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Aminopropyl-containing ionic liquid based organosilica as a novel and efficient adsorbent for removal of crystal violet from wastewaters☆

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ABSTRACT

Herein a novel aminopropyl-containing ionic liquid based organosilica (ILOS-NH₂) is prepared, characterized and applied as effective adsorbent for removal of crystal violet (CV) dye from wastewater. The ILOS-NH₂ material was synthesized by hydrolysis and co-condensation of 1,3-bis-(3-trimethoxysilylpropyl)-imidazolium chloride (BTMSPIC) under acidic conditions followed by treatment with 3-aminopropyl-trimethoxysilane in toluene under reflux conditions. This material was characterized using scanning electron microscopy (SEM), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), thermal gravimetric analysis (TGA) and energy dispersive X-ray analysis (EDAX). The material was effectively used in the removal of crystal violet at ambient temperature and showed high capacity and stability under applied conditions. The efficacy of pH, contact time, adsorbent dose, initial dye concentration, temperature, and isotherm studies and the applicability of pseudo-first, second order and Elovich kinetic models have also been investigated.

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1. Introduction

Dye contaminants dismissed from dyestuff, textile and plastic industries have to be treated due to their emphasis on water bodies and exclusively growing public concern over their carcinogenicity and toxicity. It has been rather laborious to treat dye contaminants by conventional physical, chemical and biological methods because of their complex aromatic structures. Since, innovative treatment technologies are being considered, a lot of physical, chemical and biological treatment methods such as photocatalytic degradation, advanced oxidation, electrochemical oxidation, ultrafiltration and adsorption have been successfully applied for removal of dyes from waste waters [1–7]. It is important to note that the toxic nature of dyes has resulted in only limited success in the usage of biological treatments, moreover electrochemical methods are rather expensive and usually dependent on the concentration of contaminants. While adsorption approach is simple, economical and widely used for the dye removal under moderate conditions. In this method an efficient sorbent with characteristics of simplicity in operation, high adsorption capacity and excellent removal efficiency is employed for elimination of dyes from wastewaters [8–13]. Crystal violet (CV, Fig. 1) or gentian violet is a triaminoarylmethane dye that

has antifungal, antiseptic, antibacterial and anthelmintic properties and used as a histological stain and in Gram's process of classifying bacteria. Moreover, this dye has been found to be a mitotic poisoning agent, which is recalcitrant and carcinogenic and thus regarded as a biohazard [13]. Therefore, on the basis of environmental criteria and toxicological concerns, it is essential to remove CV dye from wastewaters before its discharge [14–18].

On the other hand, ionic liquids (ILs) are one of the most important class of organic salts which have emerged as promising media in different areas of chemical and industrial processes due to their unique properties such as high viscosity, low combustibility, negligible vapor pressure, excellent thermal stability, wide liquid range, high ability for dissolving a broad range of organic and inorganic compounds and high electrochemical window [18–20]. Moreover, these compounds are also one of the most promising sorbents that offer the specificity required to separate hazardous materials and can be the aid of recycling of the synthetic dyes, plastics and metals from wastewaters [21–29]. Despite the aforementioned advantages as the potential in fine-tuning their structure in order to enhance selectivity and the possibility of their reuse, ILs suffer from some drawbacks. These compounds are usually expensive and due to their high viscosity, their handling is often cumbersome and the corresponding reactions are limited by diffusion processes. Therefore it is economically desirable to reduce the amount of utilized ionic liquids in a typical chemical process. To overcome these restrictions, the concept of supported ionic liquid phases (SILPs) has been recently introduced. The preparation of SILPs is achieved by immobilization of ILs on both inorganic solids and organic polymer

