Surface Behavior of Rhodamine and Tartrazine on Silica-Cellulose Sol-Gel Surfaces by Thin Layer Elution

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ABSTRACT

Physical and chemical interactions are the principles for different types of separation systems as the equilibrium dynamics on surface plays a key role. Surface modification is a way for selective separation at interfaces. Moreover, synthesis of gel silica by a sol-gel method is preferred due to the homogeneity and surface feature easily controlled. Cellulose can be added in situ to modified the silica features during the process. The further application for to study the interaction of rhodamine and tartrazine in its surface and their solubilities in mobile phase explains the possibility of their separation. This paper devoted to evaluating the surface behavior in term of adsorption and desorption of tartrazine and rhodamine on the silica-cellulose thin layer in different mobile phase. Some carrier liquids applied such as methanol, acetone, *n*-hexane, and chloroform. The result proves tartrazine and rhodamine are separated and have different behavior in different mobile phase. The retardation factors (R_f) of the mixtures suggest complexity behavior on silica-cellulose surface.

Keywords: silica-cellulose, surface dynamics, thin layer method

INTRODUCTION

Physical interaction on surfaces plays a role in the material making nowadays [1]. In this purpose development and characterization of the porous material of interest using sol-gel process is preferable since the formation of materials and surfaces can be followed [2]. In this case, the process can be modified according to the purpose or application of the materials. The materials themselves are usually porous with the higher surface area.

Important factors affecting physical interaction on surfaces such as particle surfaces and pore surfaces in which solvent molecules are confined. Surface behavior of simple molecules such as water or cyclohexane on porous surfaces were reported based on relaxation and diffusion NMR experiments decades ago [1,3,4]. The equilibrium dynamics on surfaces, both liquid-solid interface and liquid-gas interface shows the role of intermolecular forces as well as surface interaction. The reorientation mediated by translational displacement (RMTD) mechanism is one of several proposed mechanism to describe surface interaction. This is not the case of chemical changes on surfaces, which are not reversible.

The material used to examine the dynamics in the surface was silica from rice husk ash which is combined with hydrolyzed cellulose from *nata de coco* in nano dimension. The nanocellulose was incorporation to the silica particles via sol-gel processing [5] so that the addition of cellulose was done *in situ*. The sol-gel processing was also preferable since the

growing confinement in the gelation can be followed and controlled [6]. There were already many types of material designed for adsorbent making from agrichemical waste products, usually in the frame of environmental sustainability [7]. However, not many papers were reported for the real investigation of surface dynamics underlying separations.

The properties of the hybrid materials were compared to commercial thin layer silica plate. The idea of giving cellulose came from the good result in making adsorbent releaser system of volatile compounds which was meant to be bio-attractant for planthopper parasitoid in rice field [8]. In this case, cellulose makes the silica polarity decreased and the adsorbed biological volatile compounds can be released step by step more freely than from pure silica surface. This solid-gas equilibrium is also being studied elsewhere.

The dye molecules were used as the probe to inform indirectly the dynamics on the surface due to the colour they possess so that the separation can be followed without complex modern instrumentation. The thin layer plate were made similar to thin layer chromatography for separation of compounds in mixtures [9].
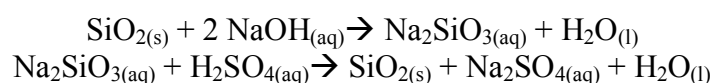
EXPERIMENT
Chemicals and instrumentation

The chemical used in this study were obtained from Sigma Aldrich and E.Merck. Most of the solutions needed were made using distilled water. Tartrazine (yellow dye) and Rhodamine B (red dye) dyes were employed as the probe to study the dynamics on surfaces. while Rf study was the simple means to learn the separation of both dyes. Chloroform, methanol, acetone, *n*-Hexane and water represent different polarity and viscosity of mobile phases with silica-cellulose as the stationary phase.

Ashing of rice husk was done in XD-1700 M, Nabertherm, dan Thermolyne furnace while gelling reactions were done on magnetic stirrer of NESCO LAB MS-H280-Pro or Thermoscientific Cimarec. Drying of the material used EYELA oven, type WFO-450ND. BET analysis using Quantachrome NovaWin - Data Acquisition and Reduction for NOVA instruments, and Scanning Electron Microscope used was the one from FEI Type Inspec S50. All bench activities used pyrex glassware.

Procedure of material preparation and characterization

The rice husk was burnt at 350°C for 2 times 3 hours before dissolving it in 6N sodium hydroxide. The filtrate was then mixed with hydrolyzed *nata de coco* to make nanocellulose particles. Hydrolysis itself was done at 55°C for 5 hours using 15 N of sulfuric acid. The cellulose fibers were made nanocellulose to be mixed with silica particles *in situ*. Both filtrate and hydrolyzed cellulose were mixed and stirred until the pH reached 2. Additional ammonium hydroxide drop by drop would increase the pH up to 8, while the silica-cellulose hybrid material formed gradually. Distilled water was used to wash away the rest of chemicals in silica gel and sodium sulfate salt prior to the drying process in oven at 50°C for 48 hours. The chemical reactions can be written as follow:

$$SiO_{2(s)} + 2\ NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$
$$Na_2SiO_{3(aq)} + H_2SO_{4(aq)} \rightarrow SiO_{2(s)} + Na_2SO_{4(aq)} + H_2O_{(l)}$$

This method is already registered in Indonesia patent number P00201-508272 dated 8 December 2015.

