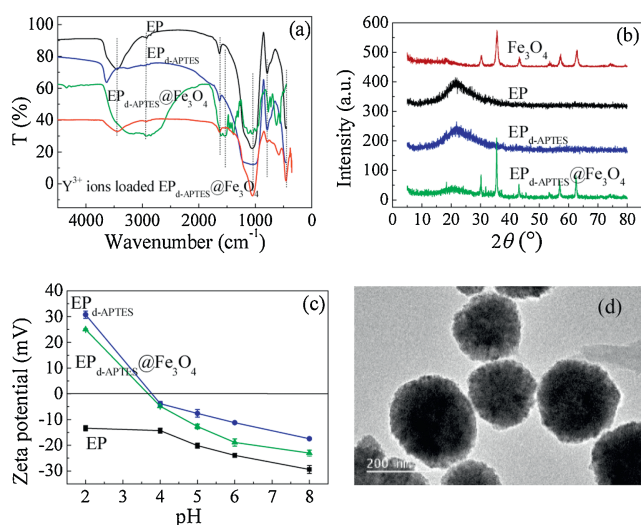
In this study, magnetic mesoporous expanded perlite was successfully synthesized by grafting the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles on amino-group functionalized EP. The precise synthesis procedure and advanced structure endow  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  high specific surface area, large number of functionalized sites to effectively adsorb/enrich the heavy REE ions from the wastewater. The synthesis processes of magnetic mesoporous expanded perlite were illustrated in Scheme 1. The detail of synthesis processes, adsorption, characterization, recycle performance and quantum chemical calculations are given in Supporting information.

The  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  composite was synthesized via a surface grafting strategy followed by a hydrothermal reaction



**Scheme 1.** Schematic illustration of the preparation of  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  composites, yttrium(III) adsorption and recycling of the  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  adsorbent.

with APTES-decorated EP (noted as  $\text{EP}_{\text{d-APTES}}$ ) and  $\text{FeCl}_3$  as raw material. Fig. 1a show the FTIR of pristine EP powder and 3-aminopropyltriethoxysilane (APTES) molecules decorated EP material. The adsorption bands at  $\sim 3458$   $\text{cm}^{-1}$  is attributed to the combination of  $-\text{OH}$  stretching of hydrogen-bonded and free  $\text{Si}-\text{OH}$  [23]. The peak at  $\sim 1627$   $\text{cm}^{-1}$  is due to the deformation band of molecular water, while the absorption peaks at  $\sim 1100$   $\text{cm}^{-1}$  and  $\sim 790$   $\text{cm}^{-1}$  are assigned to the  $\text{Si}-\text{O}$  stretching vibrations of  $\text{Si}-\text{O}-\text{Si}$  and  $\text{Si}-\text{O}-\text{Al}$ , respectively. For the FTIR spectrum of  $\text{EP}_{\text{d-APTES}}$  powder, the weak peak at  $3251$   $\text{cm}^{-1}$  was assigned to the stretching vibration of  $-\text{NH}_2$  groups, indicating the successful decoration of APTES molecules on the surface of EP particles. Besides, the strong peak at  $3500$   $\text{cm}^{-1}$  ( $\text{Si}-\text{OH}$ ) shifts to  $3650$   $\text{cm}^{-1}$  due to the disappearance of hydrogen bond. The FTIR of the  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  is characterized by a broad peak at  $3700$ – $2200$   $\text{cm}^{-1}$ , and a new peak at  $569$   $\text{cm}^{-1}$ . The broad peak at  $3700$ – $2200$   $\text{cm}^{-1}$  was attributed to the condensation of poly (ethylene glycol), ethylene glycol and sodium citrate to form new functional groups such as double bonds, triple bonds and cumulated diene. These newly formed unsaturated bonds may play a key role in subsequent adsorption of yttrium(III) ions. The new sharp peak at  $619$   $\text{cm}^{-1}$  is attributed to the vibration of  $\text{Fe}-\text{O}$  band [24]. To further validate structure of  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$ , we performed the X-ray diffraction (XRD) measurement on various materials from each stage of preparation. As shown in Fig. 1b, the broad peak of EP and/or APTES-decorated EP at  $2\theta$  of  $10^\circ$ – $38^\circ$  that corresponding to amorphous silica, several well-defined diffraction peaks at  $2\theta$  of  $30.34^\circ$ ,  $35.76^\circ$ ,  $43.3^\circ$ ,  $53.5^\circ$ ,  $57.45^\circ$  and  $62.88^\circ$  are also clearly observed, which can be indexed as (220), (311), (400), (422), (511) and (440) plane reflections of  $\text{Fe}_3\text{O}_4$ , respectively (JCPDS No. 19-0629) [36]. Zeta potential of various materials from each stage of preparation were determined as a function of pH in 1 mmol/L KCl aqueous solutions. As shown in Fig. 1c, the EP particles were negative charged with the average zeta potential value of  $-13.36$  mV with pH 2, while it became positive of  $30.73$  mV for amino-functionalized  $\text{EP}_{\text{d-APTES}}$ , which was attributed to the protonation of amino groups ( $-\text{NH}_3^+$ ) on the surface. After grafting the  $\text{Fe}_3\text{O}_4$  particles,  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  became less positive than  $\text{EP}_{\text{d-APTES}}$  due to the formation of  $\text{Fe}_3\text{O}_4$ . As the solution pH is over about 4, the zeta potentials for all the particles became negative. The zeta potential evolution of different materials further confirmed the successful synthesis strategy.



