Modified walnut shell filter material for the enhanced removal of oil from oilfield wastewater

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ABSTRACT

While polymer oil recovery greatly improves oil recovery, the polymer injected into the formation undergoes shearing, degradation, etc., and returns with the output liquid in the form of an anionic polyacrylamide of lower molecular weight, resulting in a production fluid. There is residual polymer, and this kind of polymer-containing wastewater is easy to contaminate the walnut shell filter in the sewage treatment process, resulting in failure of the walnut shell filter material, introduce hydrophilic sulfonic acid groups on the surface of the walnut shell filter material to lipophilic to hydrophilic of the surface. The dosage of NaHSO_3 is 10-20% of the mass fraction of walnut shell filter (mass ratio %). Reflux reaction, and the reaction time was 1-5 h; the surface wettability of the walnut shell reversed. The surface contact angle drops from 95° before modification to 36.75° - 66.25° . Its surface hydrophilic oleophobic performance has been significantly improved, Treatment of 150-230 mg/L of oily sewage, filtration and oil removal rate increased from 38.05% to 89.51% by modification; Backwashing and degreasing effect is increased by 4 times.

Keywords: Filter material, Modified walnut shell, Oil removal rate, Sulphite, Surface contact angle

1. Introduction

While polymer oil recovery greatly improves oil recovery, the polymer injected into the formation undergoes shearing, degradation, etc., and returns with the output liquid in the form of an anionic polyacrylamide of lower molecular weight, resulting in a production fluid [1]. This kind of polymer-containing wastewater is easy to contaminate the walnut shell filter in the treatment process, which leads to the walnut shell not being regenerated by backwashing, the failure of the knot is lost and the filtration is lost, and the service life is shortened [2].

Filter materials in the oily wastewater treatment of oilfields include quartz sand, walnut shell, microporous ceramic, membrane and fibre medium, different filter media are affected by oil contamination to a greater extent. The walnut shell can easily produce hydraulic rebound without considerable backwashing strength due to its wide range of sources, strong adsorption, interception capability, anti-oil immersion, high hardness, good abrasion resistance,

stable chemical properties and low particle density. The walnut shell can be repeatedly used in many times to restore the adsorption and degreasing effect, and it is widely utilised as the filter material in oilfield filters [3-5]. After this material is used to treat polymer-containing oily wastewater for a period, the knotting phenomenon is likely to occur. The effect of backwashing and degreasing is drastically reduced, and the degreasing rate is shortened.

Here, in order to realize the low-cost and effective filtration separation and treatment of the polymer-containing oily wastewater, the surface of the hydrophilic and oleophobic walnut shell filter material is prepared by a simple chemical modification method. In this study, a hydrophilic sulfonic acid group is introduced on the surface of the walnut shell and chemically bonded to the surface functional group of the walnut shell, a stable coating layer is formed on the surface of the walnut shell, the micropores become smaller, the surface is more dense, the surface wettability is greatly improved, and the super-hydrophilic and underwater oleophobic, and the compressive strength does not change. What

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is important is that the filtration degreasing rate is greatly improved. Filter material backwashing and oil removal is easy, prolonging the service life of walnut shell filter material. Therefore, we expect that the modified walnut shell has a wide range of potential applications in the treatment of polymer-containing oily wastewater.

2. Material and Methods

2.1. Materials

Industrial walnut shell filter used in the field was obtained from Gongyi Jingyu Filter Material Company. The walnut shell filter material with a particle size of 1.6–2.0 mm was washed with deionised water until the water was clear, and then it was dried at 105°C for 3 h. Industrial products Na_2CO_3 , NaHSO_3 and Na_2SO_3 from Hunan Zhongcheng Chemical Co., Ltd. The polymer AP-P4 (relative molecular mass of 10 million, hydrolysis degree of 19%, and hydrophobic base content of 0.1%) is water-soluble hydrophobically associated polyacrylamide, from Sichuan Guangya Technology Co., Ltd. Crude oil (API value was 13.9, 20°C density was 0.9701 g/cm³, colloid content was 21.8%, paraffin content was 1.31%, and n-pentane insoluble matter was 9.94%) from the target oilfield provided the 1,000 mL three-neck glass reaction bottle device, including stirring apparatus, thermostatic oil bath, condensing reflux unit and thermometer.

2.2. Instrument

DSA30 contact angle measuring instrument (KRÜSS), MIRA3 scanning electron microscope (Tescan), M630 NIR spectrometer (Bruker), TU-1810PC UV-Vis spectrophotometer (Beijing General Analysis), WAW-1000B universal pressure testing machine (Jinan Tianhua), GF30 high shear emulsifier (Fluko), Self-made CH-II micro-continuous sewage treatment unit and filter (DN = 40 mm, H = 400 mm).

