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Nano-structured surface modification of micro-porous ceramic membrane with positively charged nano-Y₂O₃ coating for organic dyes removal

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The purpose of this study is to develop a kind of positively charged microporous ceramic membrane which works on the electrostatic adsorption principle to promote adsorption of organic dyes with negative charge. The nano-Y₂O₃ coating which played the role of charged agent was obtained through colloid reaction and thermal decomposition process. Firstly, the precursor colloid was synthesized by chemical reaction of urea and YCl₃, and subsequently the precursor colloid was calcined in air to transform into nano-Y₂O₃, which was fixed on the surface of base membrane. The specific surface area of positively charged ceramic membrane increased 36.72% through coating process, and the nano-Y₂O₃ was evenly attached to the base membrane surface with an isoelectric point of 8.18. The EDS and XPS results demonstrated that there were new chemical bonds formed with Y element between the base membrane and the Y₂O₃ coating, which made the Y₂O₃ coating not easy to fall off. Positively charged ceramic membrane prepared in this study removed approximately 99.6% of titan yellow and 98.3% of eriochrome black T, which were both small molecule dyes with negative charges in water, and which indicates a potential manufacturing process to yield effective dye filters with superior to those of current dye filtration techniques.

Introduction

In recent years, with the development of modern industry and human society, a large number of organic dyes wastewater flows into aquatic environment which has posed a threat to the environmental safety[1]. Thus various methods of removal organic dyes from water have been researched. Among them, nano-filtration and reverse osmosis are the more effective and commercial methods[2]. However, for these methods, there are mainly two drawbacks: high cost and low flow rates[3]. Therefore, it is necessary to seek new method to remove these small molecule organic dyes from water.

Inorganic ceramic membrane is becoming increasingly application in different fields because of its incomparable advantages[4,5], such as high mechanical strength, resistant hyperthermia, fine chemical stability and so on[6-8], especially in the aspect of development and utilization of functional ceramic membrane, such as charged ceramic membrane[9]. And compared with electrically neutral membrane, charged ceramic membrane refers to the inorganic micro-porous ceramic membrane with a positive or negative charge on its internal surface, which possesses obviously technical advantage for electrical property[10].

Studies have been demonstrated that surface charge property has a significant impact on filtering performance[11] and pollution resistance[12]. This is because that charged ceramic membrane could achieve pollution resistance[13-15] by electrostatic repulsion, and it removes vanishingly small size of particles with the opposite charges through electrostatic adsorption. The principle is that charged micro-particles adsorb on the pore walls under the effect of Vander Waals and electrostatic forces[16] when passed through the opposite charged membrane with micron scale open porosity. And further studies have shown that the main dominating mechanism is electrostatic forces. So in the past, the adsorption depth filtration based on diatomaceous earth (DE; also known as kieselguhr)[17-21] and modified materials[22, 23] had drawn much attention, which gave some experiences for charged ceramic membrane preparation. Zhao et al[24, 25] studied effects of inorganic electrolytes and inorganic salt on ceramic membrane microfiltration performance. Sachdeva[26] prepared positively charged ceramic ultra filtration membrane through grafting polystyrene on the ceramic membrane surface. These researches in the literature only have been studied the surface properties and the preparation of charged ceramic membrane, which had no mention for practical application. Wegmann and coworkers[27,28] selected DE ceramic as base membrane and commercial hydrous zirconium oxide and hydrated yttrium oxide as positively charged agent to prepare positively charged ceramic membrane. These positive ceramic membrane exhibited an excess 99.99% removal rate to M_2 bacteriophages, but the applied coating on the base membrane was easily washed out by water flow when filtration test.

The result from these studies above is promising enough to guarantee further pursuit of charged ceramic membrane

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development. Thus, the goal of this study is to test the practicality of positively charged micro-porous ceramic membrane prepared by dip-coating and thermal decomposition method, and the positively charged ceramic membrane was characterized by SEM and XPS et al. Finally, removing mechanism is also simply explored to promote the removal of titan yellow, which is a small molecule organic dye with negative charge.

Experimental section

Materials

The base membrane chosen was commercial tabular diatomaceous earth-based ceramic membrane (Guangzhou pure easy hi-tech co., LTD, China) which consists of a proprietary mixture of DE and layered silicates. This abundantly available silica-based filter medium exhibits a very low isoelectric point (IEP). In operation of self-assembly device, dye wastewater was forced through the tabular ceramic bore and then flowed out.