**Fig. 1.** (a) FTIR spectra of EP,  $\text{EP}_{\text{d-APTES}}$ ,  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  and yttrium(III) ions loaded  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$ . (b) The XRD patterns of  $\text{Fe}_3\text{O}_4$ , EP,  $\text{EP}_{\text{d-APTES}}$ , and  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$ . (c) Zeta potential of EP,  $\text{EP}_{\text{d-APTES}}$  and  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$  as a function of pH in 1 mmol/L KCl. (d) TEM images of  $\text{EP}_{\text{d-APTES}}@ \text{Fe}_3\text{O}_4$ .

The morphology and structure of the various synthesized particles were observed by transmission electron microscope (TEM). The pristine EP are in irregular shaped particles with size of 200–500 nm (Fig. S1a in Supporting information). After being modified by APTES molecules, the resultant EP<sub>d-APTES</sub> still remains its irregular shape with almost same size, which is attributed to that the attached monolayer of APTES on the EP surface is very thin (Fig. S1b in Supporting information). After grafting the Fe<sub>3</sub>O<sub>4</sub> particles, the shape of the prepared EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> composites are changed from the irregular into nearly sphere with size increasing up to 150–400 nm (Fig. 1d). The changes of the size and shape is closely related to the growth of Fe<sub>3</sub>O<sub>4</sub> species on the surface of the EP<sub>d-APTES</sub> particles. High-magnification TEM image further indicates that the Fe<sub>3</sub>O<sub>4</sub> are uniformly grown on the surface of EP<sub>d-APTES</sub> particles, forming a typical EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> core-shell structure with EP<sub>d-APTES</sub> particles as core and nanofiber shaped Fe<sub>3</sub>O<sub>4</sub> as shell layer. The growth of Fe<sub>3</sub>O<sub>4</sub> on EP<sub>d-APTES</sub> surface is associated with the strong hydrogen bond between the -NH<sub>2</sub> group in APTES molecules and hydroxy group in Fe(OH)<sub>3</sub> colloids formed during the hydrothermal reaction. The compact deposition of Fe<sub>3</sub>O<sub>4</sub> nanofiber on EP<sub>d-APTES</sub> particles results in large amounts of voids and interconnected mesoporous structure and thus increase the surface area of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub>, which will be analyzed by N<sub>2</sub> adsorption/desorption isotherms (Fig. S2 and Table S1 in Supporting information). Other characterizations such as X-ray photoelectron spectrum (XPS) measurement and thermogravimetric analysis (TGA) are illustrated in supporting information (Figs. S3 and 4 in Supporting information). By combining the characterizations, it can be concluded that the Fe<sub>3</sub>O<sub>4</sub> has been coated on APTES-modified EP materials and core-shell structured EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> was successfully synthesized.

