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Marine residual fuel sorption and desorption kinetics by alkali treated rice husks

Alireza Bazargan · Chi Wai Hui · Gordon Mckay

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Abstract An oil absorbent material has been produced from waste biomass with an alkali treatment process. The simple yet effective process is carried out on the agricultural biowaste at 90 °C and ambient pressure. The present manuscript considers the transient behavior of the sorbent during application, in particular the oil sorption and desorption profiles with time. The kinetics data shows that this lignocellulosic sorbent reaches saturation in <2 min of contact with the spilled oily liquid (marine residual fuel). The results showed that the second order kinetic model accurately correlates with the experimental data. The rice-husk product is shown to significantly outperform a commercially available sorbent in terms of uptake capacity (more than 18 g/g by the husk sorbent compared to 10 g/g by Corksorb). However in gravimetric desorption experiments, the as-prepared husk exhibited less favorable behavior than the commercial competitor.

Keywords Rice husk/hull/chaff · Oil spill remediation · RMG380 marine diesel · Retention profile · Lignocellulose

Introduction

Rice husks are the protective outer layer of the edible rice grain. The husk, also known as hull or chaff is not edible and needs to be removed in the milling process. The life cycle of a rice plant takes no more than a year to complete and hence millions of tons of rice husks are discarded globally each year. From the 700 million tons of rice produced annually across the globe, about 20 %, corresponding to 140 million tons ends up as husk waste (Abbas and Ansumali 2010; Kumagai et al. 2007; Sweeney and McCouch 2007). There are various studies attempting to favourably utilize rice husks. Products such as porous silica (Tadjarodi et al. 2012), adosrbents (Mehdinia et al. 2013; Safa and Bhatti 2011), cellulose and nanocrystals (Johar et al. 2012), catalysts (Shirini et al. 2013, 2012), ethanol (Singh et al. 2014), electricity (Shackley et al. 2012), concrete (Zain et al. 2011), and particle boards (Ajiwe et al. 1998; Rozman et al. 2005), have been obtained. Nonetheless, the majority of the rice husks are not

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A. Bazargan (✉) · C. W. Hui · G. Mckay (✉)
Department of Chemical and Biomolecular Engineering,
Hong Kong University of Science and Technology,
Clearwater Bay, Hong Kong
e-mail: bazargan@ust.hk

G. Mckay
e-mail: kemckayg@ust.hk

Present Address:
A. Bazargan
Department of Chemical Engineering and Biotechnology,
New Museums Site, University of Cambridge,
Pembroke Street, Cambridge, UK

utilized and are commonly burned in open fields. Rice husks have relatively lower energy content compared to other biowastes perhaps due to their high silica ash content which makes their use as solid fuel less favorable (Houston 1972). Hence there is a need to find other applications for this abundant agricultural waste.

Spillage of petroleum products is a serious environmental threat needing extensive clean up and remediation operations. The best way to combat the negative effects of oil spills would be to contain and/or clean up the spill before it has the chance to spread. Generally mechanical, chemical, physico-chemical, and biological methods can be used for cleaning and containing oil spills. The use of dispersants, absorbents, solidifiers, booms and skimmers are commonplace (Adebajo et al. 2003; Deymeh et al. 2012; Seyedi et al. 2013; Wahi et al. 2013). Simulations and studies in regions prone to oil spills such as the Persian Gulf have shown that the oil slick thickness decreases quickly during the first 5–6 h after the spill, meaning that the liquid spreads rapidly during the first few hours (Ghiassi et al. 2012). The detrimental effects of oil spills go beyond what is visually seen. Exposure to petroleum hydrocarbons in the Persian Gulf has been shown to genetically alter the microbial and enzymatic activities in the natural microbial community in oil-contaminated sediments (Hassanshahian et al. 2010). Laboratory testing programs aimed at evaluating the effects of oil spills in the Persian Gulf for coastal engineering purposes have found that clay and sandy soils showed a decrease in strength, permeability, maximum dry density, optimum water content and Atterberg limits due to exposure to crude oil (Khamehchiyan et al. 2007). Hence it is important to adequately remediate oil spill areas as fast as possible.

