



## Binary biomaterials (inorganic material/natural resin): Synthesis, characterization and performance for adsorption of dyes

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Manuscript received online 26 April 2019, revised and accepted 20 July 2019

The sol-gel method has been reported a useful techniques for synthesizing inorganic material HSS. In this study, the sol-gel process was used in two stages. In the first step, the hydrolysis of phenyltrimethoxysilane (PTMS) was carried out under acidic conditions. In the second step, the silane condensation proceeded under basic conditions and as a result the HSS were obtained. The obtaining HSS was treated with epichlorohydrin to carry out an epoxidation process (HSEPC). Then, HSEPC was functionalized by treatment with natural resin (gum arabic) and obtained HSEPCGUM. Gum arabic has GA-GP-GA-glycoprotein, hydroxyproline glucuronic acid and polysaccharides groups. Anionic and cationic dyes were adsorbed onto HSEPCGUM and values of absorbance was measurement by UV-Visible spectrophotometers. Adsorption isotherm experiments of adsorbed dyes on HSEPCGUM were performed at 35°C with Freundlich, Langmuir and Dubinin-Radushkevich (DR) methods. Adsorption maximum capacity of HSEPCGUM ( $X_{max}$ ) was obtained 100 mg/g for BB3. Before and after dye adsorption the structure characterization of adsorbent was done by SEM and FTIR analysis.

Keywords: Hollow silica spheres, reactive blue 21, basic blue 3, adsorption, sol-gel method.

### Introduction

Dyes cause allergy, dermatitis, skin irritation, cancer and mutation in humans. Dyes are used for colouring purposes to products so they consume large amounts of water, and as a result, they produce a significant amount of coloured wastewater. Therefore, water and wastewater can be possessed of pollutant groups of these dyes. Most of the dyes structure is complex aromatic so that they have stable structures and non-degradable under light or heat. The presence of existing dyes in the environment is a worrying level because of its toxic effect to human and environment<sup>1</sup>. There are a variety of techniques for to remove dyes from aqueous media, such as: filtration, oxidation, ozonation, adsorption, biosorption, photocatalysis, electrochemical treatment and membranes<sup>2-4</sup>.

Basic dyes are in the category of cationic dyes such as basic blue 3 (BB3). BB3 is formed positively charged ions due to dissociation with positively electric charged localised over the entire molecule<sup>5</sup>. Crini *et al.* (2008) reported, adsorption of BB3 is investigated on sulfonate groups grafted chitosan<sup>6</sup>. In this work experimental data showed the maxi-

um adsorption capacity reach 166.5 mg/g. In another study, the adsorption of BB3 from aqueous solution onto Aleppo pine-tree sawdust was investigated. Adsorption contact time was studied as 5 h. In this work, adsorption maximum capacity was obtained 66 mg/g<sup>7</sup>. Liew *et al.* studied a low-cost adsorbent pomelo peel for remove BB3 from aqueous solutions. According to the experiment results, the maximum adsorption capacity of pomelo peel was found 23.87 mg/g<sup>8</sup>. In the other research was investigated removal of BB3 with tartaric acid modified sunflower. Adsorption contact time was studied as 2 h. In this work, adsorption maximum capacity was obtained between 48–53 mg/g<sup>9</sup>.

Reactive dyes are vinyl-sulphone, chlorotriazine, trichloropyrimidine compounds with different reactive groups of azo-based chromophores, such as reactive blue 21 (RB21). Reactive blue 21 has the class of copper phthalocyanine which is included in the group of sulfato ethyl sulfone. Adsorption of RB21 from aqueous solutions with clinoptilolite was studied<sup>10</sup>. After the adsorption, Langmuir ( $q_{max}$ ) were obtained as 9.6 mg/g for single RB21. In the other paper, the

study is carried out for the removal of dye reactive blue 21 (RB21) using low cost adsorbents raw fly ash. The  $Q_0$  values from Langmuir isotherm were between 0.53 and 0.19 mg/g in this study<sup>11</sup>. Removal of RB21 were studied on quaternary ammonium modified with cellulose under ultrasonic-pretreatment. In this study found that quaternary ammonium modified with cellulose adsorbed 617 mg/g RB21<sup>12</sup>. In another study, conducted for reactive blue 21 (RB21), the adsorption potential of hydrotalcite (HT) in aqueous solutions has been investigated by batch technique. The adsorption capacity of HT for RB21 was found to be 266.7 mg/g at pH 2.0<sup>13</sup>.