As described in the literature[28], yttrium oxide (Y_2O_3) was the potential adsorber to negatively charged organic dyes because of its average higher IEP of 8.8. But due to the instability of commercial colloidal yttria, the material chosen with which to coat on the base membrane in this study was the precursor colloid, which was synthesized by chemical reaction of urea and YCl_3. And subsequently, the precursor colloid was heat-treated to transform into nano-Y_2O_3, which was fixed on the surface of base membrane.

Preparation

The preparation process of positively charged ceramic membrane (as shown in Fig. 1) was mainly divided into two stages. Firstly, the precursor colloid was prepared through chemical reaction of urea (Tianjin wind ship chemical technology co., LTD, China) and yttrium chloride (Shanghai civic chemical technology co., LTD, China) for 2h at 95℃ with the concentration of Y ions 0.01mol/L. During the reaction, YCl_3 solution was slowly dripped into the urea solution with stirring and heating, and precursor colloid with a suspension station was gradually formed. The obtained precursor colloid exhibited an ideal crystal nano-particles state after heat-treated at 700℃ for 1h in air (data presented below).

And then, the base membrane pretreated with HNO_3 was dip-coated in the precursor colloid with a process of immersing for 1h under ultrasound condition and drying 1h at 110℃. This procedure was repeated three times. After dip-coating and drying, the dried membrane with precursor was calcined for 1h in air at 700℃ to fix the coating. The process of heating rate was 2℃/min from 80 to 400℃ and 1℃/min from 400 to 700℃.
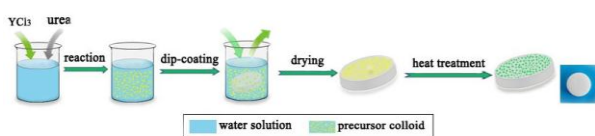

Fig. 1 Schematic illustration of preparation process of positively charged ceramic membrane

Characterization

At the first prepared stage described above, samples were crushed to powders with agate mortar and pestle, and characterized using differential scanning calorimetry-thermo gravimetric analyzer (DSC-TGA; SDFQ600, TA, America), powder X-ray diffraction (XRD; MiniFlex600, Rigaku, Japan), fourier transform infrared spectrometer (FT-IR; Nicolet 6700, Thermo Fisher Scientific, America) with KBr tablet method.

Moreover, the micro-structural analyses of charged ceramic membrane surface were characterized using scanning electron microscopy (SEM; 1530VP, LEO, Germany) in combination with energy dispersive spectroscopy (EDS; Trident, EDAX, America), which enabled elemental analyses of microstructures. Chemical bonds analyses were obtained using X-ray photoelectron spectroscopy (XPS; VG ESCALAB MKⅡ Instrument). The specific surface areas of selected samples were obtained using Brunauer-Emmet-Teller method (BET; 3H-2000PS1, Beishide instrument-S&T Co., Ltd, China). The samples for BET were cut into pieces and degassed 1h under flowing nitrogen at 200℃. The pore size and the porosity of positively charged ceramic membrane were tested by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritic Instrument Corporation, America). Zeta potential measurements were performed using electro-phoretic method (Zetamaster/ Zetasizer Nano ZS, Malvern Instruments, UK) in which the pH shift of dispersion was adjusted with either 0.01mol/L HCl or 0.01mol/L NaOH.

Retention tests were performed with titan yellow, eriochrome black T and methyl violet (Tianjin Research Institute of Fine Chemical Industry, Tianjin, China) aqueous solution by homemade filtering device. And the removal rate was calculated through the absorbance recorded before and after filtration which was measured by ultraviolet spectrophotometer (UV; DR/5000; HACH; America). Titan yellow and eriochrome black T were both small molecule organic dyes with molecule size less than 2nm and negative charge, which made them ideal simulants to represent organic dyes[29]. And methyl violet was a kind of neutral small molecule organic dye.

