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Utilization of Agricultural Residues: De-Oiled Organic Rice Bran as Adsorbent of Moisturizers for Cosmetic Products

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The objective of this research is to study the adsorption of two types of moisturizers in cosmetic, urea and glycerin, by de-oiled organic rice bran. Urea and glycerin are moisturizers which can enhances the water-binding capacity on the skin. The samples of the de-oiled organic rice bran were obtained from Surin province of Thailand. The samples were pretreated with sodium hydroxide. In equilibrium time experiments, 0.5 g of dried de-oiled organic rice bran were immersed into 50 mL of urea or glycerin 1 % wt. solutions and shaken for various times followed by the determination of remaining moisturizer in the solution. To find the adsorption capacity of moisturizers by de-oiled organic rice bran, 0.5 g of dried de-oiled organic rice bran were immersed into 50 mL of urea or glycerin solutions with different concentration levels (1, 2, 3, 4, 5, 10, 15 and 30 g 100 mL^{-1}). The solutions were shaken for 1,440 min. The equilibrium time for urea and glycerin was achieved at 40 and 60 min., respectively. The de-oiled organic rice bran could adsorb higher amounts of urea than glycerin. The adsorption isotherm could be well described by the Freundlich isotherm model. The findings of this study would be beneficial to evaluate the suitability and efficiency of adsorption of moisturizers by de-oiled organic rice bran for future application such as body scrub.

Keywords: Adsorption, Cosmetic scrub, Moisturizer, De-oiled organic rice bran.

INTRODUCTION

Rice is a staple food in many parts of the world. It is the main agricultural product in Thailand and exported to other countries. Approximately 21-26 million tons of rice are annually produced[1]. One of the major by-products is rice bran which is accounted for 8 % of milled rice[2]. Rice bran is a by-product obtained from outer rice layers and is a good source for proteins, minerals and fatty acids and has high fiber content[3]. Rice bran is used for the enrichment of some foods, biosorbent for sorption or removal of some heavy metals[4-9] and methylene blue[10], due to its high fiber content[11]. Rice bran is also used for rice bran oil[12]. The de-oiled rice bran is of very low value[13]. De-oiled rice bran is generally used for reducing the cost of animal feed or is discarded as agricultural waste. In recent years, de-oiled rice bran has been used for extraction of proteins and amino acids[14], rice bran protein[15], dipeptidyl peptidase IV[16], starch[17] and biobutanol[18]. De-oiled rice bran, an excellent source of rice bran fiber, is a byproduct of the rice bran oil process[19]. Focused on the use for this low-cost material in natural processes. Not much research has been done use de-oiled rice bran from natural sources as adsorbent. Therefore, the aim of this study is to study the adsorption of moisturizers (urea and glycerins) by de-oiled organic rice bran. Urea and glycerin are also added to moisturizers to enhances the water-binding capacity of the stratum corneum[20]. In this work, the potential of natural de-oiled organic rice bran as a biosorbent material for adsorption of moisturizers is investigated. The aim of this study is to increase the value of agricultural residues and finding possibilities to use de-oiled organic rice bran as a natural sorbent which is produced in high amounts and at low cost in Thailand. The researchers hope that this study will be useful to those interested in developing cosmetic products locally and expanded trade in the future.

EXPERIMENTAL

All reagents used were of analytical grade. Solutions were prepared using deionized water. Raw de-oiled organic rice bran used as biosorbent was obtained from a local Agricultural Cooperative at Phrasat District, Surin Province, Thailand. The raw de-oiled organic rice bran was dried in an oven at 80 °C for a period of 2 h. Then, base treated rice bran was obtained by boiling de-oiled organic rice bran with sodium hydroxide 0.1 mol L^{-1} (weight ratio 1:1) for 1 h. After cooling, the excess of the base present on the material was leached out by washing with distilled water until neutrality (tested with pH indicator paper). The treated de-oiled organic rice bran was dried in an oven at 80 °C for a period of 2 h. The resulting material was ground and sieved. Finally, the particle size, specific surface area and surface structure of de-oiled organic rice bran before and after treatment with base were analyzed by particle size analyzer, sorption analyzer and scanning electron microscope (SEM), respectively.