Over the past decades hollow silica spheres (HSS) have attracted attention by lots of researchers. HSS has low toxicity and density. It is good compatibility with other materials<sup>14</sup>. HSS uses pharmaceuticals and biochemistry because of highly biocompatible, and large surface areas<sup>15</sup>. In addition, HSS can be applied for enzymes or proteins, drug delivery systems, dyes or inks, photonic crystals<sup>16,17</sup>.

Gum arabic has higher molecular weight arabinogalactan-protein complex (GA-GP-GA-glycoprotein). Chain of gum arabic (GUM) are connected with serine and hydroxyproline groups<sup>18</sup>. GUM uses in application, such as coatings, pharmaceuticals herbal medicines and formulation of creams and lotions.

In this study, sol-gel method was applied for obtaining HSS. The sol-gel process was applied in two steps. In the first step the hydrolysis of phenyltrimethoxysilane (PTMS) was carried out under acidic conditions. In the second step, the condensation of the silane proceeded under basic conditions and as a result HSS was obtained. Between HSS and epichlorohydrin (cross-linker) were applied the epoxidation reaction for obtaining HSEPC. HSEPC was functionalized with gum arabic and as a result in HSEPCGUM obtained. Adsorption of reactive blue 21 (RB21) and basic blue 3 (BB3) dye on gum arabic functionalized HSS was studied. The absorbance values of the dyes on HSEPCGUM were monitored by UV-Vis spectrophotometer. Both BB3 and RB21 were found 45 min for the contact time necessary to reach saturation. Adsorption isotherm experiments of these dyes at four different concentrations were performed at 35°C with Freundlich, Langmuir and Dubinin-Radushkevich (DR) methods.

## Experimental

### Materials:

Phenyltrimethoxysilane (PTMS) 99% (Sigma-Aldrich), nitric acid  $\text{HNO}_3$  55–56% (Merck) ammonium hydroxide  $\text{NH}_4\text{OH}$  35% (Merck), ethyl alcohol pure (Merck), N,N-dimethylformamid (>99%) and epichlorohydrin (Sigma-Aldrich), gum arabic (Kermanlar company) are purchased. Basic blue 3 and reactive blue 21 reactive dye were taken from a textile industry company located in Turkey.

### Synthesis:

**Preparation of hollow silica spheres (HSS):** HSS was synthesized using the sol-gel method of Hah *et al.*<sup>19</sup>. In the first step of this process, phenyltrimethoxysilane (PTMS) (0.06 M) was added to the  $\text{HNO}_3$  ( $0.66 \times 10^{-2}$  M) solution in an isothermal water bath at 60°C and stirred for 4 min at a stirring rate of 260 rpm in order to achieve the hydrolysis of PTMS. Condensation of solution is the second step of process,  $\text{NH}_4\text{OH}$  solution (1.44 M) was added to the resultant solution and the solution has been transformed from colorless transparent. The resulting particles were collected by a filter, washed several times with water and ethanol and dried in vacuum oven at 80°C for 2 h<sup>19</sup>. HSS was synthesized as seen in Fig. 1.

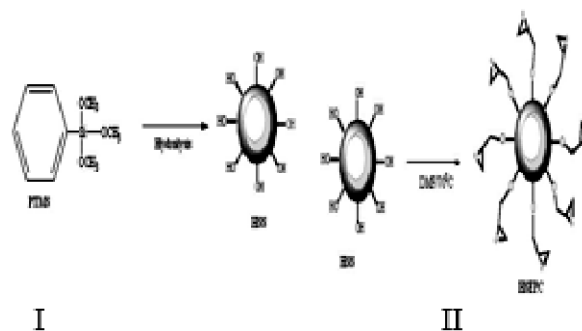


Fig. 1. (I) Synthesis of HSS and (II) the epoxidation process of HSS.

**The epoxidation process of HSS:** The epoxidation process was carried out by dispersing HSS (4.5 g) in 50 ml DMF. Epichlorohydrin was added drop wise to the solution in this process and HCl gas is released from the solution as shown in Fig. 1.

**Gum arabic functionalized HSEPC (HSEPCGUM):** In this step, after precipitation of HSEPC mixture 4.5 gram gum arabic was added and stirred for 3 h at 70°C. The precipitate

was filtered and washed with water/ethanol solution several times. It was dried at 80°C under vacuum and was obtained HSEPCGUM.

