



# Modification of Rice straw via Polyelectrolyte Layer-by-Layer Assembly for high performance Dye adsorption

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## Abstract

*Dyes released from industrial textile processing constitute major problems into the environment. Rice straw is one of agricultural plant wastes in Egypt affects the public health. In the present work, layer by layer self-assembly of Polydiiallyldimethylammonium chloride (PDADMAC)/ poly lignin sulphonat (PLS) was designed on the surface of rice straw (RS) in the presence and absence of nano-SiO<sub>2</sub>. Removal of anionic dyes from aqueous solutions by the modified rice straw (MRS) was investigated. The adsorption experiments were carried out as function of MRS dosage, contact time and dye type. The results showed that the presence of nano-SiO<sub>2</sub> between the multilayers decreases the resistance of the boundary layer surrounding the adsorbent and increased markedly the efficiency of color removal by accelerating the adsorption process. Zeta potential indicates the existence of positive-charge functional groups in the framework of MRS. The amount of adsorbed dyes was greatly influenced by molecular structure of the dyes. The highest color removal percentage was approximately 95%, provided strong evidence of the potential of MRS for the technological applications of anionic dyes removal from aqueous solutions.*

**Keywords:** Modified rice straw (MRS), polyelectrolyte layer by layer, nano-sio<sub>2</sub>, anionic dyes, adsorption.

## Introduction

Rice is one of the most abundant crops in Egypt. It is mainly cultivated in the northern east part of the country<sup>1,2</sup> especially in Kafr El-Sheikh, Al-Sharkia and Al-Dakahlia governorates. Processing of rice in Egypt yields large amounts of rice straw as residue. Rice straw residue (20%) was used for other purposes such as ethanol, paper and fertilizers production as well as fodders<sup>2</sup>. Field burning is the major and cost effective method to get quickly rides of the remaining part within a period of 30 days"<sup>3</sup>. The resulting emission significantly increases and contributes to the air pollution called the "Black Cloud, and consequently affects the public health". Many counties in Western Europe have already banned open field burning and some other countries have considered it seriously. Where, biomass burning has drawn global concerns for its effects on visibility, health and global climate by emitting particulate matters and other gaseous pollutants<sup>4</sup>.

The presence of dyes in water, even at very low concentrations, causes environmental problems in natural ecosystems since they are visible pollutants. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. Many dyes are difficult to degrade, as they are generally stable to light, oxidizing agent and are resistant to aerobic digestion. Hence, extensive use of dyes poses not only a severe public health concern, but also many serious environmental problems due to their persistence in nature and non-biodegradable characteristics<sup>5</sup>. In general, there are four main methods for reducing color in the textile effluent streams: chemical methods

such as coagulation; physical methods such as membrane technology; biological methods such as anaerobic / aerobic sequential processes; photochemical oxidation and physicochemical processes. Among the physicochemical processes, adsorption technology methods was considered to be one of the most effective technology which have a potential application in both water and wastewater treatment<sup>6</sup>.

Plant wastes are inexpensive as they have no or very low economic value. Most of adsorption studies have been focused on unwanted plant wastes such as rice straw<sup>7,8</sup>, sugarcane biomass<sup>9</sup>, maize tassels<sup>10</sup>, coriandrum sativum<sup>11</sup>, almond tree leaves<sup>12</sup>, coconut shell<sup>13</sup>, neem leaves<sup>14</sup> and rise husk ash<sup>15</sup>, bark and sawdust<sup>16</sup>, maize cobs<sup>17</sup>, and wheat barn<sup>18</sup>. Some of the advantageous of using plant wastes for waste water treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration<sup>7</sup>.

Conversion of RS as one of the agricultural plant wastes (about 45% of the volume of rice production) to valuable industrial product was achieved, by grafting different amounts of dimethylaminoethyl methacrylate (DMAEM) on it using potassium permanganate/nitric acid redox system<sup>7</sup>. The latter could become active metal scavenger for heavy toxic divalent cations such as Cu, Pb, Cd and Hg ions contaminated in water as well as efficient acid dyes removal. The metal solution should not to be acidic, for effective metal removal. Raising the levels of grafting, metal scavenging activity of the co- polymer

could be increased up to the level required for industrial application.

The synthesis of partially carboxymethyl cellulose derived from rice straw and its utilization as dye adsorbent has been investigated. The study showed that the rate of dye absorbance increased by increasing the amount of adsorbent as well as the time of adsorption. The magnitude of color removal in case of using ultrasonic technique is relatively higher than the mechanical shaking irrespective of the nature of the dye used and/or the conditions of absorbance.

In continuation of the above study, native raw rice straw, alkali treated (scoured) and scoured/bleached rice straw pulp have been chosen as dye adsorbents for some selected reactive dyestuffs<sup>8</sup>. Also, the magnitude of dye adsorption in case of ultrasonic technique is relatively higher than the mechanical shaking. Besides, the bleached rice straw acquired highest affinity for dye adsorption. The two studies gave a maximum color removal of 70%.

In this context, the agricultural waste rice straw was also employed as adsorbent to remove Malachite green (N-methylated diamino triphenyl methane) from their aqueous solutions<sup>19</sup>. Malachite green was a green menace, is extensively being used as dye for coloring silk, leather and paper. It is carcinogenic and catalyzes allergic problems. The results indicate that the rice straw was effective and has a higher sorption capacity for the removal of Malachite green reached more than 87.27% at concentration of 50 mg/L and at pH 8.