To date, several studies have evaluated the possibility of using rice husks for oil spill cleanup. It should be noted that nearly all these studies require high temperatures above 500 °C to produce silica ash from the rice husks before they can be employed for oil sorption (Angelova et al. 2012, 2011; Dimitrov et al. 2012; Kenes et al. 2012; Kumagai et al. 2007; Thompson et al. 2010; Uzunov et al. 2012; Vlaev et al. 2011). A recently published study by our research group has introduced a method for producing the highest capacity rice-husk sorbents at low temperatures and pressures (Bazargan et al. 2014). Herein, a follow-up study is presented for further elaboration of the findings. Specifically, the previous introductory study is built upon as follows:

1. Additional characterization of the sorbent including SEM, XRD, and a contact angle measurement video (supplementary material) is presented.
2. Evaluation (and modeling) of the sorption profile versus time is carried out; i.e., how much contact time is needed for the sorbent to absorb the oil?
3. Evaluation (and modeling) of the desorption profile versus time is presented; i.e., how does the sorbent lose the oil it has uptaken?
4. The as-prepared rice husk sorbent is compared with an award winning commercial sorbent: Corksorb.

Materials and methods

Materials

Rice husks were obtained through Peako Biomass Energy Ltd., Hong Kong. They were collected in mainland China, were golden brown, and <1 cm long. Marine residual fuel RMG380 was provided by Gulf Oil Marine Ltd. and was used as the petroleum sorbate. The standard specifications of the liquid provided by the supplier indicated that the viscosity at 50 °C and density at 15 °C do not exceed 380 mm^2/s and 991 kg/m^3 respectively.

Corksorb (http://www.corksorb.com) which is the name of an award-winning sorbent made from the residues of cork tree processes by Amorim Environmental Systems has been kindly donated to the research group by the Portugal-based Corksorb Ltd. company.

Sample preparation

The sample preparation is similar to that of our previous work (Bazargan et al. 2014). In short, prior to any treatment or experimentation the rice husks were sieved by a stainless steel net to remove powders and broken pieces. Subsequently, the husks were subjected to alkali treatment at temperatures of 20–90 °C and durations of 2–48 h. After the treatment the as-prepared husks were cooled to room temperature, washed to neutrality, dried and collected. All data presented in this manuscript are for the optimum sample treated at 90 °C for 24 h with 1 M NaOH.

Characterization

A JEOL 6300F scanning electron microscope (SEM) with energy dispersive analysis was used for viewing the surface of the powders. Energy dispersive X-ray analysis (EDX) was used to ascertain that the sodium had been adequately removed from the samples in the post-synthesis washing step. Contact angle measurements were carried out with a contact angle goniometer (Model 100-00, Rame-hart Inc.) coupled with a high definition Nikon camera. X-ray diffraction patterns were obtained with a Philips PW1825 diffractometer with Cu Kα radiation (40 kV and 50 mA). The angular scanning was performed in the range of $10° < 2\theta < 40°$ at a rate of $2° \mathrm{min}^{-1}$.

Uptake capacity measurement

For the oil uptake experiments 0.2 g of the as-prepared husk was submerged into RMG380 using a stainless steel net. After the desired contact time was fulfilled, the net was removed and allowed to drain. Experimental runs were also carried out to measure the amount of RMG380 uptaken by the empty net. The final sorption capacity of the sorbent can be calculated by Eq. (1) as follows:

$$q = \frac{M_T - M_N - M_H}{M_H} \tag{1}$$

where q is the sorption capacity of the as-prepared husk (grams RMG380 taken per gram of sorbent), M_T is the total measured weight of the oily net and sorbent after the sorption, M_N is the weight of the oily net, and M_H is the dry weight of the as-prepared husk used as the sorbent. The same experimental procedure was also repeated for water sorption in order to distinguish the relative hydrophobicity of the samples.

Uptake kinetics modeling

In order to further understand the sorption kinetics of the marine residual fuel by the as-prepared husk sorbent, three proposed models were used. The pseudo-first order, the pseudo-second order, and the intra-particle diffusion models were chosen (Bastani et al. 2006). The pseudo-first order model is defined as follows:

$$\frac{dq_t}{dt} = k_1(q_{e1} - q_t) \tag{2}$$

In which q_t is the sorption capacity at time t, q_{e1} is the equilibrium sorption capacity, and k_1 is the rate constant of the pseudo-first order model. By applying the initial condition of $q_t = 0$ at $t = 0$, the pseudo-first order model can be integrated to become:

$$\ln(q_{e1} - q_t) = \ln(q_{e1}) - k_1 t \tag{3}$$

The uptake kinetics were also modeled using the pseudo-second order model proposed by Ho and McKay (Gui et al. 2011; Ho and McKay 1999):