*Adsorption experiments:*

*Preparation of dyes stock solution:* Stock solutions of basic blue 3 (BB3) and reactive blue (RB21) were prepared as 500 ppm. The experimental concentrations of dyes were prepared from 500 ppm stock solution as 5, 10, 25 and 50 ppm. In this work, HSEPCGUM (0.01 g) were weighed for each concentration and placed in a glass tube. Different concentrations of BB3 and RB21 were added 10 ml, then, these samples were shaking in a water bath at 35°C and measurements were taken every 15 min. In this process was completed in 45 min. The same process was applied for 0.02 g and 0.05 g HSEPCGUM and the absorbance values monitored by UV spectrophotometer.

*Adsorption studies:*

*Effect of contact time:* Removal of dyes on HSEPCGUM was studied for 5, 10, 25 and 50 ppm at 35°C. Both BB3 and RB21 reached saturation at 45 min as seen in Fig. 2.

*Effect of adsorbent doses:* The capacity of adsorption of dyes onto the HSEPCGUM was calculated using the following eq. (1);

$$q_e = \frac{c_0 - c_e}{W} \times V \quad (1)$$

where  $c_0$  and  $c_e$  are the initial and equilibrium liquid phase concentration of dye, respectively ( $\text{mg L}^{-1}$ ),  $q_e$  is the adsorption capacity ( $\text{mg g}^{-1}$ ),  $W$  is the weight of adsorbent (g), and  $V$  is the volume of dye solution ( $\text{L}$ )<sup>20</sup>.

0.01 g, 0.02 g and 0.05 g was weighed from HSEPCGUM.  $V/W$  ratio was hold as  $1 \text{ L g}^{-1}$ ,  $0.5 \text{ L g}^{-1}$ , and  $0.2 \text{ L g}^{-1}$  during adsorption isotherms experiments and all the adsorption works were carried out at 35°C. The Tables 1-2 shows that the maximum amount of substance adsorbed in the single layer ( $X_{\text{max}}$ ) is  $\text{BB3} > \text{RB21}$  for the Langmuir isotherm. As seen in the Tables 1-2, the values of  $X_{\text{max}}$  decrease with increasing amount of adsorbent. This can be due to two reasons: the first is the adsorption maximum amount ( $X_{\text{max}}$ ), the second is the adsorption capacity ( $q_e$ ). Although units of both the above terms are same ( $\text{mg g}^{-1}$ ), they are not always the same. Adsorption capacity can be calculated by eq. (1) while the maximum adsorption amount can be estimated by Langmuir eq. (2). The eq. (1) is clarified that adsorption capacity  $q_e$  ( $\text{mg g}^{-1}$ ) decreases by increasing the weight used adsorbent  $W$  (g) because they have an inverse relationship.

*Adsorption isotherms:*

The results of adsorption studies of BB3 and RB21 at ranging from 5 to 50  $\text{mg L}^{-1}$  onto HSEPCGUM at 35°C were reported by Freundlich, Langmuir and Dubinin-Radushkevich (DR) isotherms models as seen in Tables 1-2.