Characterization of the material covers water content, ash content, Iodine adsorption, Scanning Electron Microscopy, and BET. The application of silica cellulose material as adsorbent material using thin layer was examined. The R_f study was done for the thin layer silica-cellulose in eluting every single dye and separating the mixture of both. The surface complexity can be reflected from the results of separations in the thin layers. The behavior with different eluents, methanol, acetone, *n*-hexane, and chloroform, were compared to commercial silica (E. Merck).

RESULT AND DISCUSSION
Material and characterization

The SEM picture of the material showed the porous structure of the gel which are globular and reach dimension below 100 nm. The globular shape of the gel granules implied the homogeneity of sol-gel processing which ensured good pore size distribution. This is a desired property of the good adsorbent material for separation purposes. The cellulose particles on silica surface cannot be distinguished clearly and this is also a good sign of physical interaction between silica and cellulose.

Figure 1. The appearance of silica-cellulose material (left) and the SEM picture of the same material at 80.000 times magnification

In the system studied, the pores were not empty at all. During experiments, the pores were full of solvent, in this case water, and when the elution came into action, the eluent molecules also played a role. The big of dye molecules, the probe molecules behaved differently in different circumstances. There were many possible interactions at the surface between many types of molecules.

Table 1. Characterization of materials

Adsorbents	Density (g/mL)	Water content (%)	Ash content (%)	Iodine adsorption values (%)	BET pore surface area
Silica rice-husk	0.740	14.10	17.90	3.046	-
Nata de coco Cellulose	1.305	7.249	1.697	-	-
Silica-cellulose hybride material	1.780	0.060	1.690	1.280	60.28

Physical characterization of the material shows the difference of surface properties of the silica and silica-cellulose. Iodine adsorption value shows a higher ability of silica surface to adsorb iodine compared to the silica-cellulose (**Table 1**). The presence of cellulose in this case reduce the ability of silica to adsorb iodine. However, this is not a drawback since the material can be used as a releaser for some organic compounds [8].

Application as thin layer material.

Application of the material involved tartrazine and rhodamine-B molecules. Both of them are bulky molecules and have polar functional groups. So that, chance for surface interactions are much bigger (**Figure 2**). However, the presence of these molecules must be covered by solvent molecules, and the interaction with the surface is not direct interaction. Meanwhile, there were other species in this system, eluent molecules which also have the tendency in surface interaction with silica-cellulose. Previously study reported water molecules interaction to the surface by using relaxation in NMR [1]. When water molecules are reoriented themselves in pore surface, the same analogy can be put into both tartrazine and rhodamine-B molecules including solvent and eluent molecules.
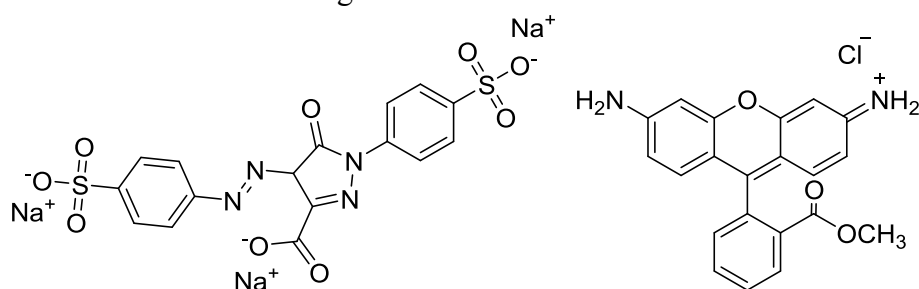
Figure 2. Molecular structure of tartrazine molecule (left) and rhodamine–B (right)

Table 2. The R_f of tartrazine and rhodamine-B and their mixtures in different solvent

R_f Systems	Solvents	Tartrazine	Rhodamine B	Mixture of Tartrazine and Rhodamine B
Commercial silica thin layer	methanol	0.42	0.75	zone 1: (Tartrazine): 0.94 zone 2:(Rhodamine B): 0.51
	acetone	0.30	0.56	zone 1 (Tartrazine) 0.57 zone 2 (Rhodamine B) 0.29
	chloroform	0	0	0
	n-hexane	0	0	0
Silica-cellulose preparative plates	methanol	0.94	0.49	zone 1(Rhodamine B) 0.75 zone 2 (Tartrazine) 0.42
	acetone	0.63	0.29	zone 1 (Rhodamine B) 0.50 zone 2 (Tartrazine) 0.093
	chloroform	0	0	0
	n-hexane	0	0	0

The silica-cellulose material was made think layer in a glass plate and used to develop tartrazine and rhodamine-B both as the single component and in the mixture. Some eluents were used with diverse polarity strength and the retardation factors can be seen in **Table 2**. It was clear that *n*-hexane and chloroform cannot act as carrier for both rhodamine-B and tartrazine molecules. Both of dyes cannot dissolve in the polar solvents and the retardation factor was zero for both. The stationary phase of silica or silica-cellulose, in this case, adsorb

both molecules. However, in polar solvents, there were some interesting facts. Methanol has the eluting power of 0.95, which is very strong, and acetone has the value of 0.56 [10].