$$\frac{dq_t}{dt} = k_2(q_{e2} - q_t)^2 \tag{4}$$

Which after the implementation of the initial condition of $q_t = 0$ at $t = 0$ and integration becomes:

$$\frac{1}{q_{e2} - q_t} = \frac{1}{q_{e2}} + k_2 t \tag{5}$$

Which can be rearranged as (Ho and McKay 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \tag{6}$$

where q_t is the sorption capacity [g/g] at time t, q_{e2} is the saturated sorption capacity, t is the contact time, and k_2 is the sorption rate constant. The sorption constant is dependent on the properties of the liquid such as viscosity and surface tension as well as the pore structure of the sorbent. The model parameters can be found by plotting t/q_t against t.

Finally, the intra-particle diffusion model is defined as follows:

$$q_t = k_i t^{0.5} + C \tag{7}$$

in which k_i is the intra-particle diffusion rate constant [$\mathrm{g/g\ min}^{0.5}$] that can be obtained from the slope of the q_t plot versus $t^{0.5}$; If the plot of q_t against $t^{0.5}$ is linear and passes through the origin, then it can be concluded that the intra-particle diffusion is the only rate limiting parameter controlling the process. Otherwise, other mechanisms are involved. Values for C provide an idea about the thickness of the boundary layer. Higher C values are indicative of larger external resistance.

Table 1 Models used for desorption retention profile

Model name	Equation	References
Lewis model	$q_t = q_0 \exp(-k_L t)$	O'Callaghan et al. (1971)
Page model	$q_t = q_0 \exp(-k_P t^n)$	Zhang and Litchfield (1991)
Two-term model	$q_t = q_0(a \cdot \exp(-k_{T1} t) + b \cdot \exp(-k_{T2} t))$	Rahman et al. (1997)

The intra-particle diffusion plots can also exhibit multi-linearity indicating more than one step (McKay 1983; Abdel Wahab 2007). The first, sharper step is representative of the external surface adsorption also known as the instantaneous adsorption stage. The second portion is where the intraparticle diffusion is rate-controlled. The third stage (which will not be witnesses herein) is indicative of where the diffusion slows down due to extremely low solute concentrations.

Retention modeling

The retention of the oil by the sorbent has been modeled by using three different equations as seen in Table 1 (Lewis model, Page model, and two-term model). These models were initially developed to model the retention of moisture by solids in drying experiments (Gunhan et al. 2005). Here, the models have been slightly modified in order to be used for the liquid desorption profile.

Where q_t [g/g] is the sorption capacity at time t, and a, b, and n are dimensionless drying model coefficients. Drying rate constants are represented by k_L, k_P, k_{T1}, and k_{T2}.

Results and discussion

Alkali treatment of rice husk can lead to endwise degradation also known as cellulose peeling (Li et al. 2007). Alkali treatment also disrupts the hydrogen bonds of cellulose and increases the surface roughness of the sample. The wax and oils covering the external parts of the husk are also removed (Li et al. 2007). Alkali treatment breaks the cell wall by dissolving hemicellulose and silica (Juliano 1985). The previous study of our group showed that the most influential factor in the high sorption capacities of the as-prepared rice husk sorbent is its low bulk density. Large void spaces existing within the lignocellulosic fiber structure that are a result of alkali attack on the husk structure result in the low bulk density (Bazargan et al. 2014). Here, additional characterization is provided for better understanding of the sorbent.

