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Investigating forward osmosis process for simultaneous preparation of brown coal slurry and wastewater reclamation

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ABSTRACT

The feasibility of using the forward osmosis (FO) process involving brown coal as draw agent to reclaim clean water from dye wastewater is evaluated in this study. It is found that brown coal not only has enough driving force for drawing water from dye wastewater but also can be reconstituted during the FO process, thus resulting in directly usable coal water slurry after appropriate FO time as an energy source equivalent to fossil oil or feedstock for chemical synthesis via gasification. In the FO process, water-drawing effect can significantly enhance the slurryability of brown coal via weakening the moisture holding capacity, decreasing the porosity and achieving the favorable particle size distribution due to the improved grindability. A possible tri-factor water-drawing and reconstitution mechanism of brown coal during the FO process is proposed to explain the effects of FO process on the properties of brown coal. The results indicate that the FO process promises to be a low-cost green process for simultaneous wastewater treatment and preparation of coal water slurry for environmental protection and energy production.

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1. Introduction

Because of the fast growth of crude oil consumption and rapid decline in its reserves, the search for a substitute for crude oil has become an urgent task. Coal water slurry (CWS) which consists of fine coal particles suspended in water makes use of coal equivalent to the use of crude oil not only as a fuel but also as a valuable chemical feedstock via gasification for a variety of chemical processes and syntheses [1–4]. Consequently, CWS is a clean, cheaper and promising alternative energy resource for fossil oil [5–7].

The desirable features of CWS include high coal loading, low viscosity, good stability, good rheological behavior, and high heating value. The characteristics of coal are the key factors that determine the properties of CWS, which is usually depicted as slurryability of coal (concentration of slurry that gives an apparent viscosity at 1000 mPa s at a shear rate of 100 s^{-1}). A valuable coal water slurry should consist of no less than 60 wt.% coal, no more than 40 wt.% water and sometimes about 1 wt.% chemical additive permitted to improve the dispersion and decrease the viscosity of the CWS according to the Chinese Standard GB/T18856.2 to achieve a metastable spatial structure based on the balance of interactions between coal, additive and water, and exhibits a pseudoplastic behavior with a viscosity no higher than 1200 mPa s at a shear rate of 100 s^{-1} [1,8].

In general, black coal is used for CWS. But with black coal becoming scarcer and more expensive, brown coal, a kind of low rank coal, is a promising choice for CWS due to its worldwide abundance, underutilization and much lower cost [2]. However, there are more hydrophilic oxygen-containing functional groups in brown coal compared with black coal, which results in more inherent moisture in brown coal. More inherent water is detrimental to slurryability because the free water as flow medium will be less at a fixed coal loading of CWS and then increase the viscosity of CWS and thus decrease the slurryability [9]. For example, slurryability of brown coals is generally less than 50 wt.% in China, which is lower than that needed for industrial application (no less than 60 wt.%). Thus, the inherent moisture of brown coal needs to be removed or liberated as lubricant between particles for improvement of slurryability. Whereas, the inherent moisture in coal is hard to be liberated by conventional mechanical grinding method, which is caused by coal's being much more resistant to pressing stresses than stretching stresses [10,11]. Namely, the particle sizes of brown coal via traditional mechanical grinding are not fine enough to liberate inherent moisture efficiently. Some other methods such as evaporative method, hydrothermal dewatering and microwave irradiation treatment to remove inherent moisture, reconstitute and upgrade brown coal were studied with obvious improvement of the slurryability of brown coal [1,12–16]. Nevertheless, energy-intensive or cleaning costs of the effluents are the challenges of the methods.

From another perspective, considering the high water-absorption propensity and swelling into a gel on wetting [17,18], brown coal is somewhat similar to the hydrogels used as draw agents in the forward

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osmosis (FO) procedure in our previous work [19–26]. Thus, it could be anticipated that brown coal can also draw water from feed solution by swelling pressure. Moreover, the dissociation of the acidic groups in the brown coal leads to the formation of an electric double layer [27, 28]. Inside the pores and crevices of brown coal the electric double layers overlap and reduce the chemical potential of water, creating an osmotic pressure [29]. Finally, soluble inorganic and organic matters of brown coal would further contribute to osmotic pressure of the coal water suspension system [9,30]. As a result, brown coal should be a satisfactory draw agent in the FO procedure.

In the present work, a FO process with brown coal particles as draw agent and dye wastewater as feed solution was designed intending to achieve liberation of inherent moisture and improvement of grindability of brown coal via fully wetting and soaking during the slow, mild and low energy-consumption FO procedure. If the concept is feasible, the resulting brown coal water mixture after appropriate FO time (according to no more than 40 wt.% water content in CWS) can be directly used as CWS after addition of a small amount of additive and following a short time of blending while avoiding recovery of the draw agent. Since a major challenge of low-cost and effective recovery of the draw agent still remains in most FO processes, without the need to recover the draw agent will be particularly attractive [31]. Additionally, the paired dye wastewater, one of the largest amounts of industrial effluents which is relatively difficult to treat, was chosen as the feed solution in the proposed FO procedure which makes water reuse and wastewater minimization together with directly usable CWS fulfilled simultaneously. This will further decrease the cost of the process. Therefore, the success of the proposed procedure promises to be a low-cost green process for simultaneous wastewater treatment and preparation of coal water slurry for environmental protection and energy production.