The adsorption behavior and mechanism of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for yttrium(III) ions were systematically investigated. It is believed that the acidity of the aqueous solution has profound influence on the adsorption behavior because it can affect the state and surface-active sites of the materials. The adsorption behavior of yttrium(III) ions (100 mg/L) on EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> was firstly studied under different pH conditions. As shown in the Fig. 2a, the adsorption capacity of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for yttrium(III) ions increased from 39.40 mg/g to 383.2 mg/g when the pH values was raised from 2 to 5.5. Obviously, the adsorption capacity is relatively low in strong acidic environment, which might be related to the increased surface positive charge because of the

protonation of the surface functional groups. For example, the -NH<sub>2</sub> groups lost their coordination ability with yttrium(III) ions due to protonation (-NH<sub>3</sub><sup>+</sup>) [37]. Such an inference was supported by the zeta potential characterization of the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> as a function of pH in Fig. 1c, in which the zeta potential was positive with the pH less than ~3.7. The electrostatic repulsion would be occurred or increased between yttrium(III) and the positive charged groups (Si-OH<sub>2</sub><sup>+</sup> and -NH<sub>3</sub><sup>+</sup>) on the surface of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> [27,34]. In addition, the H<sup>+</sup> ions would also compete with yttrium(III) ions on adsorption in strong acidic environment [38–40]. With the increase of pH value, the zeta potential would also become negative as the solution pH over ~3.7 (Fig. 1c), and the electrostatic attraction would be dominant between EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> and yttrium(III) ions. As a result, the adsorption capacity of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> significantly increased. However, as the pH value exceeded ~6.0, the ions started to form insoluble precipitation of hydroxide. Therefore, pH 5.5 was selected to be the optimum pH value for the rest of studies.

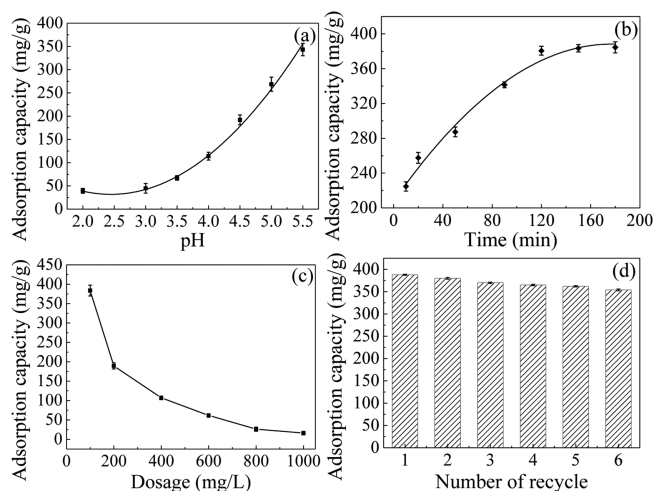
For a comparison, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles, EP and EP<sub>d-APTES</sub> were also used as adsorbents to enrich the yttrium(III) ions (Fig. S5a in Supporting information). It was found that the maximum adsorption capacity of yttrium(III) on Fe<sub>3</sub>O<sub>4</sub> nanoparticles, EP and EP<sub>d-APTES</sub> were 22.80, 30.25 and 85.32 mg/g, respectively, which were all greatly lower than that of 383.2 mg/g for the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> composites, indicating that the adsorption performance could be greatly improved by the functionalization and Fe<sub>3</sub>O<sub>4</sub> nanoparticles grafting of the EP particles.

The effect of contact time on adsorption efficiency of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for yttrium(III) ions was studied by using 10 mL of the adsorbate solution (100 mg/L) and 1 mg of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> adsorbent. As shown in Fig. 2b, it was observed that the adsorption capacity of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for yttrium(III) has reached as high as 222.4 mg/g at contact time of 10 min, and then further increased up to 370.5 mg/g at contact time of 120 min, almost approaching the maximum adsorption capacity. Therefore, the optimum contact time in this work was set as 120 min.