In this paper, we reported our preliminary investigation for the performance of modified rice straw (MRS) as an adsorbent for color removal of different reactive and acid dyes under a variety of conditions. The modification processes included: polyelectrolyte layer by layer self-assembly around the surface of adsorbents. In addition, the mono layer deposition of nano-silica between the multilayers of polyelectrolytes was the other chemistry we are carried to increase the dispersion ability of adsorbents in waterborne media. To our knowledge, there is no research on using the layer-by-layer assembly technique to coat RS and also there are no reports on using the nano-silica particles between the multilayers.

## Material and Methods

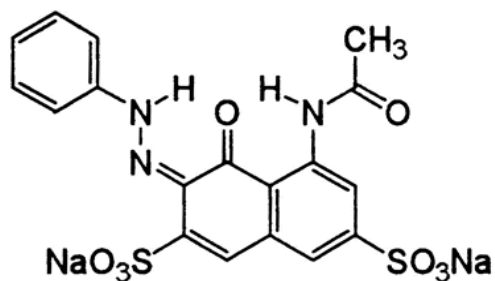
**Materials:** RS used in this study was supplied from Racta Co. for paper manufacture, Alexandria-Egypt. They were cut into segments of 5 cm length, washed with water to remove soil and dust, and then dried in oven at 60 °C for 6hr. Polyelectrolytes: Polydiallyldimethylammonium chloride (PDADMAC Mw < 200,000) and poly lignin sulphonat (PLS) were obtained from Aldrich. The dyes used in this work were: CI Reactive Orange 91 (RO91), CI Acid Red 1 (AR1), CI Reactive Yellow 145 (RY145), CI Reactive Red 4 (RR4), CI Reactive Red 195 (RR195), Reactive Violet 5 (RV5) and CI Reactive Blue 19 (RB19). These dyes as shown in (figure-1) were kindly supplied by Ciba Company-Egypt and were used as received. Nano

silicone dioxide (10-20 nm) was purchased from Aldrich, USA. All these ingredients were used without further purification and all other chemical reagents were of laboratory grade.

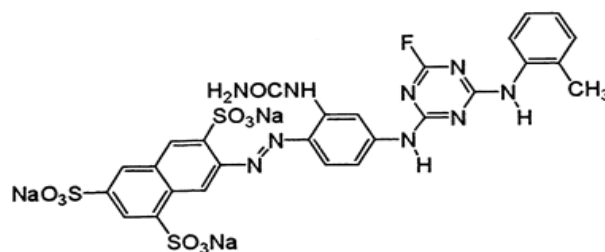
**Methods: Purification of rice straw:** The raw RS was grinded well in a mill. The grinded R.S. was then washed with water and dried at 100°C. Further, the washed rice straw was treated with a sodium hydroxide aqueous solution of 2% (w/w) for 4 h at 100 °C under mechanical stirring, washed several times with distilled water until the alkali was completely removed, and finally dried at 50 °C for 12 h in an air-circulating oven<sup>20</sup>. After this treatment, the material was bleached with a solution of hydrogen peroxide (5g/L of 45% hydrogen peroxide) and sodium silicate (3g/L). The pH was adjusted to 10.5 using aqueous sodium hydroxide solution and the bleaching process was carried out at a liquor ratio 1:20 at a temperature of 95 °C for 30 min under mechanical stirring and finally washed several times with distilled water until the alkali was completely removed then, dried at room temperature<sup>21</sup>.

**Polyelectrolyte Layer by Layer -assembly coating of RS materiel:** The purified RS is first dispersed in deionized water and then magnetically stirred for about 20 min with 1 g/L of PDADMAC as a polycations. The excess polycations was removed by washing several times with deionized water, and then dried at 60 °C. The positively charged RS materials are subjected to deposition of multilayer polyelectrolyte films by polyanions deposition using 1 g/l PLS which are deposited onto the surfaces of the precoated cellulosic materials by adding 1.7g/l NaCl. After 20 min adsorption, excess PLS was removed by washing with deionized water followed by drying. Additionally, the repetition of the above steps leads to the formation of the polyelectrolyte multilayer on the surfaces of cellulosic waste according to experimental demand. This film could provide a uniformly charged surface and facilitate subsequent nanoparticle adsorption. The outer layer is always Polycation, thus making the coated RS materials positively charged<sup>22</sup>. The MRS was designated as PE<sub>i</sub> in which i indicate the number of polyelectrolyte layers.