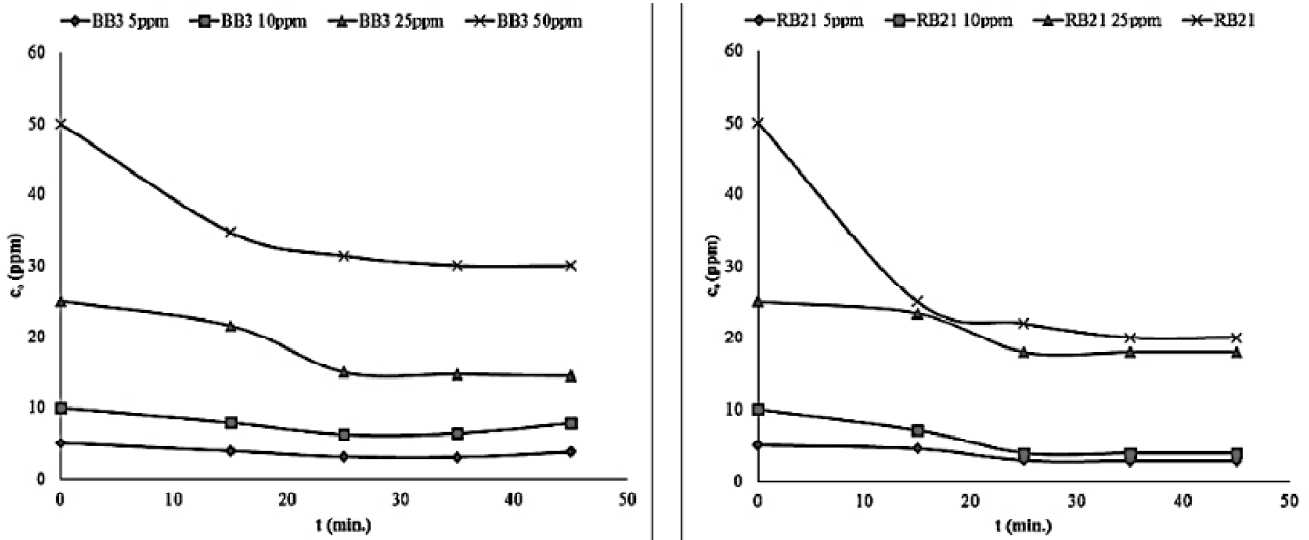


Fig. 2. Balance graphics of the dyes on HSEPCGUM at 35°C.

**Table 1.** Adsorption isotherms constants for BB3 at 35°C

Isotherm/adsorbant dose HSEPCGUM	0.01 g	0.02 g	0.05 g
Freundlich:			
<i>n</i>	0.88	0.66	1.60
<i>K<sub>F</sub></i>	0.77	0.68	0.11
<i>R</i> <sup>2</sup>	0.98	0.85	0.99
Langmuir:			
<i>b</i> (L mg <sup>-1</sup> )	0.0065	0.07	-0.04
<i>X<sub>max</sub></i> (mg g <sup>-1</sup> )	100	8.00	-4.30
<i>R</i> <sup>2</sup>	1.00	0.97	0.98
Dubinin-Radushkevich (DR):			
<i>K<sub>DR</sub></i>	3.80	2.25	2.83
<i>X<sub>max</sub></i> (mg g <sup>-1</sup> )	11.0	10.0	16.0
<i>E</i> (kJ mol <sup>-1</sup> )	9.13	8.99	3.95
<i>R</i> <sup>2</sup>	0.86	0.70	0.88

**Table 2.** Adsorption isotherms constants for RB21 at 35°C

Isotherm/adsorbant dose HSEPCGUM	0.01 g	0.02 g	0.05 g
Freundlich:			
<i>n</i>	1.98	2.40	1.20
<i>K<sub>F</sub></i>	0.035	0.002	0.04
<i>R</i> <sup>2</sup>	0.93	0.78	0.98
Langmuir:			
<i>b</i> (L mg <sup>-1</sup> )	-0.05	-0.03	-0.0009
<i>X<sub>max</sub></i> (mg g <sup>-1</sup> )	-1.95	-0.54	-66.0
<i>R</i> <sup>2</sup>	0.86	0.99	0.98
Dubinin-Radushkevich (DR):			
<i>K<sub>DR</sub></i>	14.0	16.0	6.36
<i>X<sub>max</sub></i> (mg g <sup>-1</sup> )	15.0	5.00	7.50
<i>E</i> (kJ mol <sup>-1</sup> )	5.98	5.59	7.89
<i>R</i> <sup>2</sup>	0.92	0.65	0.70

**Langmuir isotherm:** According to Langmuir equation, this process will be monolayer and there will be physical adsorption between adsorbate and dye particles on the surface of adsorbent. Following Langmuir eq. (2)

$$\frac{1}{q_e} = \frac{1}{X_{max} b C_e} + \frac{1}{X_{max}} \quad (2)$$

where *X<sub>max</sub>* is the amount of maximum adsorption at monolayer coverage (mg g<sup>-1</sup>) and *b* is the adsorption equilibrium constant (L mg<sup>-1</sup>).

**Freundlich isotherm:** Freundlich describes multilayer adsorption on adsorbent surface where heterogenous type of

adsorption occurs. Freundlich isotherm was represented as following eqs. (3), (4);

$$q_e = K_F c_e^n \quad (3)$$

$$\log q_e = \log K_F + n \log c_e \quad (4)$$

where *K<sub>F</sub>* and *n* were Freundlich constants related to adsorption capacity and adsorption intensity derived from the linear slope of log *q<sub>e</sub>* versus log *c<sub>e</sub>*.