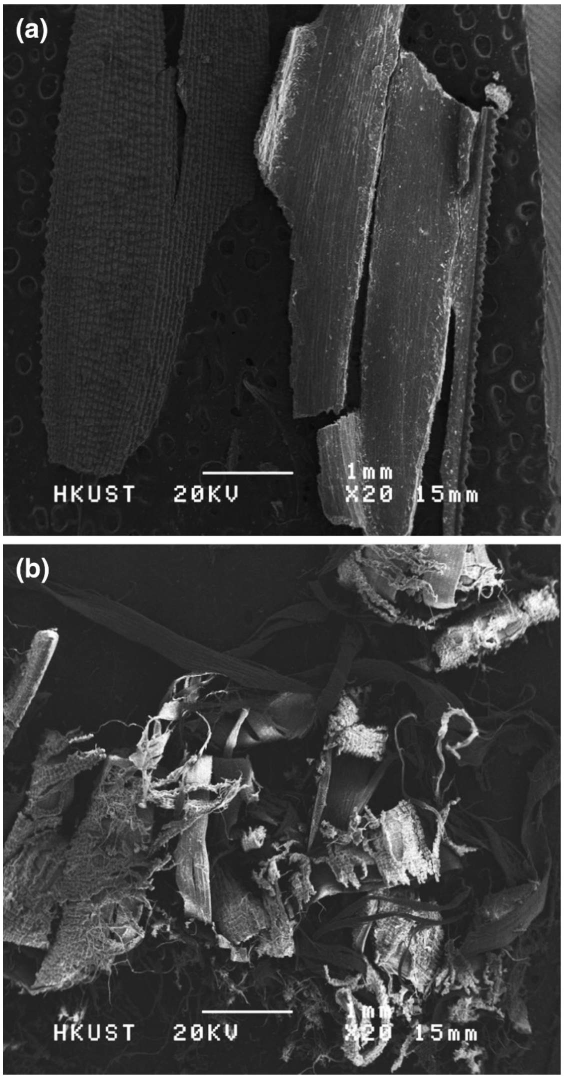
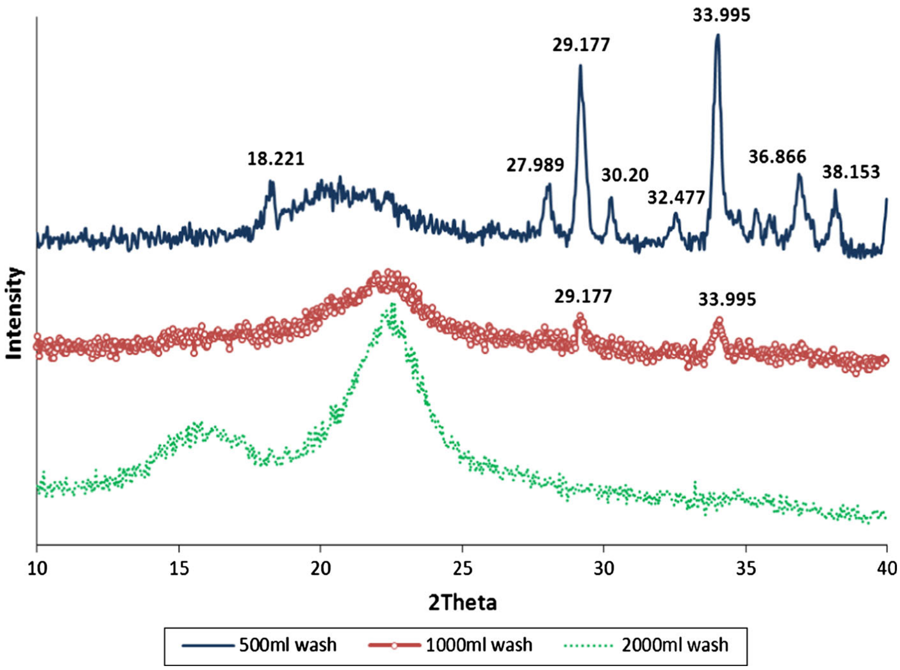


Fig. 1 Scanning electron microscope images of the husks (**a**) 20 times magnification before treatment, and (**b**) 20 times magnification after alkali treatment

Fig. 2 XRD patterns for husks with various amounts of washing



Characterization

Various analyses have been performed to better understand the nature of the sorbent. Most notably, the disruption of the rice husk structure was visible in images obtained from the SEM. As can be seen in Fig. 1, the rice husk structure is broken down as it undergoes alkali treatment. As expected, the fibers become separated and the surface becomes coarser. The process is similar to that used in the pulp and paper industry for mercerization of wood. The temperature and pressure employed here are noticeably less severe than industrial mercerization processes.

FTIR results confirmed that the alkali treatment has increased the rice husk hydrophilicity, predominantly due to the large increase in the bands associated with hydroxyl groups (Bazargan et al. 2014). The high RMG380 uptake capacity of the as-prepared husks is speculated to be due to its ability to swell. Prior to alkali treatment, the husks are stiff and do not swell when in contact with liquid. However the alkali treatment breaks down the rigid structure of the husks and makes them more susceptible to swelling. Contact angle measurement tests were attempted in order to assess the hydrophobicity of the samples. However after the alkali treatment, the husk became so susceptible to swelling that measuring contact angles were hindered. During the measurement process, the as-prepared husk soaked the liquid drop immediately upon contact and hence made contact angle measurements impossible. A video of the test is available as supplementary material of this manuscript which clearly shows the extraordinary ability of the husk sorbent to swell upon contact with the liquid.