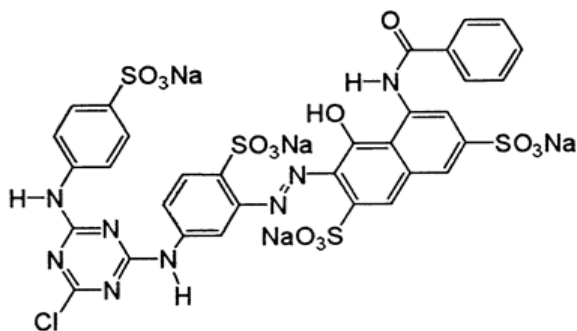
**Preparation of cellulosic materials Coated with Nano- Silica oxide:** After depositing multilayer polyelectrolyte films on MRS materials and the outermost surface layer will be always PDADMAC, thus making the coated particles positively charged, nano-SiO<sub>2</sub> particles are adsorbed on the surfaces of the cellulosic materials by adding the SiO<sub>2</sub> aqueous solution to the suspension of the precoated cellulosic material particles. The nano particles were allowed to adsorb for 20 min under continuous stirring, and then the excess nano-SiO<sub>2</sub> was removed by deionized water dispersion then drying. The electrostatic interaction between the negatively charged silica nanoparticles and positive PDADMAC utilized to build up the nanocomposite multilayers. The mono layer silica shell precoated the cellulosic materials was subjected to PDADMAC mono-layer deposition for outermost positive charges demand. The silica-coated RS were designated as PE<sub>i</sub>-SiO<sub>2</sub>.



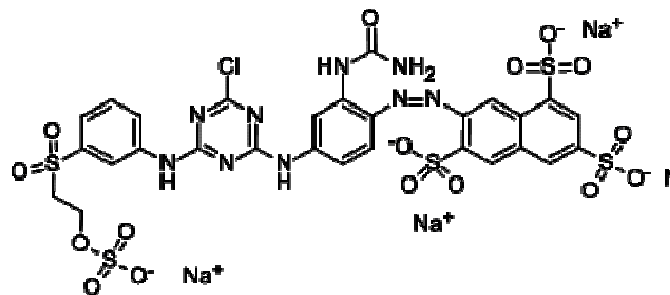
C.I. Acid Red 1



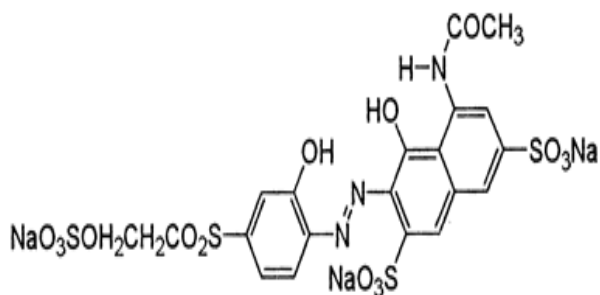
C.I. Reactive Orange 91



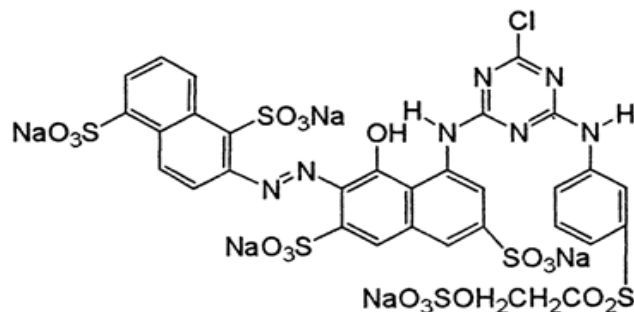
C.I. Reactive red 4



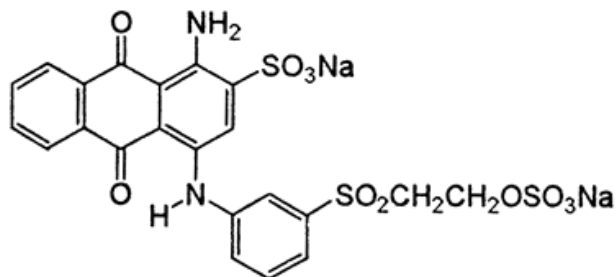
C.I. Reactive yellow 145



C.I. Reactive Violet 5



C.I. Reactive Red 195



C.I. Reactive Blue 19

Figure-1  
Chemical structures of acid and reactive dyes

**Characterization of MRS:** The nitrogen percentage of the crude or raw and MRS was determined by the Kjeldahl method<sup>23</sup>. Zeta potential measurements were carried out using Nano ZS (Malvern, UK) to determine the zeta potential of MRS and RS. The MRS and RS particles in the sediment phase were dispersed into the distilled water before determination. Cellulose percentage was performed by using by the quantitative method<sup>24</sup>. The ground raw and multi layers polyelectrolyte RS (1g from each) was placed in an oven at 105 °C for 24 hrs. Then, the moisture was evaporated to a constant weight of the sample. The dried samples were cooled and weighted, air-dried to low moisture content and the cellulose percent of RS samples was then determined. The morphology of crude or raw and MRS were characterized using a scanning electron microscope (SEM), Model Philips XL 30 with an EDX unit attached, with accelerating voltage of 30 kV and magnification between 10x up to 400.000x. All the samples were coated with gold before SEM testing.