Results and discussion

Preparation analysis

Charged agent is the key to prepare positively charged micro porous ceramic membrane. And its electrical performance, size and crystal form etc. have a great influence on the performance of charged ceramic membrane. Furthermore, the heat treatment process of the precursor colloid could strongly affect the composition and particle size of charged agent when it is fixed to the base membrane surface [30, 31]. Thus the heat treatment temperature must be kept high enough to promote adhesion of the precursor colloid to the base membrane surface and transform precursor colloid into pure nano-Y_2O_3.

In this experiment, at first the precursor colloid [27] was synthesized via chemical reaction of urea and yttrium chloride (equation 1) [32], and then positively charged ceramic membrane was prepared through dip-coating of base membrane and heat treatment (equation 2 and 3).

$$Y^{3+} +3OH^- +CO_2 \longrightarrow Y(OH)CO_3 \cdot H_2O \quad (1)$$
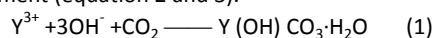
In equation 1, the precipitator OH^- derived from the ionization of ammonium hydroxide which was originated from the thermal decomposition of urea. The precursor colloid could generate slowly

and uniformly because of the tardy decomposition of urea under the heating condition.

$$Y(OH)CO_3 \cdot H_2O \longrightarrow Y(OH)CO_3 + H_2O \quad (2)$$
$$2Y(OH)CO_3 \longrightarrow Y_2O_3 + 2CO_2 + H_2O \quad (3)$$
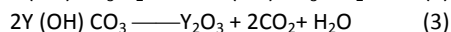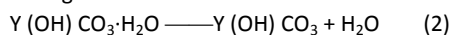
As shown in equation 2 and 3, the precursor colloid transformed to Y_2O_3 on the surface of base membrane through thermal decomposition. During the whole process of reaction, a large number of CO_2 and water vapor were to escape, so the precursor colloid was weight loss by about 38.6% in theory. However, in fact, Fig. 2 showed two distinct stages of weight loss, which were corresponding to equation 1 and 2 respectively. The first weight loss stage was from room temperature to 230℃, in which most adsorbed water escaped from precursor colloid. The second weight loss stage was from 230℃ to 700℃, and there was a sharp endothermic peak in the vicinity of 600 ℃ accompanied by a large number of weight loss, in the meantime the precursor colloid was gradually mineralized to Y_2O_3. Eventually the whole weight loss rate of precursor colloid was approximate 37.53% from room temperature to 700℃, which was consistent well with the theory analysis.

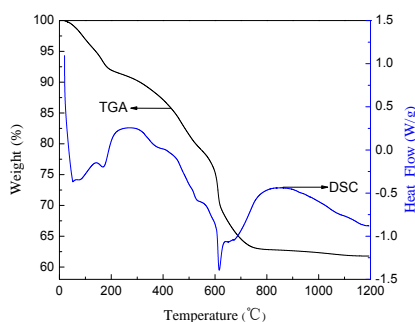Fig. 2 DSC-TGA curves of precursor colloid ramping 10℃/min to 1200℃ in air

Likewise, the XRD data in Fig. 3 also indicated an obvious crystallinity shift from precursor colloid to Y_2O_3 during heat treatment. The precursor colloid was still largely amorphous state after heat treatment at 500 and 600℃, and important crystallinity only developed at higher temperatures at 650℃. When calcined at 700℃, the sample showed fine diffraction peak. And the crystal types of sample at 700℃ were in good agreement with the diffraction pattern derived from standard yttrium oxide powders [28].
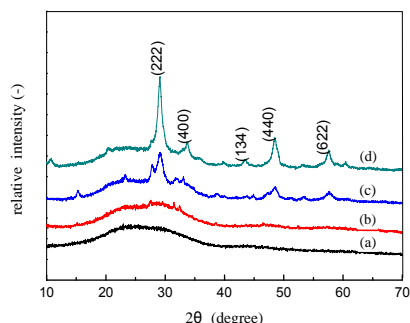

Fig.3 XRD patterns of precursor colloid dried at 110℃ and calcined 1h under air at the specified temperatures of (a) 500℃, (b) 600℃, (c) 650℃ and (d) 700℃