Characterization of de-oiled organic rice bran (before and after treatment with base): The particle size of de-oiled organic rice bran was analyzed by particle size analyzer. The characteristic surface areas of de-oiled organic rice bran particles before and after treatment with sodium hydroxide 0.1 mol L^{-1} and after sorption of moisturizers were analyzed by SEM micrograph (magnification: × 1000). In addition, the specific surface area ($m^2 g^{-1}$) of the solid was measured by using physical adsorption of nitrogen on an automatic volumetric sorption analyzer (Quantachrome autosorb automated gas sorption system). The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method which is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules.

Effect of contact time: In order to study the time required for equilibrating urea or glycerin solutions with the de-oiled organic rice bran, equilibration times were selected at 0, 10, 20, 30, 40, 50, 60, 120, 180, 240 and 1440 mins, respectively. The sorption experiments were conducted by shaking 0.5 g sample of de-oiled organic rice bran in 50 mL of 1 g 100 mL^{-1} urea or glycerin solutions at 100 rpm at room temperature. At the end of the shaking period, the mixture was filtered. The de-oiled organic rice bran with urea or glycerin adsorbed were dried in an oven at 80 °C for a period of 2 h. The amount of urea or glycerin adsorbed, was calculated using the following equation by eqn. 1:

$$N = (M_2 - M_1)/M_1 \quad (1)$$

where N is the amount of urea or glycerin adsorbed (g g^{-1}), M_1 is the dry mass of de-oiled organic rice bran without moisturizer adsorbed (g) and M_2 the dry mass of de-oiled organic rice bran with moisturizer adsorbed (g).

Adsorption isotherm models for equilibrium conditions: The adsorption capacity of moisturizers by de-oiled organic rice bran was studied by adding 0.5 g of the adsorbent to 50 mL of urea or gylcerin solutions with different concentration levels (1, 2, 3, 4, 5, 10, 15 and 30 g 100 mL^{-1}). Each flask was shaken at 100 rpm. The adsorption capacity experiments were conducted by shaking to equilibrium time. At the end of the shaking time, the mixture was filtered. The de-oiled organic rice bran with urea or glycerin adsorbed were dried in an oven at 80 °C for a period of 2 h. The amount of urea or glycerin adsorbed was calculated. Each experiment was repeated three times and the results are given as averages.

In the present investigation the data have been correlated with Freundlich and Langmuir isotherms. The linearized Freundlich isotherm equation was adopted in this study as expressed by eqn. 2:

$$\log N = \log K_F + (1/n) \log C_e \quad (2)$$

where K_F and n are the Freundlich parameters that were adjusted to fit eqn. 2 to the experimental data.

The equation for the Langmuir isotherm equation was adopted in this study as expressed by eqn. 3:

$$\frac{C_e}{N} = \frac{1}{K_a n} + \frac{1}{n} C_e \quad (3)$$

where C_e is the equilibrium concentration (g 100 mL^{-1}), N is the amount of urea or glycerin sorbed (g/g), n is N for a complete monolayer (g/g), K_a is a sorption equilibrium constant (100 mL g^{-1}). A plot of C_e/N *versus* C_e will yield a straight line for data which fits the Langmuir expression.