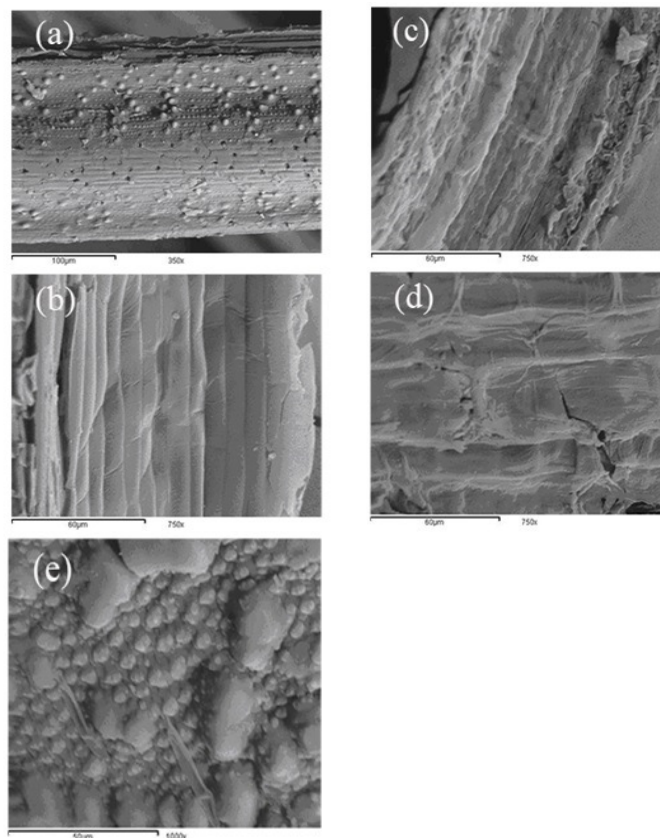
**Adsorption studies:** Aqueous solutions of dyes were prepared by dissolving a constant dye concentration (500 mg/l) in distilled water. The pH of the solutions was adjusted to 8 in case of reactive dye and pH= 4 in case of acid dye. The MRS (1 - 20 g/l) was then added to the dye solution (100 ml). The dispersion was shaken for different intervals of time ranging from 30-180 min at room temperature (26 °C ± 0.5 °C) with constant stirring at 400 rpm. The colored rice straw adsorbent was then removed by filtration and the filtrate was used to evaluate the dye concentration calorimetrically using UV-Vis Shimadzu Spectrophotometer at the maximum wavelength of each dye used. The color removal % of each dye was calculated from the following formula<sup>8, 25-26</sup>:

$$\text{Color removal \%} = [(A_0 - A_t)/A_0] \times 100 \quad (1)$$

Where:  $A_0$  is the initial dye absorbance and  $A_t$  is the final dye absorbance of the dye solution after time  $t$ .

## Results and Discussions

**Characterization of RS Coated with polyelectrolyte- nano-SiO<sub>2</sub> particles:** Since the surfaces of RS were usually negatively charged, the colloidal nano-SiO<sub>2</sub> particles obviously could not be directly adsorbed onto the surfaces of the RS. Therefore, we first used polyelectrolytes PDADMAC and PLS to be sequentially and alternatively adsorbed onto the surfaces of the RS and then coated by nano-SiO<sub>2</sub> particles. The outer layer is always Polycation, thus making MRS materials positively charged. The layer-by-layer assembly technique has been applied to fabricate the electrostatically aqueous colloidal particles adsorbed on the surfaces of charged RS for anionic dye removal. The electrostatic interaction between the negatively charged silica nanoparticles and positive PDADMAC utilized to increase dispersion ability of MRS. The original and pre-coated RS were imaged in order to evaluate the morphology and distribution of the coatings of multi layers polyelectrolyte with SiO<sub>2</sub> nanoparticle using SEM (figure-2).



**Figure-2**  
SEM micrographs of original RS (a), PE<sub>3</sub>-coated RS (b), PE<sub>4</sub>-SiO<sub>2</sub>-coated RS (c), PE<sub>5</sub>-coated RS (d), and PE<sub>6</sub>-SiO<sub>2</sub>-coated RS (e)

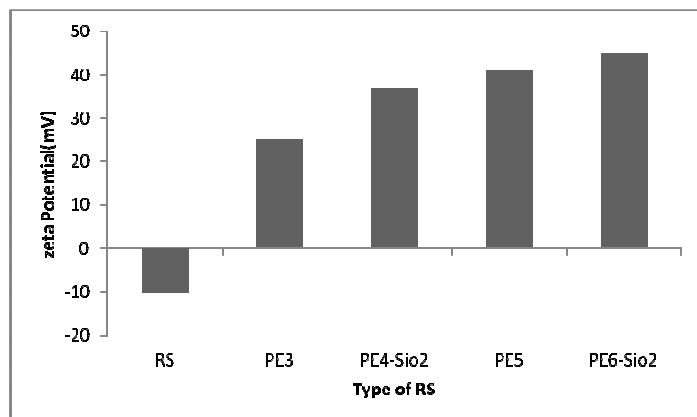
The surface of original RS clearly shows a relatively smooth and uneven surface. In contrast such characteristics completely disappeared on the surface of polyelectrolyte -pre-coated RS, where the deposition of multilayers polyelectrolyte (PE<sub>3</sub>-coated RS and PE<sub>5</sub>-coated RS) could improve the surface evenness of pre-coated RS (see figure-2 b, d). It can be also obviously seen grooves and cracks on the surfaces of PE<sub>3</sub>-coated RS and PE<sub>5</sub>-coated RS. However, there was no obvious difference in morphology between the RS deposited with different layers of polyelectrolytes. Meanwhile, deposition of SiO<sub>2</sub> between the multilayers obviously increased the surface roughness (figure-2 c,e).

The coverage of RS by nano-SiO<sub>2</sub> particles between the multilayers was sufficient for three layers of polyelectrolyte-pretreated RS (figure-2 c). Figure 2e shows the SEM image of PE<sub>6</sub>-SiO<sub>2</sub>. Clearly, more nano-SiO<sub>2</sub> particles were adsorbed onto the surfaces of MRS between the layers compared with PE<sub>4</sub>-SiO<sub>2</sub> and had a relatively rougher surface.