As shown above, samples of the precursor colloid were calcined at various temperatures (1h in air). Among these samples, selected results (110 and 700℃) of FTIR spectra were shown in Fig. 4. It indicated that the significant amounts of C-O group whose wave was about 1457cm^{-1} had disappeared, and the stretching vibration absorption peaks of Y-O about 1529 and 1406cm^{-1} appeared when calcined at 700℃, despite the O-H group in 3433 and 1633cm^{-1} being still presented in material.
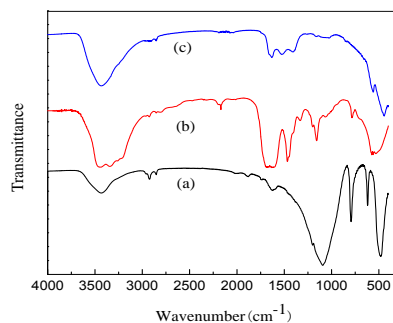

Fig. 4 FTIR spectra of (a) base membrane, precursor colloid (b) dried at 110℃ and (c) calcined at 700℃ 1h in air

These analysis results of DSC-TGA, XRD and FTIR data demonstrated that the optimum heat treatment temperature was 700℃ considering the economic factors and the need of complete conversion of precursor colloid into inorganic Y_2O_3.

Surface analyses

Through the heat treatment process, nano-Y_2O_3 particles were attached to the base membrane surface resulting in an increase of specific surface area, which would contribute to the available for organic dyes to adsorb on. As expected, from the Table 1, the specific surface area of positively charged ceramic membrane with nano-Y_2O_3 coating exhibited an approximately growth rate of 36.72%. Furthermore, there was slightly decrease about both the porosity and the average pore size of charged ceramic membrane, which were 41.09% and 445.3nm, respectively. SEM microstructure images of base membrane and charged ceramic membrane (Fig. 5) explained the reason of increasing specific surface area. Observing Fig. 5d, nano-scale particles of charged agent Y_2O_3 were uniformly distributed on the internal surface of base membrane compared with Fig. 5b. Table 1 and SEM images also confirmed that the electrostatic adsorption of individual particles on charged ceramic membrane surface, not a sieving mechanism, was responsible for the removal of organic dyes from water. Because the charged agent had little impact on the micro-porous structure of charged ceramic membrane, whose pore size was much larger than the organic dyes molecule.

Table 1 Characteristics of base membrane and positively charged ceramic membrane

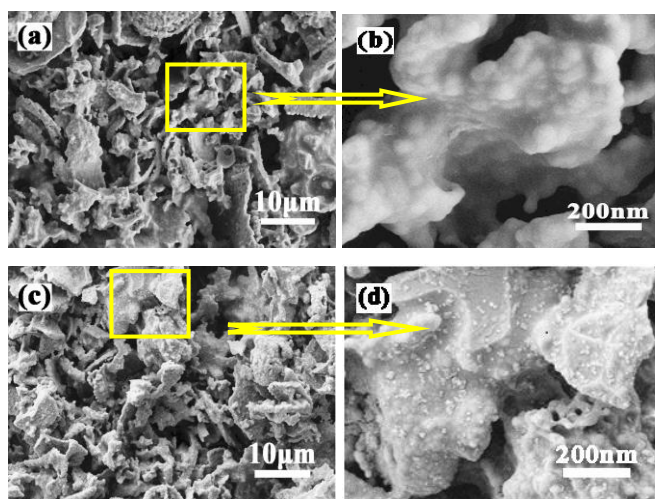| Membrane type	Base membrane	Positively charged ceramic membrane
Diameter	27mm	27mm
Thickness	5mm	5mm
Pore size [a]	989.3nm	445.3nm
Porosity [a]	43.22%	41.09%
Specific surface area [b]	1.28 m^2/g	1.75 m^2/g

[a] Mercury intrusion porosimetry
[b] BET

Fig. 5 SEM images of (a) base membrane, (b) magnification of the selected area of base membrane, (c) charged ceramic membrane and (d) magnification of the selected area of charged ceramic membrane