XRD patterns were obtained to distinguish the effects of alkali treatment. In addition to confirming that no conversion of Cellulose I to Cellulose II had taken place due to the treatment, the patterns showed that adequate washing was required to remove the NaOH and sodium compounds formed on the husk. Figure 2 shows that washing 4 g of the treated husks with 500 ml of deionized water was not at all adequate to remove the sodium. Even 1,000 ml of water did not remove the sodium completely. SEM-EDX images confirmed that the sodium was effectively removed when approximately 2,000 ml of water was employed.

Sorption profile

The duration of time that the sorbent and sorbate are in contact is known as the contact time. A sorbent which can take up large amounts of oil within the shortest

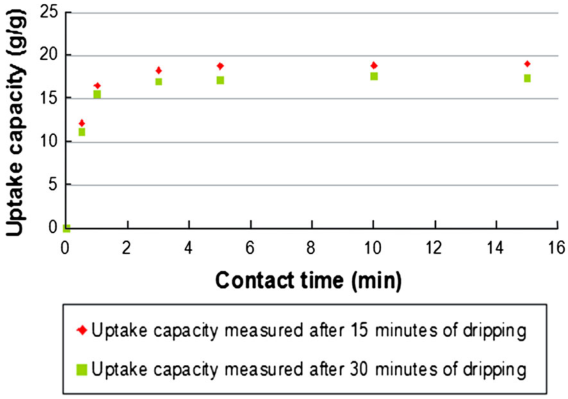


Fig. 3 Sorption profiles of the as-prepared rice husk sorbent for RMG380

contact time is desirable. In order to evaluate the uptake kinetics, the samples were allowed to be in contact with the oil for different durations. The sorption capacity was then measured for different contact times and sorption profiles shown in Fig. 3 were obtained. The results show that the uptake capacity does not increase considerably when more than 3 min of contact time is allowed; i.e. the sorbent reaches equilibrium after 3 min and is saturated with RMG380. It is noteworthy that the amount of time the sorbent is allowed to drain before measuring the sorption capacity is of importance. Figure 3 shows the sorption profiles for samples which have been left to drain for 15 and 30 min. Observably, the shorter the drainage time, the higher the measured uptake capacity became. This is because in the initial several minutes of drainage the system has not yet lost all of the sorbate due to gravimetric desorption. The values in Fig. 3 would be much higher if the drainage period was further shortened or avoided altogether. For example the uptake capacity was measured at values near 40 g of RMG380 per gram of as-prepared husk when the sorbent was not allowed to drain and weighed immediately after removal from the bath. This is because the oil that is loosely connected to the outer surfaces of the husk would also (inaccurately) be counted as part of the uptake capacity. Although some studies neglect to include an adequate drainage period (Sun et al. 2004) it seems that by including ample drainage more accurate results mimicking the real-world application of the sorbents can be obtained.

Table 2 Model parameters of the employed sorption kinetic models

Model name	Parameters	R^2
Pseudo-first order	$q_{e1} = 18.88$ (g/g), $k_1 = 0.94$ (min^{-1})	0.989
Pseudo-second order	$q_{e2} = 19.27$ (g/g), $k_2 = 0.35$ (g/g.min)	0.999
Intraparticle diffusion	$k_i = 1.67$ (g/g $\text{min}^{0.5}$), $C = 13.77$ (g/g)	0.593