**Dubinin-Radushkevich (DR) isotherms:** Dubinin-Radushkevich (DR) is generally expressed as follows equations (5), (6)

$$\ln q_e = \ln X_m - K_{DR} \epsilon^2 \quad (5)$$

$$\epsilon = RT \ln (1 + 1/c_e) \quad (6)$$

where *X<sub>m</sub>* theoretical isotherm saturation capacity (mg g<sup>-1</sup>); *K<sub>DR</sub>* Dubinin-Radushkevich isotherm constant. This constant is related to the average free energy of adsorption per mole of adsorbate. This constant is related to the average free energy of adsorption per mole of adsorbate. This energy can be calculated using the following relationship eq. (7);

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (7)$$

*E*; the mean sorption energy (kJ/mol).

## Results and discussion

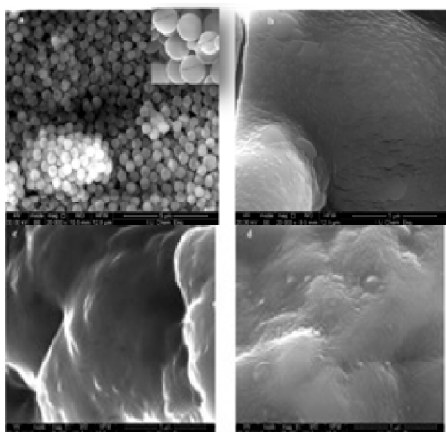
### Characterization:

**SEM of hollow silica spheres (HSS):** The surface structure of the resulting hollow silica spheres is shown as in Fig. 3. Particle size of the spherical structures are between 600 nm and 500 nm.

**SEM of gum arabic modified (HSEPCGUM):** The surface of gum arabic modified hollow silica sphere is shown as in Fig. 3. Between gum arabic and silica was monitored no phase separation and homogeneous distribution of silica phase was defined in gum arabic.

**SEM of basic blue 3 (BB3)/gum arabic modified hollow silica sphere (HSEPCGUM-BB3):** BB3 loaded on the surface of gum arabic modified hollow silica sphere showed difference as seen in Fig. 3. The surface of HSEPCGUM was deformed by BB3 dye and the dye is penetrated into the surface of adsorbent.

**SEM of reactive blue 21 (RB21)/gum arabic modified hollow silica sphere (HSEPCGUM-RB21):** Fig. 3 shows that the surface of HSEPCGUM was deformed with RB21 dye



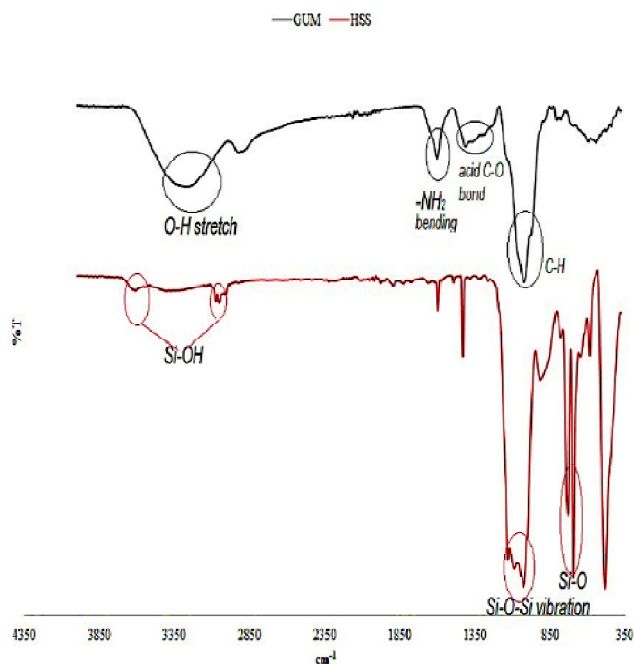
**Fig. 3.** SEM image of (a) HSS, (b) HSEPCGUM, (c) HSEPCGUM-BB3 and (d) HSEPCGUM-RB21 (mag. 20 000 x).

but RB21 is superficial adsorption onto the surface of adsorbent.