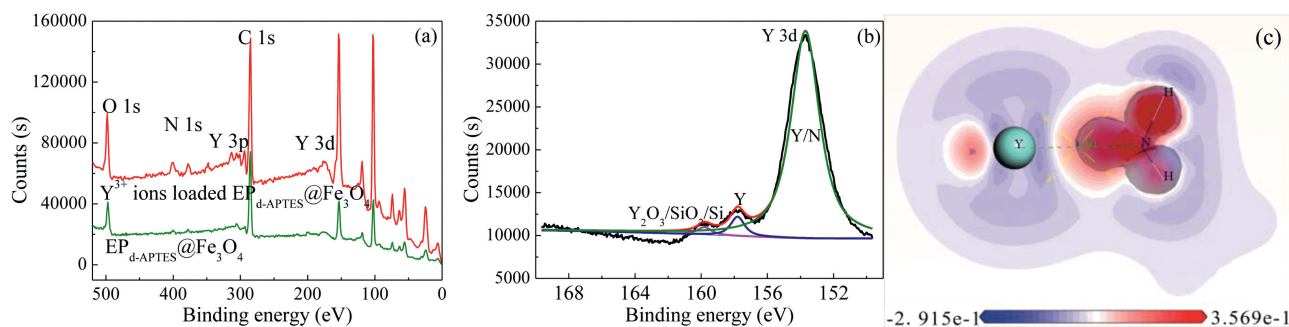
Adsorbent dosage is an important factor to affect the adsorption efficiency of the adsorbate. In this study, effect of the adsorbent dosage on adsorption capacity of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for Yttrium(III) was also investigated. As shown in Fig. 2c, when the dosage was increased from 100 mg/L to 1000 mg/L, its adsorption capacity was correspondingly decreased from 371.6 mg/g to 16.10 mg/g. The decrease of adsorption capacity with increase of dosage is due to the insufficient use of the active sites. Therefore, the optimum dosage was set as 100 mg/L for the rest of adsorption experiments. By combing Figs. 2a-c, it can be concluded that the synthesized EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> possesses excellent adsorption performance with maximum adsorption capacity of 383.2 mg/g for rare earth ions of yttrium(III), which is much higher than those in previous reports [41]. The excellent adsorption performance of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> was attributed to the high specific surface area and the large amount of adsorption active sites of amine groups.

The good magnetic property of the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> enables it to be well recycled under the external magnetic field (Fig. 5Sb in Supporting information). As shown in Fig. 2d, for the first adsorption cycle, the adsorption capacity was 388.2 mg/g. Encouragingly, after being recovered and eluted in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution, it still has a good adsorption performance with a high capacity of 354.4 mg/g after six cycles (91.23% of initial adsorption capacity). The findings demonstrate that the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> adsorbent possesses good recyclability and is a promising material for enrichment of the yttrium(III) ions from rare earth wastewater.

To study the adsorption thermodynamics of yttrium(III) ions on EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub>. Three isotherms of langmuir [42], Freundlich [43] and Dubinin-Radushkevich model (D-R isotherm model) [28,44], are used to study the adsorption behavior (Fig. 6S in Supporting



**Fig. 2.** Effect of solution pH (a), contact time (b) and adsorbent dosage (c) on adsorption capacity of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> for yttrium(III). (d) The recyclability of the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> as adsorbent to adsorb yttrium(III).



**Fig. 3.** (a) XPS spectra of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> before and after adsorption of yttrium(III) ions. (b) High-resolution XPS spectra of Y 3d after adsorption of yttrium(III) ions. (c) The electron density differences on the cross section parallel to the surface formed by three atoms (N/Y) for the most stable configuration of yttrium(III) ions interacting with amino group.

information). The result indicated that Freundlich isotherm model could better describe the adsorption process ( $R^2 = 0.9953$ ). Calculated from D-R isotherm model, the average adsorption energy was 24.1 kJ/mol, indicating that the adsorption is mainly through a chemical adsorption. The adsorption kinetics were also studied in this work [45]. The fitting results show that the *pseudo*-second-order kinetics is suitable for the adsorption of yttrium(III) on the surface of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> ( $R^2 = 0.9934$ ). In order to investigate the effect of temperature on the adsorption, the thermodynamic parameters were also calculated. The enthalpy change ( $\Delta H^0$ ) had a value of 15.68 KJ/mol at 298.15 K. The positive  $\Delta H^0$  indicates that the adsorption is endothermic reaction. The Gibbs free energy change ( $\Delta G^0$ ) of adsorption was calculated to be 5.81 KJ/mol. Therefore, the increase in temperature is beneficial to the adsorption of rare earth ions on EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> surface.