2.3. Polymer-containing Oily Wastewater Sample

The experimental water sample was obtained from an oilfield on-site wastewater with a salinity of 9374.13 mg/L. The mass concentration of the polymer simulating the water was 50 mg/L. Then, the water sample added with the polymer was heated at 60°C, added with the standard crude oil of the oilfield and emulsified by a high shear emulsifier at 12,600 r/min for 5.00–10.00 min to obtain a water sample surface free from oil slick; its oil content was 150.00–230.00 mg/L. The water sample oil content was determined in accordance with the ‘determination of oil content in oilfield waste-

water-spectrophotometric method’ (SY/T 0530—2011).

2.4. Surface Modification of Filter Material

A certain amount of walnut shell filter material m_1 , adding different amounts of ionized water, then adding three kinds of reaction agent m_x (mass ratio $m_x/m_1\%$), reacting at different temperatures for different time, the series reaction conditions are shown in Table 1.

A certain amount of washed walnut shell filter material is added to the reaction bottle provided with the stirring device and the condenser, and deionized water is added until the filter material is completely immersed in a certain ratio of chemical solution under reflux for different time. After the reaction is completed, the filter material was poured out, rinsed with clear water until colorless and dried in an oven at 105°C for 3 h. The unmodified filter material is No. 0, and the reaction conditions are changed to obtain a series of modified filter materials No. 1–6 of different reaction conditions.

2.5. Characterisation of Filter Material

The surface morphologies of No. 0 unmodified and No. 3 modified filter materials were analysed via scanning electron microscopy (SEM). Treatment process: spray-gold treatment to enhance the conductivity of the filter material. Test condition: 15.0 kV. The types and contents of the surface elements of the filter materials were analysed via energy-dispersive X-ray spectroscopy (EDS) and XPS, respectively.

2.6. Determination of the Surface Wettability of Filter Materials

The surface contact angle of the series of surface modified and unmodified filter materials was determined using the sitting drop method, and the diameter of the bayonet glue needle was 0.247 mm.

2.7. Filter Material Compression Resistance Test

The steel pipe with an inner diameter of 40 mm was filled with walnut shells pressed using a steel piston. The test machine started the compression resistance test by slowly pressurising the filter material with a force speed of 0.10 kN/s to obtain the stress-deformation curve before and after modification.

2.8. Filter Structure and Filter Material Filling Method

Filter packing: DN400, Filter was filled with 360.00 mm of Walnut shells, the structure of which is shown in Fig. 1.

Table 1. The Dosage and Reaction Conditions of the Filter Materials

Serial number	Walnut shell/g	Deionized water/g	NAC/%	YNS/%	NHS/%	Temperature/°C	Reaction time/h
1	250	250	10	10	0.10	95	1
2	250	250	10	5	0.15	105	5
3	250	250	20	10	0.10	105	3
4	200	240	10	5	0.10	105	3
5	200	240	10	10	0.15	100	3
6	200	240	5	5	0.20	105	3

Fig. 1. (a) SEM image of oral walnut shell and (b) Modified walnut shell.

2.9. Continuous Dynamic Degreasing Experiment with Different Filter Materials

The unfiltered filter material No. 0, modified filter material No. 1 and modified filter material No. 3 were used to carry out the continuous filter dynamic degreasing experiment. The filling methods of the five kinds of walnut shell filter materials are shown in Table 2.

The sewage (60°C) is continuously into the filter by the pump, and the filter material is completely immersed in the water during the filtration process, and the pump is set to stabilize the same filtration speed for the filtration experiment. Each time the 3L water sample of the filter outlet is collected, total of 5 filter batches.

Table 2. Filter and Filter Material Filling Method

Filter filling Item	Filter material filling method
Filter a	0# filter material
Filter b	1# filter material
Filter c	3# filter material
Filter d	3# and 0# filter materials 1:1(m/m)
Filter e	1# and 0# filter materials 1:1(m/m)

Fig. 2. Comparison of oil removal rate of different filled filter materials.

Fig. 3. Comparison of filtration time for filtering the same amount of water.

Record the filtration time of five filtered batches and analyze the oil content of the filtered water sample. After each batch of filter material is filtered, the same conditions as the filter pump are used to pump the 2 L (60°C) field sewage from the lower end of the filter to reverse backwash the filter material. Collect the backwash water sample at the outlet at the top of the filter to measure the oil content. The trend of the experimental degreasing rate and filtration time of the filter materials a to e filled with different filter materials is shown in Fig. 2 and Fig. 3.