The cellulose percentage which is the main polycation sites was determined according to Jayme method<sup>24</sup>. The contents of the cellulose % were 41.69 % and 38.92 %, for raw rice straw and purified or bleached rice straw respectively. The mass loss of

cellulose % during the purification or bleached process can be related to two factors: (i) the breakdown of cellulose chains during bleaching and (ii) the loss of material inherent in various filtering processes and mass transfer<sup>27</sup>.

As shown in (figure-3) the zeta potentials of RS is negative. In contrast with the RS, the zeta potential of MRS is positive, which indicates the existence of positive-charge functional groups in the framework of MRS. However, a gradual increase in zeta potential of MRS is observed with the increase of polycation layer on the surface of RS.



**Figure-3**  
Zeta potential of RS and MRS types

Table-1 displays the nitrogen content of the pre-coated multi layers polyelectrolyte RS in comparison with bleached RS. An intensive increase is observed in the nitrogen contents (0.03–0.24%) for PE<sub>3</sub> which indicates that the coating proceed efficiently and quite a number of amino groups from the polycation PDADMAC have been introduced into the framework of modified RS. Besides, a gradual increase in nitrogen content of modified RS is observed with the increase in polyelectrolyte layer. This result may be attributed to the polycation layer dependent amino groups existing in modified RS. The polycation coating will exhibit an increase of the

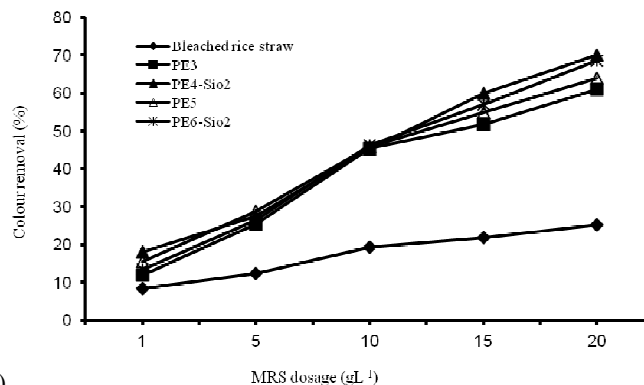
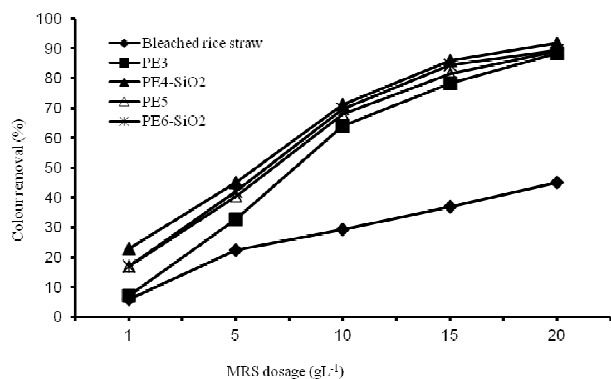
number of amino groups, which results in the increase in the nitrogen content of modified RS. It seems likely that the assembly of SiO<sub>2</sub> between the layers of polycations has no effect on the magnitude of nitrogen content, but increases the deposited quantity of PDADMAC was located at the outermost layer of MRS. Therefore, the nitrogen content of MRS will increased. Also, the results show that the deposition of nano-SiO<sub>2</sub> between PE<sub>3</sub> and PE<sub>4</sub> and between PE<sub>5</sub> and PE<sub>6</sub> dramatically increases the nitrogen content from 0.24% to 0.47% and from 0.51% to 0.68% respectively. This may be attributed to the presence of nano-SiO<sub>2</sub> between the layers changes the MRS from sediment phase to dispersed phase which, increased polycation uptake in the outermost layers and nitrogen content.

**Table -1**  
Nitrogen percent of bleached and multi-polyelectrolyte layer rice straw adsorbents

Adsorbents	<sup>a</sup> N %
Bleached rice straw	0.03
PE <sub>3</sub>	0.24
PE <sub>4</sub> -SiO <sub>2</sub>	0.47
PE <sub>5</sub>	0.51
PE <sub>6</sub> -SiO <sub>2</sub>	0.68

a. Average of three determinations

**Effect of modified RS dosage on the colour removal %:** The effect of MRS dosage at various modifications on the color removal of RO91 and AR1 was studied by varying the concentration of the adsorbent from 1 to 20 g l<sup>-1</sup> while using keeping the other experimental conditions constant. The percentage of color removal of RO91 and AR1 versus MRS dosage is shown in (figure-4). The results indicate that, the percentage of color removal increased with increasing MRS dosage which was observed in both two dyes (figure-4 a, b), regardless of the type of modification. This may be due to the availability of more electrostatic positive charge at the outermost layer for anionic dye adsorption at higher MRS dosage.