**FTIR characterization:** For FTIR of HSS, Si-O-Si bond peaks belonging to structure of phenyltrihydroxylsilane are in the range of 1116–1019  $\text{cm}^{-1}$ . Also, Si-O peaks band to the phenyl structure were observed between 726 and 694  $\text{cm}^{-1}$ , as seen in Fig. 4. For FTIR of GUM, O-H peaks between 3300–3200  $\text{cm}^{-1}$  were observed. -NH<sub>2</sub> bending of amine groups of hydroxyproline-rich glycoprotein is observed at 1590  $\text{cm}^{-1}$ . The symmetrical stretching C-O and O-H band peaks of glucuronic acid in gum arabic structure was observed respectively 1420 and 1325  $\text{cm}^{-1}$ . C-H peaks between 1020 and 1010  $\text{cm}^{-1}$  belonging to structure of polysaccharide is seen as in Fig. 4.

**For FTIR of HSEPCGUM:** -NH<sup>+</sup> amine structure observed in the form of double peak at 1650–1590  $\text{cm}^{-1}$  because of result of opening to the epoxy ring of HSEPC. Also, reaction of HSEPC with zwitterionic hydroxyproline was observed by C=O stretching band belonging to conjugate ester at 1740  $\text{cm}^{-1}$ , as seen in Fig. 5.

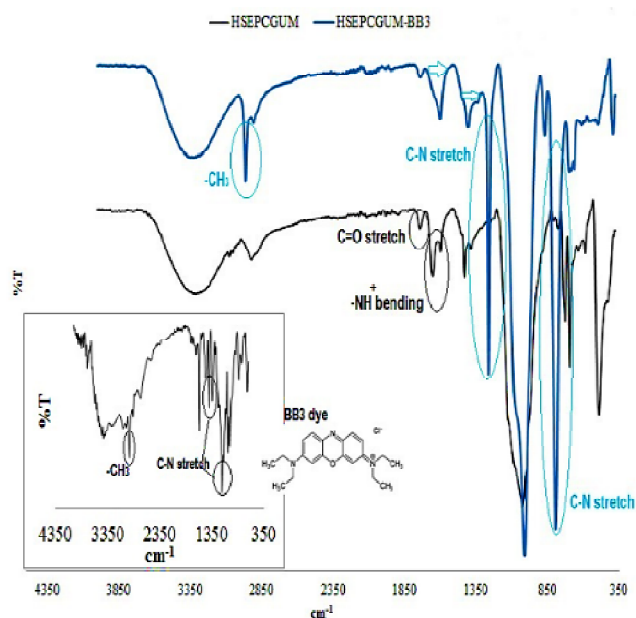
**For FTIR of HSEPCGUM-BB3:** The BB3 dye have the CH<sub>3</sub> functional group bands at 2970–2870  $\text{cm}^{-1}$  and the C=N stretching bands at 1590  $\text{cm}^{-1}$ . The aryl C-N and alkyl C-N stretching bands peaks of BB3 were observed respectively, 1340–1267  $\text{cm}^{-1}$  and 1150–1000  $\text{cm}^{-1}$ , as seen in Fig. 5 (small Figure). The C-O peak belonging to glucuronic acid in HSEPCGUM structure expanded towards 1400  $\text{cm}^{-1}$ . The C-N conjugate strong band was observed at 1257  $\text{cm}^{-1}$ . It



**Fig. 4.** Image of FTIR.

supposed that BB3 can be connected to the C-N bond with C-O symmetric stretching band belonging to glucuronic acid (HSEPCGUM), as seen in Fig. 5.

**For FTIR of HSEPCGUM-RB21:** The N-H stretch of RB21



**Fig. 5.** FTIR spectrum of gum arabic/hollow silica sphere/dye (HSEPCGUM-BB3).

amine ring appears at  $3315\text{ cm}^{-1}$ . -NH bond peak appears at  $1590\text{--}1480\text{ cm}^{-1}$ . S=O tension and S-O tension of sulphonate structure appear at  $1114\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$ , respectively. S=O tension of sulfoxide acid appears at  $1025\text{ cm}^{-1}$ , as seen in Fig. 6 (small Figure). For HSEPCGUM, C-H peaks belonging to structure of polysaccharide between  $1020$  and  $1010\text{ cm}^{-1}$  is seen as in Fig. 6. After adsorption, peaks of RB21 were quite small. It supposed that S-O and S=O group belonging to RB21 can be linked to C-H bond from polysaccharides group of HSEPCGUM, as seen in Fig. 6.