The further evidence for nano-Y_2O_3 coating effectively screening the base membrane could be obtained from the EDS results and XPS spectra, which gave the composition information of charged ceramic surface. Table 2 clearly showed the elemental analysis of base membrane and charged ceramic membrane. Compared with base membrane, the content of Y element of charged ceramic membrane obviously improved from 1.18 to 25.68wt%, which proved a successful import about Y element on the ceramic membrane surface. Fig. 6 presented the XPS spectra of Y3d and survey spectrum of charged ceramic membrane. The survey spectrum (Fig. 6a) showed the presence of Y, O and Si element, while little quantity of C, Al and Fe element were also detected which was likely and mainly originated from the diatomaceous earth. As for comparison, Fig. 6c displayed that the Y3d peak of pure Y_2O_3 split into double peaks at 157.04 and 158.18eV which were attributed to Y-O bond. And Fig. 6b showed the Y3d peak of charged ceramic membrane surface which was fitted for four peaks of 160.33, 158.48, 156.94 and 153.86eV. This kind of peak shape indicated a considerable change about Y^{3+} bond energy, although 158.48 and 156.94eV should still belong to Y-O bond. However, since 158.48 and 156.94eV peak areas had a greater transformation compared with Y-O peak areas of pure Y_2O_3, it implied a new Y-O bond where the O element originated from base membrane. And

the peak at 160.33eV indicated a combine between Y^{3+} and carbonate (CO_3^{2-}) being from base membrane or pyrolysis product of precursor colloid. Furthermore, Y was quite reactive with SiO_2 and they could react to form Y silicide [33]. Thus the new chemical bond at 153.86eV could be concluded Y-Si bond which formed between Y element and Si element of base membrane [34, 35]. In brief, the shift of these bonds contributed to enhance adhesive force between nano-Y_2O_3 coating and base membrane surface. This was also the reason why Y_2O_3 particles were not easy to fall off from the base membrane surface in the subsequent filtration experiment.

Table 2 EDS results of the surface of base membrane and positively charged ceramic membrane

Membrane	Element /Wt%					
	C	O	Al	Si	Y	Fe
Base membrane	01.25	51.13	02.35	42.40	01.18	01.69
Positively charged ceramic membrane	03.22	40.05	00.45	29.81	25.68	00.79
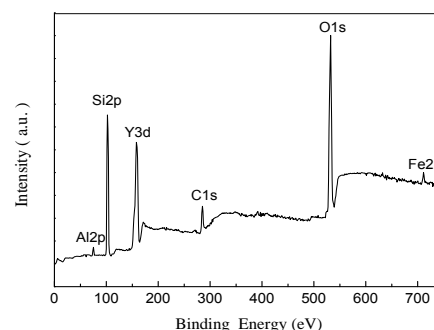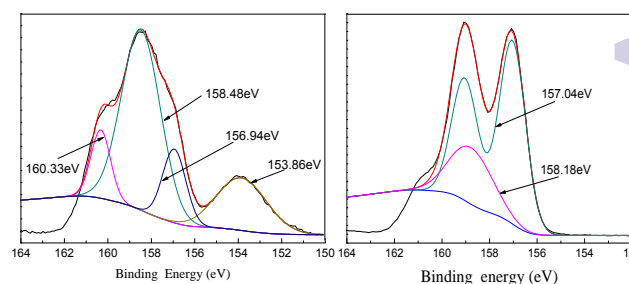
Fig. 6 XPS spectra of the samples: (a) survey spectra of charged ceramic membrane surface, (b) Y3d region of charged ceramic membrane surface and (c) Y3d region of pure Y_2O_3 particles for comparison

Electrical analysis

Electrical property which was normally characterized by zeta potential or isoelectric point (IEP) is a key indicator for charged ceramic membrane. Normally, the material is positively charged in water at lower pH values, and negatively charged at higher pH values than IEP value. Fig. 7 showed the zeta potential change of precursor colloid following various calcining temperatures. It was positive values when calcining temperature was at and above 400℃. And the zeta potential values increased gradually along with the rise of calcining temperature which indicated a significant effect of

electrical property. This was another reason to choose 700℃ as the finally calcined temperature. Furthermore, zeta potentials of base membrane, precursor colloid and charged ceramic membrane following pH values are shown in Fig. 8. As seen from the Fig. 8a, the abundantly available silica-based membrane exhibited a whole negative charge when immersed in water ranging pH from 4 to 10, which was correspond with the literature [36]. And compared with the IEP 8.44 of precursor colloid suspension (Fig. 8b), the IEP 8.18 of charged ceramic membrane (Fig. 8c) was slightly lower, while the both possessed a similar change trend among the same pH range. That is, nano-Y_2O_3 coating onto silica-based membrane resulted in a stronger positive surface charge and a change of isoelectric point to higher pH value. The major reason is that Y_2O_3 surface has much more positive charge sites and is more easily to adsorb H^+ than diatomaceous earth. This confirmed that the nano-Y_2O_3 coating strongly impacted the surface charge properties of composite ceramic membrane.