RESULTS AND DISCUSSION

Characterization of de-oiled organic rice bran: The average particle size by particle size analyzer of treated de-oiled organic rice bran (after treatment with base) was equal to 172.8 μm. The surface structure of de-oiled organic rice bran was analyzed by SEM before and after treatment with base and after adsorption of moisturizer as shown in Fig. 1. The de-oiled organic rice bran particles after treatment with base (Fig. 1 (b) and (c)) had more pores than particles before treatment with base Fig. 1 (a). The micro granules reveal clearly the presence of granular structures after urea sorption Fig. 1 (c); these structures were absent before the sorption process Fig. 1 (b). The presence of granules on the de-oiled organic rice bran particles can also be observed after urea adsorption. It was further detected by SEM that the de-oiled organic rice bran particles had a rather smooth surface area before treatment with sodium hydroxide compared to particles after base treatment. The characteristic of the surface area corresponds with

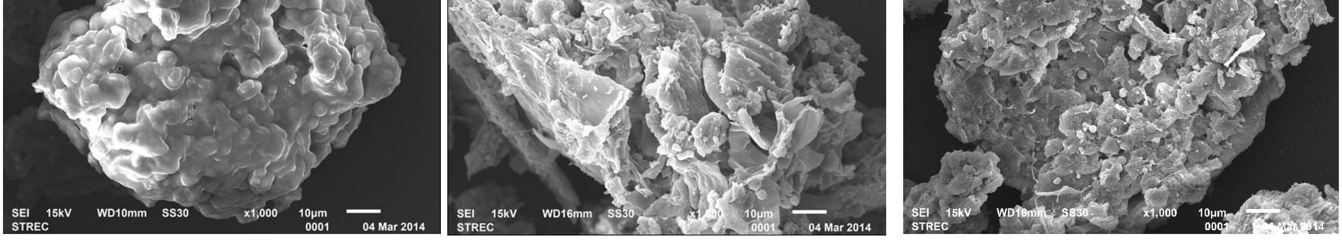

Fig. 1. Typical SEM micrograph of de-oiled organic rice bran (magni-fication: ×1000) (a) before moisturizer adsorption (b) after treatment with base (before sorption) and (c) with urea adsorbed

the specific surface area determined by BET measurements. The de-oiled organic rice bran particles before treatment with base had a lower specific surface area than particles after base treatment (before sorption). The de-oiled organic rice bran particles after base treatment had a rough characteristic surface area and larger specific surface area. The specific surface areas by the BET measurement before and after base treatment were 23.540 and 40.850 $m^2 g^{-1}$, respectively (Table-1). Table-1 shows that pretreatment with sodium hydroxide 0.1 mol L^{-1} can increase the specific surface area by more than 40 % which should increase the amount of adsorbents. This specific surface area is much larger than that of rice bran, a sorbent commonly used for the removal of metal ions in aqueous samples, which presents a very small surface area (0.46 $m^2 g^{-1}$)[7].

TABLE-1
SPECIFIC SURFACE AREAS OF DE-OILED ORGANIC RICE BRAN BEFORE AND AFTER MOISTURIZER ADSORBED

De-oiled organic rice bran	Specific surface area ($m^2 g^{-1}$)
Before urea adsorbed	23.540
After urea adsorbed	40.850

Effect of contact time: In this study, the effect of contact time on the adsorption of urea and glycerin studied with batch experiments are shown in Fig. 2. The solution concentration of urea or glycerin was 1 wt. % while the adsorbent quantity was 0.5 g. The results show that the adsorption process is clearly time dependent. Urea needed 40 min to reach equilibrium while glycerin needed 60 min. In addition, the amounts of adsorbed urea moisturizers on de-oiled organic rice bran are higher than for glycerin moisturizers as shown in Fig. 3. Fig. 3 shows the relationship between adsorbed amount of urea on de-oiled organic rice bran and it equilibrium concentration in solution. The amount of moisturizers adsorbed increased with the increase of moisturizers concentration. Therefore, this de-oiled organic rice bran was able to adsorb the moisturizers such urea and glycerin. Different works have been carried out using rice bran as natural sorbent for the sorption of heavy metals from aqueous solutions[4-9].

Adsorption isotherm models for equilibrium conditions: Fig. 4 confirmed that the adsorption behavi-our of moisturizers on de-oiled organic rice bran correspond with the Freundlich isotherm (linear relation log N *vs*. log C_e with high R^2 values). All correlations R^2 of Freundlich isotherms are higher than 0.90 while all correlations R^2 of Langmiur isotherms are lower than 0.90.