The simultaneous preparation of CWS and wastewater reclamation using FO technology is schematically illustrated in Fig. 1. In this work, two typical Chinese brown coals are chosen as draw agents and methylene blue as a model dye in the FO experiments. The possible water-drawing mechanism of brown coal and the effects of FO process on the properties of brown coal are discussed.

2. Materials and methods

2.1. Chemicals and materials

Methylene blue was purchased from Sigma-Aldrich and used as received. Two types of Chinese brown coal samples, HongMiao (HM) and BaiYinHua (BYH), were collected from Inner Mongolia, the largest brown coal production place in China. The proximate and ultimate analyses of the raw brown coals are shown in Table 1. All air dried brown coal samples were first crushed in a jaw crusher to below 10 mm in particle size. Then the crushed coals were ground in a ball mill to obtain the coal powders. The coal powders were screened through a 100-mesh screen (150 μm pore size) for use as draw agent to extract clean water from dye wastewater and produce brown coal water slurry. Sodium naphthalene sulfonate formaldehyde condensate (Anyang Shuanghuan Auxiliary Co., Ltd, China) was used as a dispersant. Deionized (DI) water from Milli-Q (Millipore) system was used to prepare 2000 ppm NaCl solution as feed solution in comparison with methylene blue solution. The FO membrane used in this work was kindly provided by the Hydration Technologies Inc. (Albany, OR). The membrane characteristics have been reported in several previous studies [32–34].

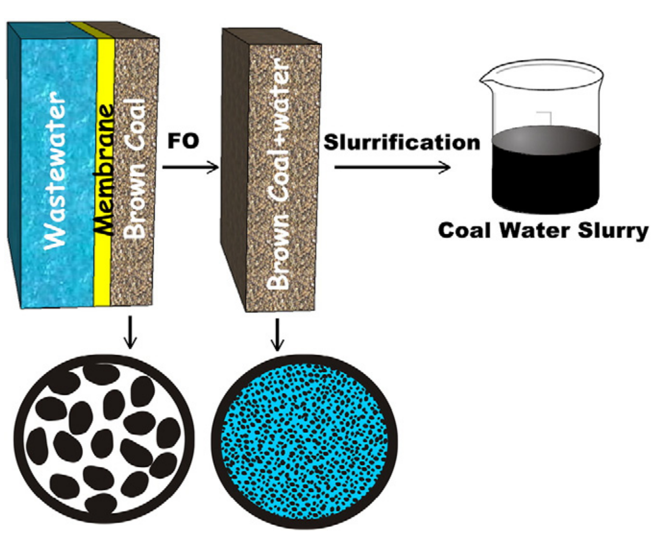

Fig. 1. Schematic representation of brown coal driven FO process for simultaneous wastewater reclamation and preparation of coal water slurry.

2.2. FO procedure

The membrane was soaked in DI water for 30 min before use. The two kinds of air dried brown coals HM and BYH were tested as draw agents. The coal samples obtained after the FO process were denoted as FO-HM and FO-BYH, respectively. 1 g of brown coal sample was placed on the porous support layer of FO membrane with an effective area of 1.33×10^{-4} m^2, while the feed solution was placed on the active side (skin layer) of the membrane under magnetic stirring. The feed solution in all of the FO processes in this work is 50 mL of 80 ppm methylene blue solution except the one with 2000 ppm NaCl solution as the feed solution to test FO performance with brown coal as draw agent. As the water permeated through the membrane from the feed solution into the brown coal draw agent, the mass of the draw agent increased. The mass of water permeated was determined by measuring the mass increase of brown coal draw agent using a digital balance at a given time interval. The volume of the water permeated was calculated from its mass increase. Water flux, F, in L/(m^2 h) (or LMH), was determined by

$$F = V/(A \times t)$$

where V is the volume of water permeated through the membrane (L), which is based on the mass increase of the swollen brown coal draw agent measured over a given period of time in the FO process, t (h); A is the effective area of FO membrane (m^2) (1.33×10^{-4} m^2) used in the permeation cell. All FO experiments were carried out at room temperature.

2.3. Methylene blue and NaCl concentration analyses

The aqueous solutions of methylene blue exhibit maximum absorbance at 665 nm. Therefore, the concentration of methylene blue was determined by UV–vis spectrophotometry with a TU-1901 double-beam UV–vis spectrophotometer (Purkinje General, Beijing, China). The concentration of NaCl aqueous solution was measured by using an electric conductivity meter (Multi 3430, TetraCon 925, WTW, Germany).

Table 1
Proximate and ultimate analyses of coal samples.

Samples	Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
	M_{ad}[a]	A_d[a]	V_{daf}[a]	C	H	N	O	S
HM	15.89	18.23	42.59	70.96	4.47	0.88	20.42	3.27
BYH	11.20	14.32	41.23	73.00	4.82	1.47	20.11	0.60

[a] M_{ad} — moisture, air dry basis; A_d — ash, dry basis; V_{daf} — volatile, dry and ash free basis.

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