Full Length Article

Spherical polymer brushes bearing imidazole groups as novel nickel remover for crude oil

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ABSTRACT

Nickels in crude oil often deactivate the hydrocracking and catalytic cracking catalysts. Strong acids are widely applied to remove these nickels, although they cause severe corrosion to the subsequent catalytic cracking and processing equipment. Polymer brushes bearing specific groups which can adsorb nickel ions are considered as desirable non-corrosive nickel removal agents. In this work, micro-sized spherical polymer brushes bearing imidazole groups (PVIm@SiO$_2$) are first applied to remove trace nickels in crude oil with the help of electric demulsification. The effects of polymer brushes concentration, oil/water ratio and electric demulsification temperature on nickel removal efficiency are investigated. Compared with the monomer (VIm) and polymer (PVIm) bearing imidazole groups, polymer brushes exhibit a much higher nickel removal efficiency than the other two, which is approximately 66.7%. In addition, the regeneration of polymer brushes are achieved by a rapid and simple process using diluted HCl. As well as, the removal efficiency of Ni remains 62.5% in 5 consecutive cycles. Consequently, these spherical polymer brushes bearing imidazole groups are reasonable nickel remover for crude oil.

1. Introduction

Nowadays, fossil fuels are still the major sources of the energy demand [1]. Unfortunately, metals in heavy oils are deleterious to hydrocracking and cracking catalysts and lead to the reduction of light oil yield and the increase of inferior products [2–4]. Especially, nickel contained in the crude oil is the most troublesome metal complex although it is only present in trace quantities (from trace to 200 ppm) [5]. Removal of nickel can not only alleviate the negative impacts on the refining process, but improve the quality of follow-up products, which has attracted more and more attentions in recent years. The main nickel usually exists as the oil-soluble organometallic compound with a stable structure, such as metalloporphyrins and nonporphyrins [6–10] so that it is extremely difficult to be separated.

Tremendous efforts have been devoted to addressing the above mentioned problem of nickel removing and various novel approaches are developed. Shang [11] reported that the microwave technology was a new approach for removing Ni/V with the help of chemical reagents. Gonzalo [12] developed low-cost chabazite-based catalysts to remove Ni and V during coking operations. However, a recent tendency is the

usage of demetallization agent which is a facile and effective method, compared with others. The widely applied demetallization agents are acids [13–15], such as organic acids and their salts, monocarboxylic acids, dicarboxylic acids, aminocarboxylic acids and/or their salts, as well as inorganic acids. Most of them are strong acids which will cause severe corrosion to the subsequent catalytic cracking and processing equipment [16]. Therefore, searching for a clean, non-corrosive demetallization agent has a practical significance. Krambeck [17] and Kukesl [18] employed phosphorus compounds to remove porphyrin nickel and porphyrin vanadium with a high removal efficiency of 39% and 41%, respectively. Nguyen [19] investigated the effect of isocyanate/ester on the removal of nickel and increased the nickel removal efficiency to 30%. Organic demetallization agents, such as cationic starches (CS), carboxymethyl chitosan (CT), and chitosan schiff [20–23] exhibit high removal efficiencies of Ca, Cu and other metals owing to their amino (−NH$_2$) and carboxylic (−COOH) groups [20,24]. But Ni is hardly removed by these agents. Therefore, an efficient and non-corrosive nickel removal is highly demanded by the oil refinery industry. Since the nickels in crude oil exist as the porphyrin complexes, a considerable competitive coordination with nickel is required for the novel

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nickel removal agents.

Nowadays, polymer brushes have demonstrated good performance in many fields [25], especially in heavy metals adsorption, due to their distinctive structures. Because of the strengthened Donnan effect [26,27], the polymer brushes are ideal candidates for the removal of heavy metals. It is reported that the metal selectivity and sensitivity [28–30] of polymer brushes can be regulated by changing the grafted functional groups. Liu [31,32] synthesized functional 3D graphene by grafting functional groups on the surface, which can adsorb Pb^{2+}, Na^+ and Cl^- by capacitive deionization. Zhou [33] found that the amphi-philicity of the silica nanoparticles could be adjusted by changing the grafting ratio of the hydrophilic-lipophilic groups. Chao [34] fabricated the poly(1-vinylimidazole) oligomer (FSPV) brush with magnetic core as a novel adsorbent to remove Hg(II) from water which possesses the adsorption capacity of 346 mg/g. Takafuji [35] proved that the poly(1-vinylimidazole) oligomer on the magnetic nanoparticles had a great efficiency of adsorbing Cu^{2+}, Ni^{2+}, and Co^{2+} from water and the ability of ions adsorption followed the rule $Cu^{2+} \gg Ni^{2+} > Co^{2+}$. Besides, those polymer brushes are easily recovered [27] by desorption of heavy metal with aqueous HCl solution.

From the above, it is obvious that polymer brushes possess outstanding merits of adsorbing heavy metal ions from water. If cooperated with appropriate process, they have great potential to remove the heavy metals in crude oil. Different from water, the viscosity of crude oil is very high. If following the similar process of removing metals from water, the polymer brushes are hardly separated out from crude oil after they adsorb nickels. Considering about that, dispersing polymer brushes into water and preparing water/oil emulsion will increase the contacting of polymer brushes and nickel-porphyrin complexes at the water–oil interface. According to the Donnan effect, spherical polymer brushes can adsorb more nickels into their interlayer, thus seize nickels from oil to water. Afterwards, with the help of electric field, dipolar force and dielectrophoretic force triggered by alternating current promote the mutual attraction and collision between the water droplets, which causes small droplets emerge into large droplets. Eventually, the water is separated out and removal of nickels from crude oil is achieved.