To understand the adsorption mechanism of yttrium(III) ions on the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> surface, the FTIR spectrum, XPS measurement and the electron density difference (EDD) were analyzed after EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> adsorbing the Yttrium(III) ions. As shown in Fig. 1a, the FTIR spectrum for the yttrium(III) ions loaded EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> exhibited a new characteristic weak band at  $\sim 460\text{ cm}^{-1}$ , which was attributed to the vibration of Y–N coordination bond. In addition, the broad peak at  $3500\text{--}2800\text{ cm}^{-1}$  becomes narrower, and the peaks at  $565\text{ cm}^{-1}$  and  $1532\text{ cm}^{-1}$  disappeared, which further supports the coordination of nitrogen atoms with the yttrium(III) ions [46]. Moreover, the intensity of bands at  $3437\text{ cm}^{-1}$  and  $2927\text{ cm}^{-1}$  decreased, which might be associated with the coordination of yttrium(III) ions changing the environment of  $\text{-NH}_2$  groups. Meanwhile, the XPS spectroscopy is a useful tool to understand the surface chemical states. Fig. 3a shows the XPS spectra of EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> before (Fig. S2 in Supporting information) and after adsorption of yttrium(III) ions. For the yttrium(III) ions loaded EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> sample, it is obviously observed that two characteristic peaks appear at 299–301 eV and 150–160 eV correspondingly assigned to Y 3p and Y 3d. The high-resolution spectrum of Y 3d is shown in Fig. 3b, which can be fitted to three peaks. Peak at 159.8 eV was assigned to Y<sub>2</sub>O<sub>3</sub>, which might be resulted from the oxidation of the adsorbed yttrium(III) ions during the drying process of materials after adsorption. The peak at 157.7 eV was attributed to the free yttrium(III) ions adsorbed by a physical process. As to the main peak at 153.7 eV, it was assigned to the yttrium(III) ions coordinated with the functional groups such as  $\text{-NH}_2$ . Compared with that of the free yttrium(III) ions, the coordination of yttrium(III) ions with  $\text{-NH}_2$  groups induces a 4 eV shift toward lower binding energy, which was due to the electron donor effect by the lone electron pair of nitrogen atom. To confirm such a conclusion, the EDD between yttrium(III) ions and amino groups was calculated by using quantum chemical theory.

As illustrated in Fig. 3c, the EDD map reveals the origination of the electronic structure differences upon the bond between the yttrium(III) ion and amino group. The enhanced red regions indicate the electron enrichment, while the enhanced blue regions represent electron deficiency. It can be clearly observed that the electron density of yttrium(III) ion is significantly increased as indicated by the enhanced red color, suggesting that the yttrium(III) ion gains more electrons from amino group. Therefore, it can be concluded that the strong adsorption of yttrium(III) ion on the surface of the synthesized EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> composite is closely associated with the coordination of yttrium(III) ions with various functional groups [47].

We have successfully synthesized a magnetic EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> composite by amino-functionalizing the EP nanoparticles followed by a Fe<sub>3</sub>O<sub>4</sub>-decoration process. The synthesized magnetic composite shows a good adsorption behavior for rare earth ions with a high adsorption capacity of 383.2 mg/g for yttrium(III) ions. The adsorption energy from Dubinin-Radushkevich isotherm was estimated to be 24.1 kJ/mol at 298.15 K, indicating that the adsorption of the yttrium(III) on EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> is mainly through a chemical adsorption. Adsorption isotherm analysis indicated that the Freundlich isotherm model could better describe the adsorption process of yttrium(III) on EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> surface, while the adsorption kinetics complies with the *pseudo*-second-order model. The excellent adsorption properties of the EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> materials for yttrium(III) ions are attributed to the porous structure of the materials with high specific surface area on the one hand, and a large number of functional groups of  $\text{-NH}_2$  on the surface of the materials on the other hand. The yttrium(III) ions have strong coordination with various functional groups, which were confirmed by FTIR, XPS characterizations and the quantum chemical calculation. More importantly, the synthesized EP<sub>d-APTES</sub>@Fe<sub>3</sub>O<sub>4</sub> composite materials could be recycled for at least six times without significant degeneration in adsorption capacity, indicating that the prepared composites have a high stability and recyclability, and might find its application in treatment of the ionic rare earth wastewater.

#### Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Highly Efficient Enrichment and Adsorption of Rare Earth Ions (Yttrium(III)) by Recyclable Magnetic Nitrogen Functionalized Mesoporous Expanded Perlite”.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccl.2020.08.017>.

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