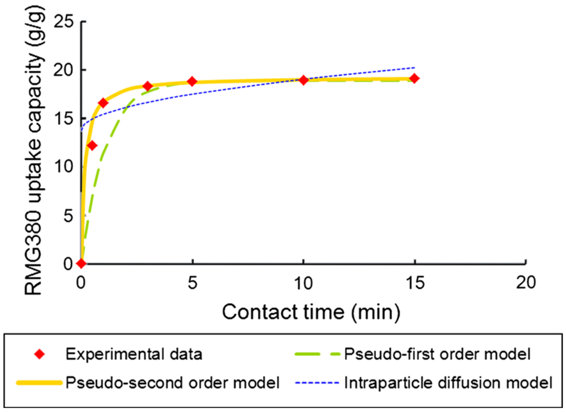


Fig. 4 Agreement of various kinetic models to the sorption data

The ASTM F726 standard for sorbent performance testing suggests a draining period 30 s or 2 min depending on the sorbate viscosity. Interestingly nearly all previous research groups examining rice husk sorbents have ignored the ASTM F726 guidelines. Kumagai et al. (2007) allowed 5 min of drainage. Kenes et al. (2012), Uzunov et al. (2012), and Angelova et al. (2011, 2012) have allowed 10 min of drainage. Meanwhile, Vlaev et al. (2011), Thompson et al. (2010), and Dimitrov et al. (2012) have neglected any information regarding the sample drainage period and have simply mentioned that the samples were strained before being weighed. Herein we have obtained the highest sorption capacities for rice-husk-derived materials even though we have allowed for longer drainage periods compared to the aforementioned studies.

In order to model the sorption kinetics of the sorbent, the pseudo-first order, the pseudo-second order, and intra-particle diffusion models were used. In order to avoid redundancy, the uptake capacity data for 15 min of dripping was used. Table 2 shows the model parameters and R^2 values obtained indicating that the pseudo-second order model showed the best fit

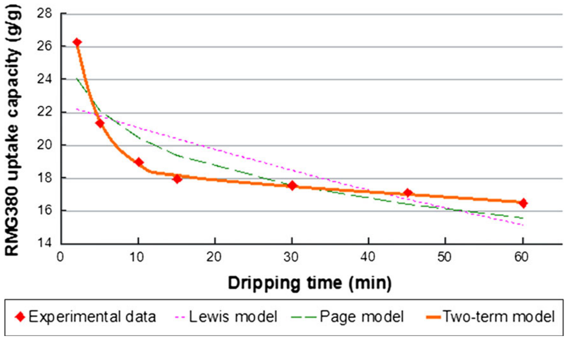


Fig. 5 Desorption profile of RMG380 from the rice husk sorbent due to gravitational forces

Table 3 Model parameters of the employed desorption models

Model name	Calculated parameters	R^2
Lewis model	$q_0 = 22.5$ (g/g), $k_L = 0.0066$	0.58
Page model	$q_0 = 37$ (g/g), $k_P = 0.01$, $n = 0.22$	0.85
Two-term model	$q_0 = 25.7$ (g/g), $a = 0.72$, $k_{T1} = 0.57$, $b = 0.002$, $k_{T2} = 31$	0.99

for the system. Multi-linearity was observed for the intraparticle diffusion model. Figure 4 visually confirms the better fit of the pseudo second order model. This suggests that chemisorption is the rate-limiting step with valency forces through exchange of electrons between the sorbate and the sorbent (Yaneva and Koumanova 2006).

The "half-time", t_h, which is defined as the contact time needed by the sorbent to reach half of the saturation sorption capacity can be used to characterize the sorption rate. A low t_h indicates fast uptake (Gui et al. 2011). Here, the corresponding t_h is calculated as approximately 15 s meaning that it takes only 15 s of contact between the as-prepared husk and the RMG380 for the sorbent to uptake 50 % of its maximum capacity. The short half-time is further proof of the ability of the sorbent to swell quickly upon contact with the liquid.

Desorption profile

As mentioned before, after the sorbent has been in contact with the sorbate, it is removed from the liquid bath and allowed to drain. The sorbent retains the liquid by capillary forces which build liquid bridges overcoming the gravitational pull. If these capillary forces are not strong enough to hold the liquid, the oil is lost due to dripping. As evident from Fig. 5, the loss of oil is fairly quick in the initial moments of the drainage. This is due to loss of the oil on the external surfaces and larger macropores of the sorbent. After this fraction of the oil is lost, the remaining oil which is kept by stronger forces shows more resistance towards dripping. At some point in time, the desorption profile begins to steady out reaching a plateau. At the plateau, some sorbate still remains within the sorbent. This fraction is kept by forces stronger than the gravitational pull. Hence this fraction of the sorbate will remain within the sorbent unless it is forced out by other means such as physical compression of the husk. The general trend of the liquid loss from the as-prepared rice husk sorbent is in agreement with other sorbents reported in the literature (Wei et al. 2003).

Figure 5 demonstrates the models used to fit the experimental data. The R^2 value for each model as well as the model parameters are presented in Table 3. Evidently, the two-term model is in better agreement for the sorbent-sorbate system.