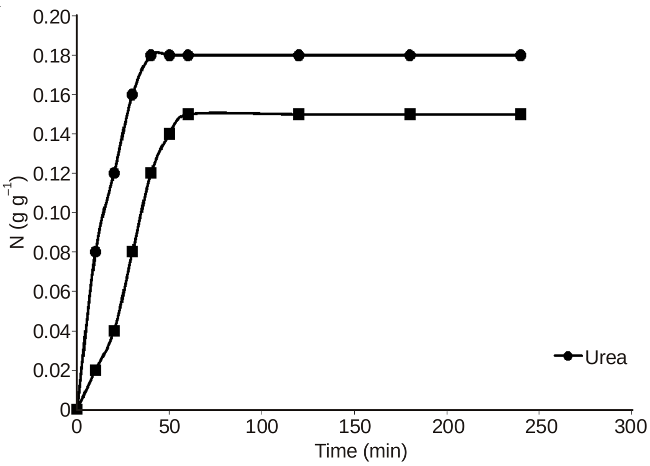

Fig. 2. Effect of contact time on adsorption of urea and glycerin by de-oiled organic rice bran

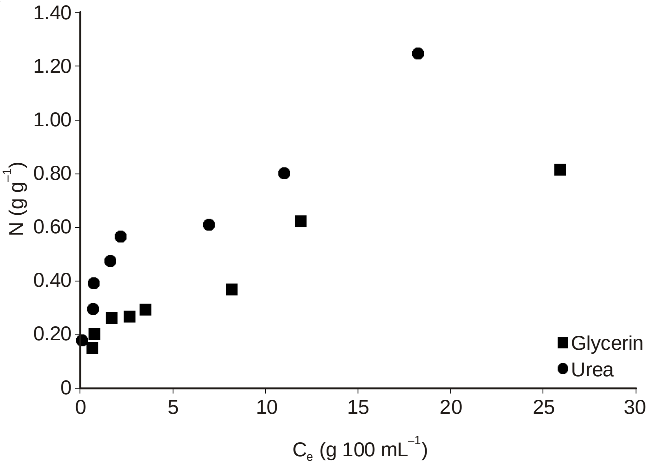

Fig. 3. Typical amount of adsorbed urea and glycerin on de-oiled organic rice bran depending on the solution concentrations

The experimental results (Table-2) show that practically all of the parameters 1/n (or slopes) are lower than one. This indicates that the adsorption ability of moisturizer is increased rather slowly with higher solution concentrations. Therefore the slope of the Freundlich isotherm is not steep at high solution concentrations. The determined values of the Freundlich adsorption parameters, K_F and n, are summarized in Table-2. It may be concluded that the adsorption behaviour of moisturizers on de-oiled organic rice bran tend to be of multilayer type confirmed by the Freundlich isotherm.

TABLE-2
FREUNDLICH ADSORPTION PARAMETERS FOR UREA AND GLYCERIN SOLUTION ADSORPTION

Parameters	Urea	Glycerin
Freundlich isotherm		
K_F	0.39	0.19
1/n	0.34	0.42
n	2.91	2.40
R^2	0.95	0.94
Langmiur isotherm		
K_a	2.17	4.38
1/n	0.83	1.14
n	1.20	0.88
R^2	0.88	0.86

Conclusion

De-oiled organic rice bran is a suitable biomaterials for adsorption of moisturizers such as urea and glycerin. Experimental results were analyzed by using the Freundlich and Langmuir equations and the correlation coefficients for fitting the Freundlich model were significantly better than the coefficients for the Langmiur isotherm. De-oiled organic rice bran may be an efficient biomaterial in cosmetics to enhance the water-binding capacity.