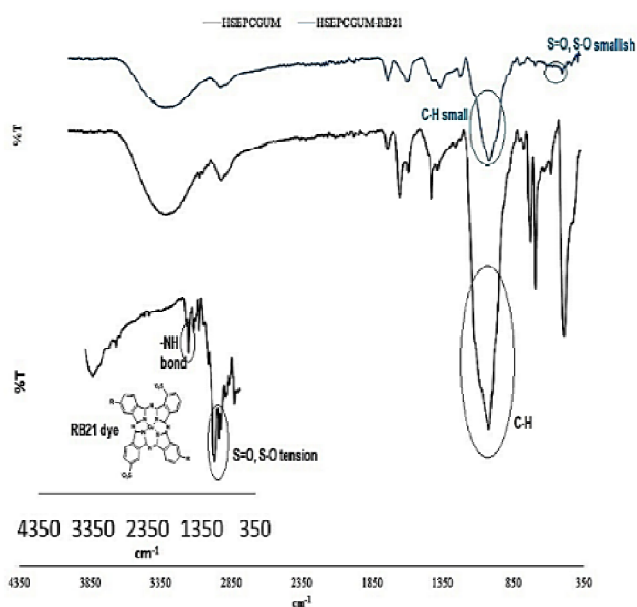


Fig. 6. FTIR spectrum of gum arabic/hollow silica sphere/dye (HSEPCGUM-RB21).

## Conclusions

It can be implied that BB3 was linked to C-N bond with C-O symmetric stretching band belonging to glucuronic acid in HSEPCGUM. C-O<sup>-</sup> bond belonging to zwitterionic hydroxyproline or glucuronic acid is formed by C=N<sup>+</sup> bond belonging to cationic dye a strong ionic bond. As a result, between imine groups (C-N) and the carboxyl groups (C-O) in HSEPCGUMBB3 is formed ionic structure. It can be suggested that, S-O and S=O group belonging to RB21 was connected with C-H bond from polysaccharides group of HSEPCGUM. C-H bond of polysaccharides group in HSEPCGUM is formed a weak hydrogen bond with S-O and S=O group belonging to anionic dye. Hydrogen bonds were

happened between sulphonate and sulfoxide acid bonds of RB21 and polysaccharides belonging to HSEPCGUM. As is known, the ionic bond is stronger than the hydrogen bond. Therefore, the adsorption of basic blue 3 that is called cationic dye has been quite strong on HSEPCGUM. Compared to other studies, the adsorption time of HSEPCGUM is very fast for the basic dye (BB3).

The  $n$  value for BB3 was found to be less than one ( $n < 1$ ). But the value of  $n$  is greater than 1 for RB21 as shown in Tables 1-2. The value of  $n < 1$  explains that binding energy decreases with increasing surface concentration and resulting in desired adsorption. The  $K_F$  is constant the adsorption capacity at Freundlich isotherm. The values of adsorption capacity ( $K_F$ ) are listed as BB3 > RB21 as seen in the Tables 1-2. Hence, it is concluded that HSEPCGUM better adsorbed basic blue 3. For the Freundlich isotherm, correlation coefficient average of adsorption of dyes is 96%. Adsorption of the dyes on HSEPCGUM is best suited to Langmuir isotherm as seen in Tables 1-2. According to these operating conditions, the highest value of  $X_{max}$  was found to be  $100\text{ mg g}^{-1}$  for adsorption of BB3 dye on  $0.01\text{ g}$  HSEPCGUM. However, for RB21 this value was found to be at least  $-1.95\text{ mg g}^{-1}$ . The  $E$  values of the Dubinin-Radushkevich isotherm are also shown in the Tables 1-2. For BB3, average free energies of adsorption per mole of adsorbate ( $E$ ) were calculated for  $0.01\text{ g}$ ,  $0.02\text{ g}$ ,  $0.05\text{ g}$  doses of adsorbent, respectively  $9.13$ ,  $8.99$  and  $3.95\text{ kJ mol}^{-1}$ . For RB21, these values were calculated the same doses of adsorbent, respectively  $5.98$ ,  $5.59$  and  $7.89\text{ kJ mol}^{-1}$ . Values of average free energy of adsorption per mole of adsorbate ( $E$ ) is between  $10$  and  $4\text{ kJ mol}^{-1}$ . It can be understood, between the dyes and HSEPCGUM is observed physical adsorption for these values. Weak Van der Waals forces are effective between adsorbent and adsorbate molecules. The adsorbed layer can be single or multi-layer. Also, the mean free energy was calculated as BB3 > RB21 for  $0.01$ ,  $0.02$ ,  $0.05$  grams of adsorbent dose.

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