In brief, these electrostatic results may effectively explain the performance of the charged ceramic membrane when challenged with negative organic dyes in the close to neutral solution. In this condition, the surface of charged ceramic membrane possessed more positive charges, which could effectively remove negatively charged organic dyes smaller than the pore size of ceramic membrane by the interaction of electrostatic adsorption.
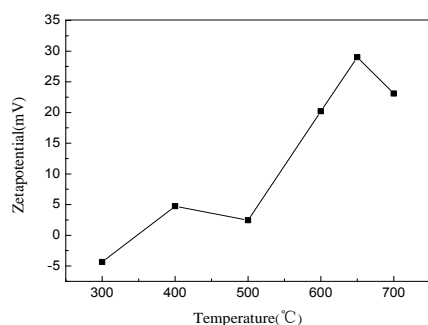

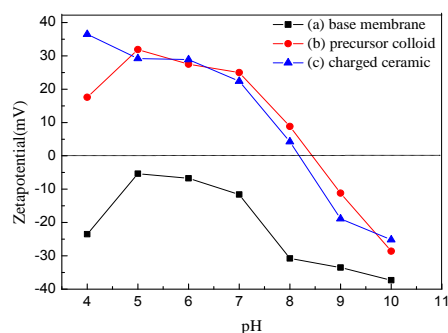Fig. 7 Zeta potentials of precursor colloid at different calcined temperatures

Fig. 8 Zeta potentials of (a) base membrane, (b) precursor colloid and (c) charged ceramic membrane calcined at 700℃

Filtration performance

Filtration performance of ceramic membrane (characteristics of membrane were shown in Table 1) was firstly researched using titan yellow as organic dye pollutant. When operating pressure was

at 0.06MPa, bright-yellow titan yellow solution with 10mg/L was manually pumped through the charged ceramic membrane, and the colour of permeate solution was obvious reduction (Fig. 9a). In addition, the results of UV measurements showed a removal rate of 99.6%, which matched with the performance of Fig. 9b. That is, titan yellow adsorbed on charged ceramic membrane after filtrated, which made the white base membrane shift to yellow one. To further demonstrate the electrical property and practical application of positively charged ceramic membrane, the retention tests of other two organic dyes were also studied. As shown in Table 3, there were higher removal rates for titan yellow and eriochrome black T, which both carried negative charges. However, positively charged ceramic membrane had only 3.2% removal rate for neutral molecule of methyl violet. Furthermore, contrasted with the results above, there was almost no retention to organic dyes for the base membrane. In conclusion, compared with neutral organic dyes, negative organic dyes presented a desirable removal in practical after filtrated by positively charged ceramic membrane.
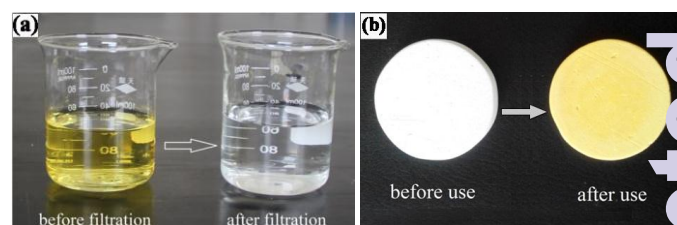

Fig. 9 Photograph of (a) titan yellow aqueous solution before and after filtration respectively, (b) the as-fabricated positively charged ceramic membrane before and after filtrated titan yellow aqueous solution

Table 3 Removal rates of different organic dyes after filtrated by charged ceramic membrane

Membrane	Removal rates of organic dyes /%		
	Titan yellow	Eriochrome black T	Methyl violet
Base membrane	1.6	2.1	2.7
Positively charged ceramic membrane	99.6	98.3	3.2