Sodium ion in tartrazine and chloride ion in rhodamine-B would be readily ionized. They can influence the surface interaction and the tendency of both to stay on the surface for a certain retention time before dissolving back to the pore liquid. The diffusion of the molecules and also the water solvent tend to be anomalous on surfaces but become normal in bulk liquid [1]. Moreover, there are also some other cations or anions present as additional charged particles that would contribute in the competition on the surface. Presumably, the big body of tartrazine and rhodamine-B themselves interact with surface and undergo surface diffusion as well. Moreover, when the solvent is not water then the behavior of both molecules differ again due to different solubilities in the organic solvents. To add to the complexity, the different viscosities toward pore network would lead to different migration rate across the silica-cellulose material.

Table 3. Surface tension, viscosity and solvent strength of relevant eluents

Eluents	Surface tension	Viscosity (dyne/cm)	Solvent strength
methanol	2.67	0.43	0.95
acetone	2.50	0.40	0.56
n-hexane	2.33	0.37	- (0.00 for *n*-pentane and 0.04 for cyclohexane)
chloroform	2.67	0.42	0.4

In **Table 3** above, the alternate eluent power of methanol and acetone in bringing the rhodamine and tartrazine due to the presence of cellulose. In commercial silica, both methanol and acetone brought rhodamine-B molecules easier compared to tartrazine when they were not mixed. But in the homogeneous mixture, they both were separated but tartrazine leads the way and left rhodamine behind. In this case, rhodamine and tartrazine could be described as competitors in staying and diffused along the surface pores. In this situation, it is clear that the dynamics on the surface is not a simple process to describe. The attachment of rhodamine in silica was greater than tartrazine or the solubility of tartrazine in methanol or acetone was better than rhodamine.

However, there were other factors still have to be taken into account. The dynamics of solvent molecules and the behavior of all towards tortuosity of the porous system can play particular role as described previously [1,11]. The reorientation cannot be explained here since there were no means to get into dynamics in details. It is also interesting that tartrazine molecules in mixture with rhodamine moved farther than they did when without another competitor (R_f 0.94 compared to 0.42 in methanol and 0.57 compared to 0.3 in acetone). Tartrazine leads the way in both methanol and acetone eluents leaving rhodamine-B behind. The Rf of rhodamine reduced in the presence of tartrazine.

In the presence of cellulose in silica surface, the tendency of migration for both dyes altered. With additional cellulose surface, tartrazine moves faster and longer than rhodamine for one elution period. R_f of Tartrazine were greater than rhodamine can be originated from the weak interaction with the cellulose. But also interesting was the fact that when both were in the mixture, rhodamine would move easier towards the end of the plate compared to tartrazine, exactly the other way around the first experiment with commercial silica. Seemed

that in this situation tartrazine molecules were adsorbed onto the surface for a longer period of time and won the competition with rhodamine.

For both situations, the eluting strength of methanol plays the key role in elution process regardless which one eluted first. Acetone on the other hand made the separation clearer in the silica-cellulose system. Tartrazine was almost fully absorbed in the surface while rhodamine-B could be diffused halfway. Note that the surface tension, as well as viscocity of the four solvents, were not much differ compared to each other. In this case, the pore filling process cannot be considered the same due to surface tension and viscosity of both eluents.

The adsorption must be considered as physical adsorption since the zones move. In chemical adsorption, the molecules would be retained forever since chemical bondings were formed along the process. In this physical adsorption, the Langmuir or Freundlich isotherm cannot be counted as the way to describe the process. The solid-liquid dynamics can be a key model for different other systems. However, the more quantitative calculation must be considered for further investigation. The probe of molecules are much higher to be measured the dynamics but there must be a better way to describe molecular tumblings on different surfaces as a complex dynamics.

CONCLUSION

There is specific behavior of rhodamine and tartrazine molecules on surfaces of silica-cellulose. This specific dynamic involves interaction with solvent molecules in the surroundings, as well as the eluent-adsorbent interaction. The retardation factors of rhodamine-B and tartrazine alternate by elution with different solvent based on the eluent's polarity towards surface and adsorbates. The presence of cellulose on surface changes the sequence of separation molecules. In mixture of both the complexity of dynamics can be seen from the greater desorption of tartrazine due to greater rhodamine-B competitiveness.

In the future, the different behavior due to the different interaction with surfaces can be a key role for specific material making directed to special purposes. Desorption itself also important for surface releaser agents such as for in molecular dispenser used in the agricultural area. The releasing mechanism can be the key role in designing better dispenser day by day.

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