3. Results and Discussion

3.1. Optimum Conditions for Filter Material Modification

The main components of walnut shells include acid-insoluble lignin, cellulose and hemicellulose. Although differences are found in the surface composition of walnut shells in different varieties and regions, the content of acid-insoluble lignin present in walnut

shells is relatively high, accounting for more than 50% of the components. As the basic structure of the acid-insoluble lignin in the walnut shell exhibit mainly hydroxyl groups, phenolic groups, α -C and γ -C, that confer high chemical activity to the walnut shell. The introduction of hydrophilic groups at these sites with higher chemical activity gives the walnut shell filter material the ability to resist oil stain adhesion and easy backwash regeneration. Lignin has three structural units, namely, guaiacyl (G type), syringyl (S type) and hydroxyl-phenyl (H type), whereas the walnut shell acid-insoluble lignin mainly includes G and S types. The sulphite constant temperature reaction can be used to modify the lignin on the surface of the walnut shell; it is divided into three stages: soaking, sulfonating and dissolving [6-9]. To avoid serious damage to the lignin structure or dissolution of lignin during modification, the factors affecting the modification reaction (reaction temperature, drug mass fraction and reaction time) were optimised. The chemical reaction process is represented at Fig. S1.

3.2. Filter Material Characterisation and Mechanical Property Analysis

3.2.1. Analysis of the surface morphology of the filter material SEM (Fig. S2) results show that at different magnifications, the filter material surface before modification was oleophilic and had large and numerous micropores, thereby easily adsorbing emulsified oil and blocking the micropores. The filter material surface after modification became dense and had small micropores, thereby easily forming a trapping layer that prevented the blocking of micropores. In addition, the pollutant catching capacity of the modified filter material was easily restored by backwashing.

3.2.2. EDS analysis

Table 3 shows the EDS results of the filter material surface. The unmodified walnut shell contains four elements: C, O, Ca and K. In addition to these elements, the modified walnut shell also has Na, S and Mg, it is indicated that the surface of the Walnut shells successfully introduces a hydrophilic sulfonic acid group.

Table 3. Walnut Shell Filter Material EDS Analysis (Raw and Modified Walnut Shell)

Element	Element content of raw walnut shell/%	Element content of modified walnut shell/%
C	58.73	49.03
O	32.11	25.96
Au	5.94	9.02
Na	--	5.69
S	--	3.85
Ca	2.03	3.06
Si	--	1.92
Mg	--	1.47
K	1.2	--

3.2.3. XPS analysis

The XPS test (Fig. 4) shows that the unmodified walnut shell consists mainly of O (binding energy of 532.6 eV) and C (binding energy of 284.92 eV), with element contents of 27.43% and 67.77%, respectively. After hydrophilic modification, O (binding energy of 532.77 eV) and C (binding energy of 286.21 eV) are considered main elements but their contents are changed. The content of O is increased to 29.68%, and that of C is decreased to 65.14%. The binding energies of the two elements are also changed. The peak binding energy of O is increased by 0.17 eV, and a new peak appears at 500 eV. The peak binding energy of C is increased by 1.29 eV, indicating that the chemical changes of the surface group of the walnut shell have occurred. The increase in the content of O element is due to the introduction of sulphonic acid group after sulphonation.

A significant S binding energy peak (168 eV) is not observed on the XPS wide scan spectrum of the modified walnut shell due to the high content of C and O in the walnut shell and the limited introduction of sulfonic acid groups. The comparative results before and after modification show that on almost no S element is found on the surface of the unmodified walnut shell, and the hydrophilic sulphonic acid group is introduced into the surface of the modified walnut shell.

Fig. 4. XPS spectrum of walnut shell before and after modification. (a) Wide scan spectrum. (b) Narrow scan spectrum.

3.2.4. Evaluation of the surface wettability of filter materials

The contact angle (θ) is an important measure of the relationship between the material and the wettability of the liquid. $\theta = 90^\circ$ can be used as the boundary between wetting and nonwetting. When $\theta < 90^\circ$, it can be wetted; when $\theta > 90^\circ$, it cannot be wetted [10-13]. Table 4 shows that the contact angle of the unmodified walnut shell filter material is 97° , and the water droplets are rounded on the filter material surface, indicating that the surface is hydrophobic. The water droplets are spread on the surface of the modified walnut shell filter material, and the contact angles are reduced to 36.5° – 66.25° . The results indicate that the surface wettability of the modified walnut shell is significantly improved, and the surface becomes hydrophilic and oleophobic. The hydrophilic modification degree of the No. 1 filter material is the highest, and that of the No. 3 filter material is the lowest.

Therefore, the optimum conditions of the filter reaction, the ratio of the agent to the filter material are: Na_2CO_3 20.00%, NaHSO_3 10.00% and Na_2SO_3 0.10%, and the reaction temperature is 105°C reflux reaction time 3 h.