These results of electrical analysis and filtration performance indicated the separation mechanism for organic dyes removal. When the organic dye molecules and the charged ceramic membrane surface had opposite charges, the retention was excellent, and declined while they both possessed the same charges according to the data in Fig. 8. And Fig. 10 showed the major separation mechanism of positively charged ceramic membrane. When negative organic dyes (such as titan yellow) passed through the bigger micro pores of positively charged ceramic membrane, negative organic dyes were adsorbed on the positive wall of hole, which achieved the purpose to retain the organic dyes from water. During the process, electrostatic adsorption rather than Vander Waals attractive forces and physical sieving played a significant role. These analyses above were consistent well with the micro-porous structure of charged ceramic membrane represented in Fig. 5 and Table 1.
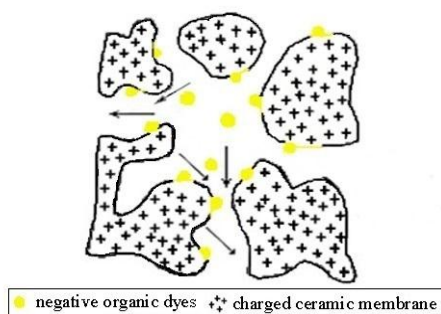
Fig. 10 Schematic diagram of separation mechanism of positively charged ceramic membrane

The membrane fouling is the key factor to affect its use. Based on electrostatic adsorption mechanism, positively charged ceramic membrane reached the adsorption saturation because of the excessive organic dyes after long period operation. This certainly resulted in a decrease of removal rate for negative organic dyes. Therefore, the regeneration of membrane was particularly crucial for the application of charged ceramic membrane. According to the electric properties of charged ceramic membrane in Fig. 8, the polluted membrane was back rinsed with weak alkaline cleaning solution. And the cleaning solution was 1×10^{-4} mol/L NaOH aqueous solution whose pH value was slightly higher than the isoelectric point of charged ceramic membrane. The result showed that the removal rate of organic dyes could be almost fully recovered through back rinse. This was due to that the surface of charged ceramic presented negative charge at higher pH value than IEP (shown in Fig. 8c), which had the same electrical property with organic dyes. Thus under the effects of electrostatic repulsion and water flow, organic dyes desorbed from the charged ceramic membrane and the polluted ceramic membrane was reused again.

Conclusions

Using $YCl_3 \cdot 6H_2O$ as raw material and urea as precipitator, the precursor colloid was synthesized by heating and stirring at 95℃, which was simple and economical. And that it was feasible to prepare positively charged ceramic membrane through dip-coating and thermal decomposition process. These various characterization analyses indicated that the prepared nano-Y_2O_3 coating attached to the base membrane surface irregularly and equably, which had scarcely any influence to the micro porous structure of base membrane. Moreover, the nano-Y_2O_3 coating was not easy to fall off during filtering process because of the formation of chemical bonds between Y element and base membrane, which enhanced the adhesion with both by chemical reaction on charged ceramic membrane surface.

Furthermore, the zeta potential analyses of charged ceramic membrane presented a positive charge between pH 4 and 8 with an IEP 8.18. And filtration performance also showed a 99.6% high removal rate to 10 mg/L titan yellow solution and a 98.3% removal rate to 10 mg/L eriochrome black T solution at 0.06MPa. These indicated that effective adsorption occurred because of the opposite charges between the positively charged ceramic membrane and the negative charge molecules of titan yellow. That means it mainly relies on electrostatic adsorption rather than physical sieving intercept to remove the organic dyes.

From these promising results, using the electropositive nano-Y_2O_3 coating to modify a commercial DE-based membrane is indeed a potential course to develop dye filters working on the electrostatic adsorption principle. However, there is a problem about the current research, mainly the limited adsorption capacity about dyes. The future development of charged ceramic membrane which works on resolving the problem is urgently in need.

Acknowledgements

References

[1] A. Aouni, C. Fersi, B. Cuartas-Uribe, A. Bes-Pia, Alcaina-Mirand and M. Dhahbi, Desalination, 2012, 297, 87-96.

[2] E. Kurt, D.Y. Koseoglu-Imer, N. Dizge, S. Chellam and I. Koyuncu, Desalination, 2012, 302, 24-32.

[3] B. Vander Bruggen, M. Manttan and M. Nystrom, Sep. Purif. Technol., 2008, 63, 251-263.

[4] X. W. Chen, K. G. Khoo, M. W. Kim and L. Hong, ACS Appl. Mater. Inter., 2014, 6, 10220-10230.