In the present work, micro-sized spherical polymer brushes (PVIm@SiO$_2$) are synthesized and creatively applied to remove nickels from crude oil. In the presence of the polymer brushes, the nickel removal efficiency of crude oil is investigated from these parameters, such as oil/water ratio, polymer brushes concentration and electric demulsification temperature. Spherical polymer brushes exhibit much better performances on the removal of nickels than the monomer and polymer bearing imidazole groups. Consequently, the nickel removal mechanism for spherical polymer brushes is proposed. Besides, these polymer brushes can be regenerated by diluted HCl and the removal efficiency of nickel remains 62.5% in 5 consecutive cycles. Such results thus suggest a promising potential for their industrial application.

2. Experimental section

2.1. Materials

Methacryloxy propyl trimethoxyl silane (99%) and 2,2-azobis (2-methylpropionitrile) (98%) are purchased from Energy Chemical. 1-vinylimidazole (99%) and micro-sized silica powder are from Aladdin. HCl (36–38 wt%), HNO$_3$ (65–68 wt%) are purchased from Shanghai LingFeng company. NaOH (99%), absolute methanol (99.5%), absolute ethanol (99%) and acetone (99%), N,N-dimethylformamide (99%) and methylbenzene (99%) are purchased from Titan and used as received. Crude Oil sample is provided free by Petroleum Liaohe oil field Company with a density of 0.8977 g/cm^3 and viscosity of 3.0 mPa·s (at 50 °C). The content of saturates, aromatics, resin and asphaltenes is 63.7, 18.5, 13.4 and 3.8 wt%, respectively. The water content is 0.5 wt % and the Ni content is 80 ppm.

2.2. Preparation of PVIm

Poly(1-vinylimidazole) (PVIm) is prepared by radical polymerization of 1-vinylimidazole (VIm) with AIBN as the initiator [36]. A typical polymerization process is shown as following: 10.00 g of VIm, 0.33 g of AIBN and 100 mL toluene are added into a 250 mL three-neck bottle and stirred. N$_2$ is charged into and discharged out of the bottle for three times to fully remove oxygen from the reaction system. The polymerization is proceeded at the temperature of 70 °C for 48 h. After that, the crude product is dissolved in methanol, and then precipitated in acetone. The precipitated polymer is filtered and vacuum dried at 60 °C for 24 h.

2.3. Preparation of PVIm@SiO$_2$

The preparation of PVIm@SiO$_2$ is according to the previous Ref. [37]. Before reaction, micro-sized silica is acidized by 1 M HCl solution to generate more active silanol groups (Si-OH) on the surface. After that, 5.00 g acidized silica, 50 mL toluene and 5.00 g KH570 are added into a three-necked flask and mixed together. Above solution is heated at 125 °C with stirring and reacted for 6–7 h. Then, KH570@SiO$_2$ is obtained by washing with toluene, ethanol and acetone in sequence to remove the solvent and reactant. Next, certain amount of VIm is mixed with dried 5.00 g KH570@SiO$_2$ in 50 mL DMF with 0.16 g AIBN as the initiator. Under the nitrogen protection, the reaction is proceeded for 10 h at 80 °C. By washed with DMF and methanol to remove homopolymers and unreacted monomers, then dried in a vacuum oven at 80 °C for 12 h, PVIm@SiO$_2$ is finally acquired [35].

2.4. Characterization of PVIm@SiO$_2$

2.4.1. FT-IR
Obtained KH570@SiO$_2$ and PVIm@SiO$_2$ are analyzed using a FT-IR spectroscopy (Nicolet 6700, Thermo Fisher Scientific., USA) by KBr pellet.

2.4.2. TGA
The grafting ratios of PVIm on SiO$_2$ are measured by thermogravimetric analyzer (Pyris 1 TGA, PerkinElmer., USA).

2.4.3. Elemental analysis
The elemental composition of PVIm@SiO$_2$ is characterized by using elemental analyzer (Vario EL III, Elementar., Germany). Grafting ratios of PVIm are calculated by the results of nitrogen contents. The calculation method is as follows:

$$PVIm\% = \frac{N\%}{2M_N/M_{VIm}}$$

where M_N and M_{VIm} are the molecular weights of nitrogen and 1-vinylimidazole.

2.4.4. GPC
The molecular weight and molecular weight distribution of PVIm are measured by gel permeation chromatography (PL-GPC50, Agilent., USA).

2.4.5. SEM and TEM
The morphology and particle size of PVIm@SiO$_2$ are characterized by SEM (S-4800, Hitachi, Japan) and TEM (JEM-2100, JEOL, Japan).

2.5. Removing nickel from crude oil

Nickel is removed by using electric desalter instrument (YS-3, Shuangyang, China). In a common process, crude oil sample is preheated at 90 °C for half an hour. After the temperature is stabilized, certain amount of water, desired dose of nickel removal agent and