Table 4. Contact Angle of Different Walnut Shell Filter Materials ($^\circ$)

Serial number	Once	Twice	Average value
original filter material 0	93	97	95
modified filter material 1	64	68.5	66.25
modified filter material 2	66	66.5	66.25
modified filter material 3	36.5	37	36.75
modified filter material 4	56.5	55.5	56
modified filter material 5	56.5	56	56.25
modified filter material 6	47	44	45.5

3.2.5. Analysis of the mechanical property of filter materials

Fig. S3 shows the stress–strain curves of Nos. 0 and 3. The two filter materials have a slight deformation of 0.01 mm at a force of 0.050 kN. When the destructive force reaches 50.00 kN with a force increase speed of 0.10 kN/s and the breaking strength is 39.80 MPa, the strains of Nos. 0 and 3 are 59.85% and 60.76%, respectively. No comminute changes in the two samples are found, indicating that the mechanical properties of the walnut shells before and after modification are unchanged, and they still have the advantages of high hardness and good wear resistance.

3.3. Effect of Filter Material on Filtration Oil Removal and Backwashing

3.3.1. Filtration oil removal effect

Continuous dynamic degreasing experiment was conducted on No. 0, 1 and 3 filter materials. Fig. 2 and Fig. 3 show the degreasing rate and filtration time of the series of experiments, respectively. The emulsified and suspended oils are affected by various forces during filtration, including gravity sedimentation, hydraulic collision and Brownian diffusion during migration. The contact flocculation, electrostatic attraction, adsorption, molecular attraction and coalescence effect during adsorption affect the filtration and degreasing efficiency [14, 15]. Fig. 2 shows that the average oil removal rates of Nos. 0, 1 and 3 are 38.05%, 55.26% and 89.51%, respectively.

The degreasing rates of No. 1 and 3 modified filter materials are improved, and the degreasing effect of No. 3 is the best. This finding is caused by change in the surface properties of the modified walnut shell from lipophilic to hydrophilic and from oil wettability to water wettability during filtration. The contact angle between the oil granule and walnut shell in the water is changed from immersion adsorption to oil bead particle adsorption. Therefore, the contact area of the emulsified oil with the surface of the walnut shell is reduced, and the total amount of adsorption increased. The adsorption force of the oil beads follows the principle of chemical flotation kinetics ($F = 4\pi r\sigma$), wherein a large particle size of the oil bead shows a strong adhesion. Moreover, the large particle size of the oil beads has a high strength of coalescence. Fig. 3 shows that the average filtration time of No. 3 is 9.28 min and that of other filter materials is between 3.6 min and 5.1 min. The filtration time of No. 3 is considerably larger than that of other filter materials. The reason is that in addition to the resistance of the filter layer formed by the walnut shell intercepting the emulsified oil and the blocking effect of the suspended particles, the surface of the modified walnut shell compared with the unmodified filter material has additional capillary resistance due to water wettability [16-18]. Thus, the filtration speed becomes slow, and the filtration time becomes long. Therefore, the emulsified oil in the water is in contact with the filter material for a long period, and its adsorption, retention and capture effects are enhanced.

3.3.2. Filter backwashing evaluation

Table S1 displays that the oil content of the backwashed effluent of No. 3 reaches the highest value of 405.15 mg/L, indicating that the oil adsorbed by No. 3 is easily removed by backwashing, and its backwashing effect is greatly improved compared with those of the other materials. The surface of the modified walnut shell becomes hydrophilic and oleophobic. Thus, oil concentrates in the gap of the filter layer in the form of oil droplets; it is easily backwashed under water flushing. No. 3 captures a large amount of oil during filtration; thus, its backwashed effluent contains a large amount of emulsified oil.

4. Conclusions

The walnut shell filter was modified by sulphite reflux reaction under alkaline conditions. The best modification conditions were as follows: mass ratio (m_2/m_1) Na_2CO_3 20.00%, NaHSO_3 10.00% and Na_2SO_3 0.10%, the reaction temperature is 105°C reflux reaction time 3 h. The surface wettability of the walnut shell filter material before and after modification reversed from lipophilic to hydrophilic. For the treatment of polymer (50.00 mg/L) and oil (150.00–230.00 mg/L) containing wastewater, the degreasing rate of modified filter material was greater than 88%, which was increased by more than 50.00% compared with that of the filter material before modification. The oil content in the backwashed effluent of modified filter material was 405.15 mg/L while in the oral filter material backwashed effluent was 100 mg/L, indicating that the backwashing degreasing effect was also greatly improved.

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Author contributions

X.Y. (Professor) conducted all the experiments. J.Z. (Ph.D. & Chief Engineer) performed the experiments. X.J.W. (Ph.D.) performed the experiments. M.J.Z. (Ph.D.) wrote the manuscript.

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