[5] J. Kujawa, S. Cerneaux, S. Koter and W. Kujawski, ACS Appl. Mater. Inter., 2014, 6, 10220-10230.

[6] T. V. Gestel, C. Vandecasteele and A. Buekenhoudt, J. Member. Sci., 2002, 207, 73-89.

[7] Y. P. Lei, Y. D. Wang and Y. C. Song, Ceram. Int., 2012, 38, 271-276.

[8] Y. P. Lei, Y. D. Wang, J. G. Xue and Y. C. Song, Composites: Part B, 2013, 51, 254-259.

[9] C. Deng, M. F. Zhu, P. Chen, J. Ma, H. B. Su and T. Tian, Mater. Res. Innov., 2015, 19, 335-338.

[10] N. Kattamuri, J. Shin, B. Kang, J. Lee and C. Sung, J. Member. Sci., 2005, 40, 4531-4539.

[11] Q. Zhang, W. H. Jing and Y. Q. Fan, J. Member. Sci., 2008, 318, 100-106.

[12] J. E. Atwater and J. R. Akse, J. Member. Sci., 2007, 301, 76-84.

[13] W. Peng, I. C. Escobar and D. B. White, J. Member. Sci., 2004, 238, 33-46.

[14] A. Tiraferri and M. Elimelech, J. Member. Sci., 2010, 389, 499-508.

[15] D. W. Lu, T. Zhang and J. Ma, Environ. Sci. Technol., 2015, 49, 4235-4244.

[16] C. Gerba, Adv. Appl. Microbiol., 1984, 30, 133-168.

[17] Y. F. Lin, C. H. Chen, K. L. Tung, T. Y. Wei, S. Y. Lu and K. S. Chang, Chem. Sus. Chem., 2013, 6, 437-442.

[18] Y. F. Lin, C. C. Ko, C. H. Chen, K. L. Tung and K. S. Chang, RSC Advances, 2014, 4, 1456-1459.

[19] V. Vasuhdivan, Appl. Environ. Microbiol., 1991, 57, 2502-2506.

[20] B. Lau, G. Harrington, Anderson, M. Anderson and I. Tejedor, Water Sci. Technol., 2004, 50, 223-228.

[21] S. Farrah, D. Preston, G. Toranzos, M. Girard, G. Erdos and V. Vasuhdivan, Appl. Environ. Microbiol., 1991, 57, 2502-2506.

[22] Y. F. Lin and F. L. Liang, Cryst. Eng. Comm., 2015, 17, 678-685.

[23] Y. F. Lin, J. H. Chen, S. H. Hsu and T. W. Chung, Cryst. Eng. Comm., 2013, 15, 6506-6510.

[24] Y. J. Zhao, W. H. Xing, N. P. Xu, Sep. Sci. Technol., 2005, 42, 117-121.

[25] Y. J. Zhao, W. H. Xing, N. P. Xu, J. Member. Sci., 2005, 254, 81-88.

[26] S. Sachdeva, A. Kumar, J. Appl. Polym. Sci., 2008, 110, 210-227.

[27] M. Wegmann, B. Michen, T. Luxbacher, Water Res., 2008, 42, 1726-1734.

[28] M. Wegmann, B. Michen, T. Graule, J. Euro. Ceram Soc., 2008, 28, 1603-1612.

[29] M. F. Zhu, C. Y. Gong, J. Y. Su and H. M. Chen, Industrial Water Treatment, 2001, 21, 23-25.

[30] Y. P. Lei, Y. D. Wang and Y. C. Song, Mater. Lett., 2012, 71, 91-93.

[31] Y. P. Lei, Y. D. Wang and Y. C. Song, Ceram. Int., 2013, 39, 6847-6851.

[32] L. W. Liao, G. Q. Yin, Y. D. Cui and J. Q. He, Chinese Rare Earths, 2005, 26, 41-45.

[33] Z. M. Wang, J. X. Wu, Q. Fang and J. Y. Zhang, Appl. Surf. Sci., 2005, 464-469.

[34] J. J. Chambers and G. N. Parsons, Appl. Phys. Lett. , 2000, 77, 2385-2387.

[35] T. M. Pan and J. D. Lee, J. Electron. Mater. , 2007, 36, 1395-1403.

[36] C. Oulman, E. Baumann, J. Am. Water Works Assoc., 1964, 56, 915-930.

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