Comparison with corksorb

The experiments carried out for the rice husk sorbent were duplicated by the commercial Corksorb sorbent for comparison. The desorption profile of the liquid by the as-prepared husk in this study is compared to Corksorb in Fig. 6. The experiments showed the superior final uptake capacity of the husk sorbent compared to the award-winning commercial sorbent. The superiority of the husk sorbent is attributed to its ability to swell as opposed to the Corksorb sample which is rigid. However, Corksorb exhibited a better retention profile after the removal of the sorbent from the liquid bath. This is attributed to the hydrophobic nature of the Corksorb. Unlike the husk sorbent which is hydrophilic, Corksorb benefits from oleophilic properties.

In order to investigate the hydrophobicity/hydrophilicity of the sorbents the water uptake capacity of each sample was separately tested. Figure 7 shows that Corksorb has considerably less water uptake compared to the husk sorbent and untreated husk.

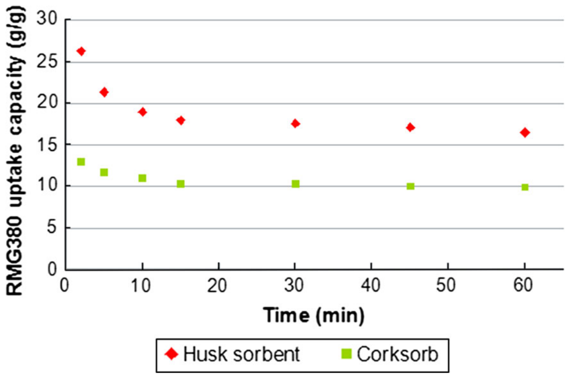


Fig. 6 Retention of RMG380 by the as-prepared husk sorbent compared with Corksorb (commercial sorbent)

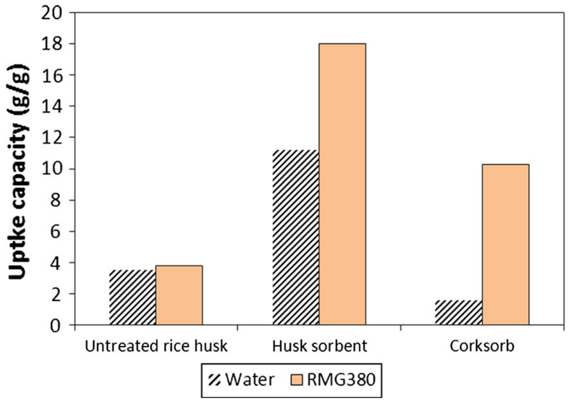


Fig. 7 Comparison of RMG380 marine residual fuel and water uptakes

From Figs. 6 and 7 it can be concluded that the ability of the sorbent to swell is an important parameter leading to high sorption capacities. However, if the sorbent does not possess oleophilic properties, much of the oil will be lost due to dripping. On the other hand, if a sorbent is oleophilic (such as Corksorb), it has good resistance against gravitational forces and can retain a large fraction of the oil it has uptaken. Hence, the combination of both oleophilicity and the ability of the sorbent to swell should be ideally sought in order to benefit from a good retention capability against gravitational force as well as high uptake capacities. In future studies, if the full potential of the as-prepared husk sorbent is to be realized, the sorbent could be subjected to further chemical treatment such as with acetic anhydride and/or fatty acids to increase its oleophilicity (Cunha and Gandini 2010; Peydecastaing et al. 2011; Vaca-Garcia and Borredon 1999).

Conclusion

With alkali treatment at modest temperatures, rice husk waste has been modified to form a sorbent which can be used to combat oil spills. Double-digit sorption capacities are consistently obtained by the developed husk sorbents. The kinetic studies showed that in nearly 15 s, the rice-husk sorbent could absorb 50 % of its final uptake potential. The full uptake capacity is reached after approximately 3 min of contact between the sorbent and the RMG380 marine residual fuel sorbate. In addition, the performance of the material has been compared to an award-winning commercial sorbent, Corksorb. The as-prepared husks exhibit superior final uptake capacities in the comparison. However, due to the lack of oleophilicity, in gravimetric experiments the husk sorbent loses a considerable amount of its liquid. Although Corksorb lacks the ability to swell, it has the advantage of retaining a high percentage of the oil showing more resistance towards gravimetric desorption.

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