**Figure-4**  
(a) C.I. Reactive Orange 91 (RO91) and (b) C.I. Acid Red 1 (AR1). Initial dye concentration: 500mgL<sup>-1</sup>; shaking time 60 min and pH 8 (RO91), 4 (AR1)

Effect of MRS dosage on the color removal (%) of: (a) C.I. Reactive Orange 91 (RO91) and (b) C.I. Acid Red 1 (AR1). Initial dye concentration: 500mgL<sup>-1</sup>; shaking time 60 min and pH 8 (RO91), 4 (AR1)

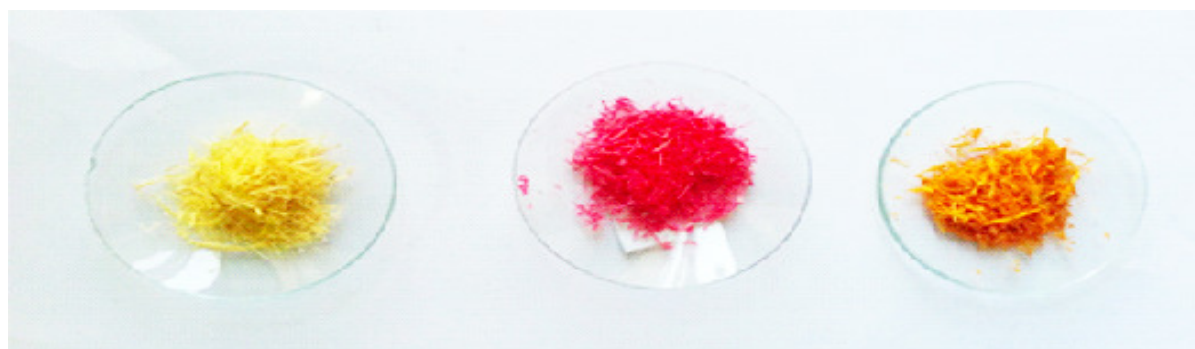
Along with the increase of adsorbent dosage of PE<sub>3</sub> from 1-20 g/L the percentages of dye removal increase from 7.10 to 88.40 % and from 11.95 to 60.94% in RO91 and AR1, respectively. Generally, in all cases the MRS is more effective for RO91 removal than AR1. As shown in figure-1, the number of the sulphonic groups (-SO<sub>3</sub>H) in the dye structure which are the adsorbent site for electrostatic adsorption plays an important role in the color removal of dyes. This may give an explanation for the higher degree of color removal for RO91 (contains three -SO<sub>3</sub>H groups) than AR1, which contains two groups of -SO<sub>3</sub>H. The assembly of nano-SiO<sub>2</sub> between the layers of polycations promoted markedly the efficiency of color removal, irrespective of the type of dye. It is clear that the presence of nano-SiO<sub>2</sub> enhances greatly the color removal. Based on the color removal (%) in the presence of nano-SiO<sub>2</sub> between the layers of polycations as was illustrated in PE<sub>4</sub> - SiO<sub>2</sub>, the highest enhancement (%) for both dyes at 20 g/L was RO91(91.83) and AR1(70.0). At 20 g/L of modified RS, the highest degree of color removal was achieved in the case of the RO91 in the presence of PE<sub>4</sub> - SiO<sub>2</sub>, while the lowest color removal was in the case of the AR1 in the absence of nano-SiO<sub>2</sub> using PE<sub>3</sub>. The enhancement of color removal in presence of nano-SiO<sub>2</sub> between the layers may largely depend on the increase in electrostatic interaction between the functional groups on the adsorbent surface sites and the color. This may be also a result of the increase in dispersion ability and surface area of adsorbent due to the presence of nano-SiO<sub>2</sub> which in term may decrease the resistance of the boundary layer surrounding the adsorbent so that the transfer of color in the boundary layer increases<sup>5</sup>. Schematic prototype of adsorption of acid and reactive dye on the modified rice straw was illustrated in (figure-5).

**Effect of contact time on the colour removal %:** The adsorption processes were carried out for different contact times with adsorbent dose selected as 20 g/L. The results in (figure-6) indicate that the color removal % increased as the contact time increasing from 30 to 90 min, irrespective of the type of dye. However, a significant equilibrium time for both RO91 and AR1

adsorptions is observed at 120 min in the absence of nano-SiO<sub>2</sub> between the layers. The fact that the adsorption of dyes is in favor of contact time indicates that the increase in time would increase the opportunity of electrostatic interaction of the large dye ions with the outer most shell of MRS, polycation, thus enabling the large amount of dye molecules to be adsorbed. It is clear that, the further increase of contact time beyond 120 min has no significant increase of color removal % for MRS, PE<sub>3</sub> and PE<sub>5</sub>.

Furthermore, there is a clear decrease of equilibrium time (90 min) needed to reach a maximum adsorption of dye in the presence of nano-SiO<sub>2</sub> between the multi layers which are illustrated in PE<sub>4</sub> - SiO<sub>2</sub> and PE<sub>6</sub> - SiO<sub>2</sub>. Along with the increase of contact time from 30 to 90 min the percentages of adsorbed dyes on PE<sub>4</sub> - SiO<sub>2</sub> increase from 85.10 to 94.66 % and from 51.24 to 78.22 % in RO91 and AR1, respectively. However, the percentage of color removal of RO91 and AR1 on the PE<sub>4</sub> - SiO<sub>2</sub> keeps almost constant with the further increase of contact time beyond 90 min. It suggests that the adsorption equilibrium has been reached at 90 min in the presence of nano-SiO<sub>2</sub>. It is worthy to mention that the contact time supplied for 90 min is not adequate to accomplish the maximum adsorption balance of dyes on using PE<sub>3</sub> and PE<sub>5</sub>. In other word, the adsorption process is accelerated by deposition of nano-SiO<sub>2</sub> between the multi layers, which can be explained as a strong electrostatic attraction between the positively charged outer most shell, polycation and anionic dyes.