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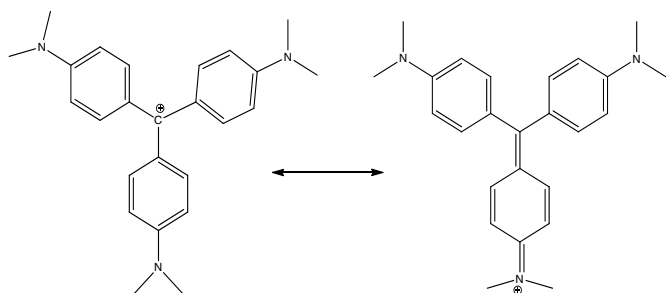


Fig. 1. Chemical structure of CV.

supports via different approaches such as simple impregnation, chemical attachment, co-condensation and encapsulation or pore trapping. Among the inorganic supports, particularly silica has the advantages of low cost and ease of preparation. Along this line, more recently we developed a new strategy for the chemical immobilization of ionic liquids via co-condensation and self-assembly of alkylimidazolium ionic liquids under moderate acidic conditions. The prepared materials were applied as capable support in a number of chemical processes and showed nice efficiency and recyclability [23,31]. In continuation of these studies, herein for the first time a novel amine-functionalized ionic liquid based organosilica (ILOS-NH₂) is prepared, characterized and successfully applied as powerful sorbent for the removal of CV dye from wastewaters (Fig. 2).

2. Experimental

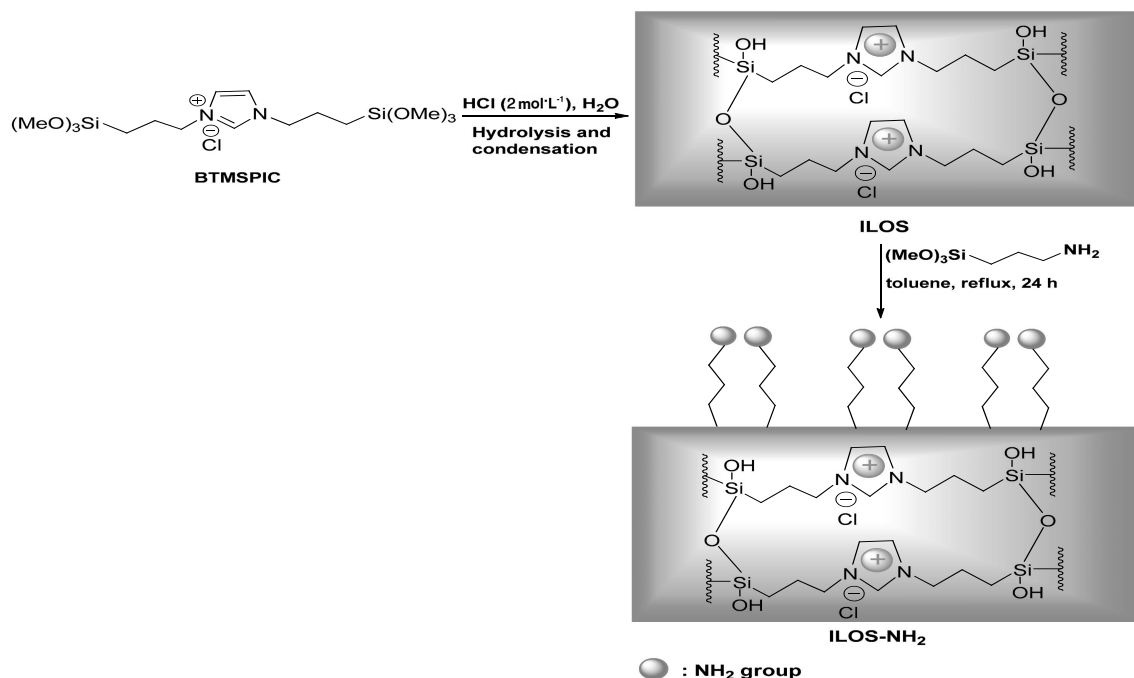
2.1. Instruments and reagents

The CV concentration evaluation was carried out using Jasco UV–visible spectrophotometer model V-530 (Jasco, Japan) at a wavelength of 590 nm, while the pH/ion meter model-686 thermometer