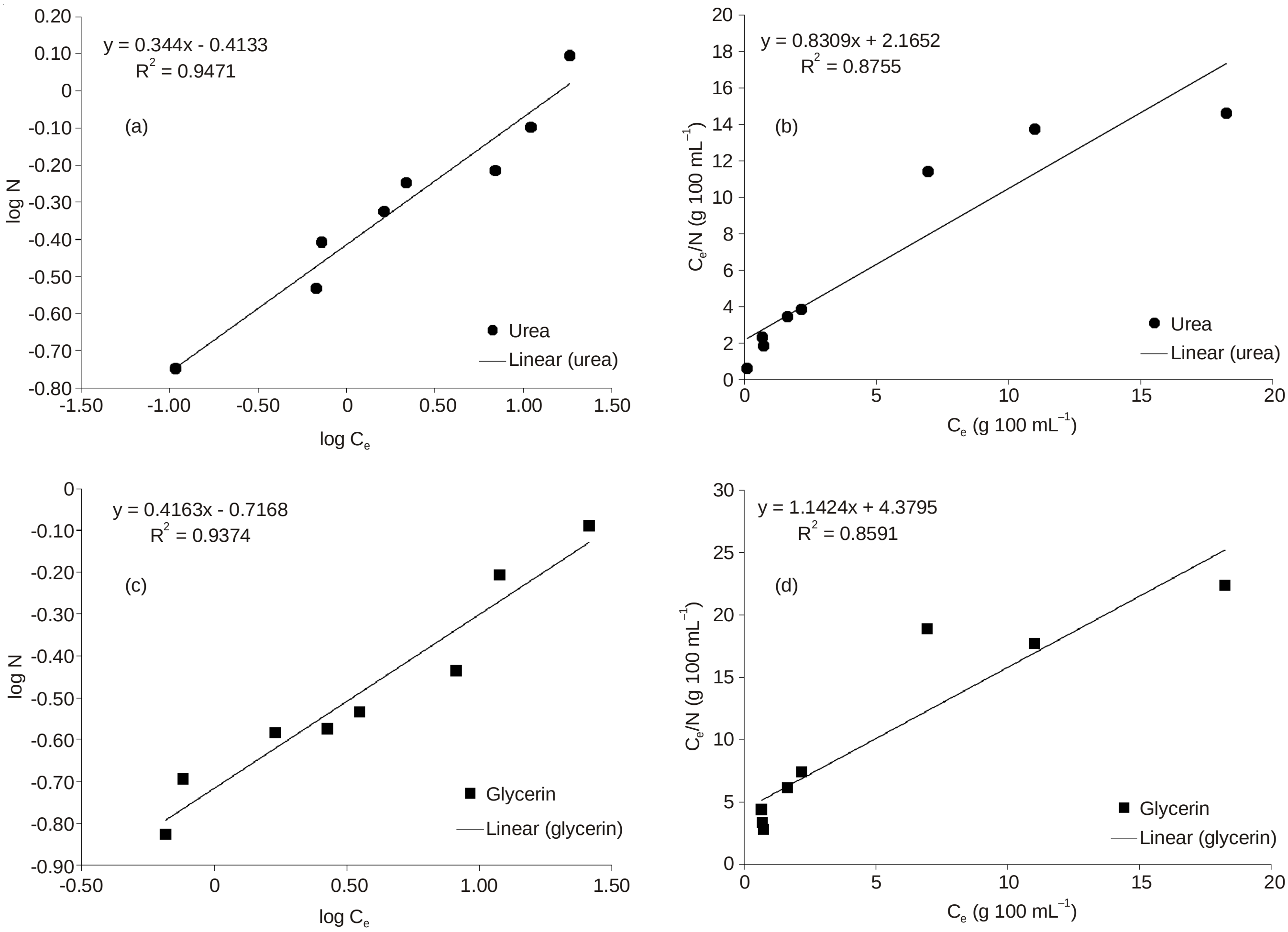

Fig. 4. Typical Freundlich and Langmiur isotherms of moisturizer adsorbed on the de-oiled organic rice bran (a) Freundlich isotherm of urea adsorbed (b) Langmiur isotherm of urea adsorbed (c) Freundlich isotherm of glycerin adsorbed (d) Langmiur isotherm of glycerin adsorbed

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