**Effect of dye type on the adsorption process:** The color removal percent of different types of reactive dyes namely Reactive Yellow 145 (RY145), Reactive Red 4 (RR4), Reactive Red 195 (RR195), Reactive Violet 5 (RV5), Reactive Blue 19 (RB19) and Reactive Orange 91 (RO91) were estimated under the optimized conditions deduced from the previous studies (figure-7). The measurement of each dye adsorbed must be at the maximum wave length of each dye which was as follows: 422, 520, 530, 575, 595, and 450 nm respectively.



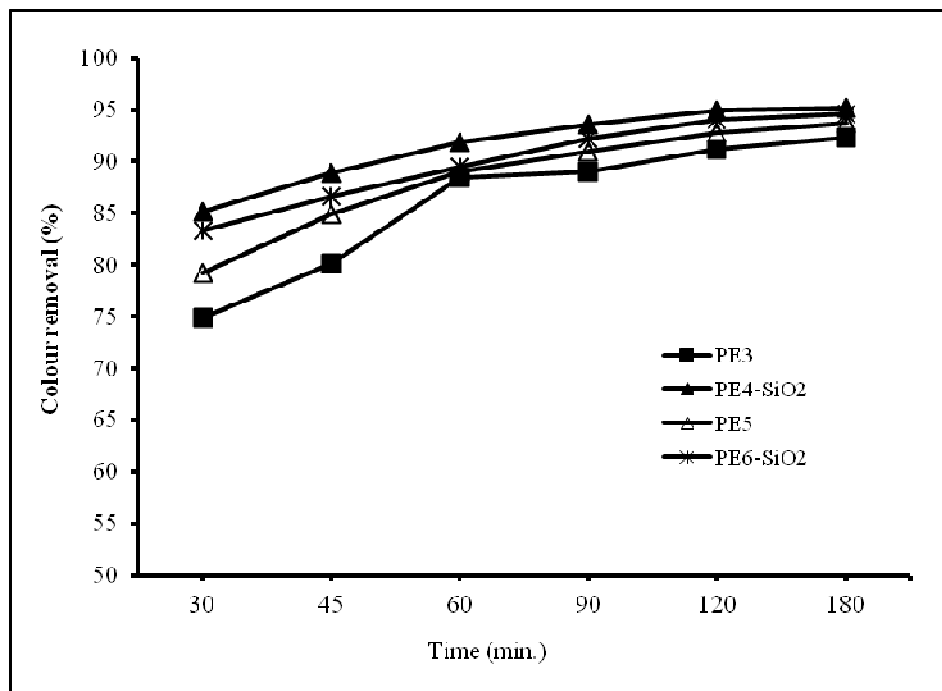
Raw rice straw

Acid dye adsorption

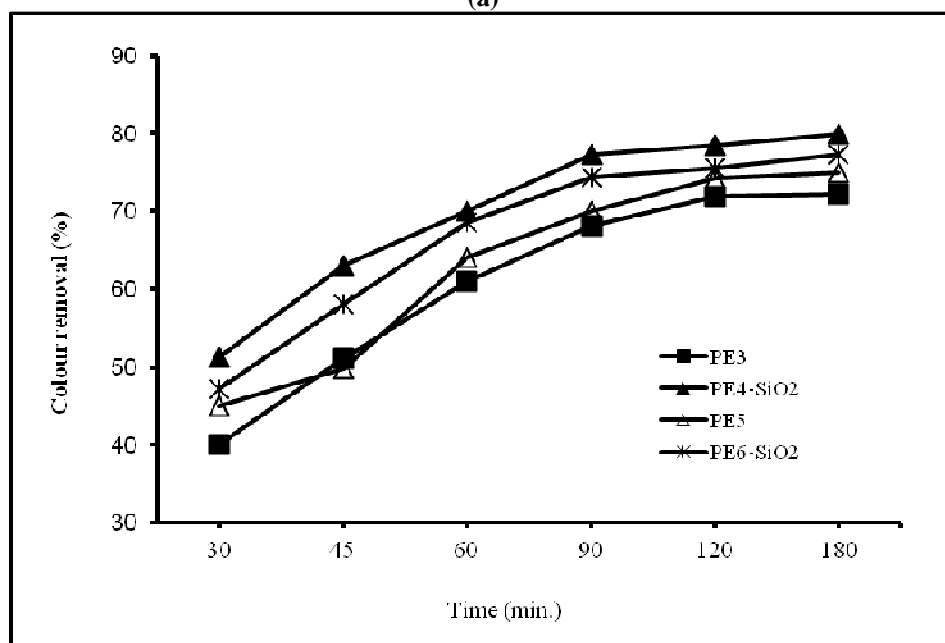
Reactive dye adsorption

Figure-5

Schematic prototype of adsorption of acid and reactive dye on the modified rice straw



(a)



(b)

Figure-6

Effect of contact time on the color removal (%) of: a) C.I. Reactive Orange 91 (RO91) and b) C.I. Acid Red 1 (AR1). Initial dye concentration:  $500\text{mgL}^{-1}$ ; MRS dosage,  $20\text{ g l}^{-1}$  and original solution pH 8 (RO91), 4 (AR1)

It was seen from (figure-7) that, the capacity of dyes removal follows the order: Reactive Yellow 145 (RY145) > Reactive Orange 91 (RO91) > Reactive Blue 19 (RB19) > Reactive Red 195 (RR195) > Reactive Red 4 (RR4) > Reactive Violet 5 (RV5) irrespective of the type of MRS. Also, the amount of dye adsorbed for all dyes in questions increased by deposition of nano-  $\text{SiO}_2$  between the multilayers of polyelectrolytes.

Moreover, acid groups, molecular size and stereochemistry of the dyes appeared to be greatly influence the amount of dye adsorbed on MRS. It seems likely that the adsorption mechanism of dyes on modified RS may be as follows: first anionic dyes were dissolved in an aqueous solution after which the sulphonate groups of anionic dyes ( $\text{R-SO}_3\text{Na}$ ) became dissociated and converted to anionic dye ions. The adsorption

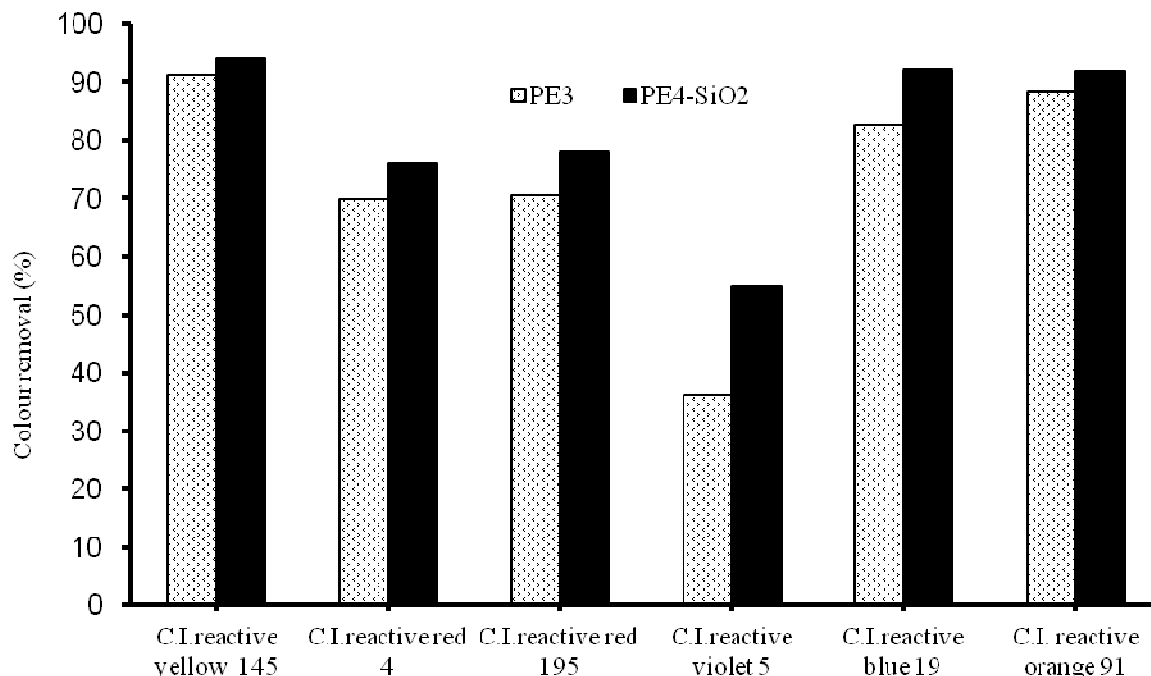
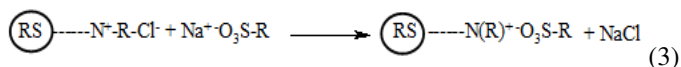
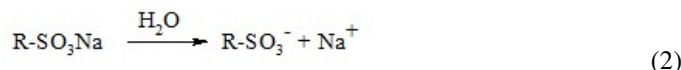


Figure 7

Effect of dye type on the color removal (%) in presence and absence of nano- SiO<sub>2</sub>. Initial dye concentration: 500mgL<sup>-1</sup>; MRS dosage, 20 g l<sup>-1</sup> and contact time 90 min.

process then proceeded due to the interaction between the anionic dye ions and the outermost shell, polycation of MRS formulated as follows:



## Conclusion

This study investigated the utilization of polyelectrolyte layer by layer self-assembly in the presence and absence of nano-SiO<sub>2</sub> for modification of the Egyptian agricultural waste, RS. The potential use of MRS as an adsorbent for removal of anionic dyes was also investigated. The highest dye removal percent, 95%, could be achieved in the presence of nano-SiO<sub>2</sub> between the multi layers which are illustrated in PE<sub>4</sub> - SiO<sub>2</sub> and PE<sub>6</sub> - SiO<sub>2</sub>. A clear decrease of equilibrium time (90 min) needed to reach a maximum adsorption of dye was also observed in presence of nano-SiO<sub>2</sub>. Moreover, acid groups, molecular size and stereochemistry of the dyes appeared to greatly influence the amount of dye adsorbed on MRS.

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