Metrohm was used for measurement of pH adjustment (Metrohm, Switzerland, Swiss). The morphology of the ILOS-NH₂ was taken by scanning electron microscopy model KYKY-EM 3200 (China). The diffuse reflectance infrared Fourier transform (DRIFT) spectrum was determined using a Bruker-Vector 22. Thermal gravimetric analysis (TGA) was conducted in an air flow using a Pheometric Scientific analyzer. The energy dispersive X-ray (EDX) spectra were determined using a Seron AIS 2300 (Korea). All chemicals including NaOH, HCl, KCl and Crystal violet (CV) with the highest purity were purchased from Merck (Dermasdat, Germany). The stock CV solution was prepared by dissolving appropriate amounts of solid dye in double distilled water and the desired concentrations of test solutions were prepared by diluting the stock solution. All other chemicals were used as received and purchased from Merck or Fluka.

2.2. Preparation of ionic liquid based organosilica supported propyl-amine (ILOS-NH₂)

The ILOS-NH₂ was prepared by simultaneous hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)-imidazolium chloride (BTMSPIC) under acidic conditions followed by treatment with 3-aminopropyl-trimethoxysilane (Fig. 2) [23–29]. Firstly, the 1,3-bis(3-trimethoxysilylpropyl) imidazolium chloride (BTMSPIC) ionic liquid was prepared according to our previous reported procedure with a slight modification [23–31]. Then, the BTMSPIC (50 mmol) was added in a flask containing 25 ml of deionized water and 105 ml of HCl (2.0 mmol·L⁻¹) and stirred at 35 °C for 24 h. The mixture was then heated at 100 °C for 72 h under static conditions. Next, the obtained material was completely washed with a 1:1 mixture of deionized water and ethanol solvents (4 times). The resulted sample was dried at 70 °C for 12 h and denoted as ionic liquid based organosilica (ILOS). The ILOS (1 g) was then added into a flask containing toluene (30 ml) and stirred at room temperature. After complete dispersion of the ILOS in toluene, 0.6 mmol of 3-aminopropyl-trimethoxysilane was added and it was refluxed under argon atmosphere for 24 h. After cooling the

Fig. 2. Preparation of amine-functionalized ionic liquid based organosilica (ILOS-NH₂) material.

reaction to room temperature, the resulted mixture was filtered and completely washed with ethanol. Finally, the obtained material was dried at 70 °C overnight and denoted as ionic liquid based organosilica supported propyl-amine (ILOS-NH₂).

2.3. Measurements of dye uptake

The dye concentrations in the aqueous solution were estimated quantitatively using the linear regression equations obtained at different CV concentrations. The adsorption experiment was carried out in a stirring batch mode as follows: specified amounts of dye solution at a known concentration (10 mg·L⁻¹) and initial pH of 8.0 with a known amount of adsorbent (0.05 g per 25 ml) were poured into the flask and maintained the desired stirring time (45.0 min) in temperature of (35 ± 2) °C ((308 ± 2)K). At the end of the adsorption experiments, the sample was immediately centrifuged and analyzed. The experiments were also performed in the initial CV concentration range of 10–40 mg·L⁻¹ to obtain adsorption isotherms. The amount of adsorbed dye (q_e , mg·g⁻¹) was calculated by the following mass balance relationship:

$$q_e = (C_0 - C_e) V / W \quad (1)$$

Where C_0 and C_e (mg·L⁻¹) are the initial and equilibrium dye concentrations in aqueous solution, respectively, V (L) is the volume of the solution and W (g) is the mass of the adsorbent.

3. Results and Discussion

Aminopropyl containing ionic liquid based organosilica (ILOS-NH₂) was prepared by simultaneous hydrolysis and co-condensation of 1,3-bis(3-trimethoxysilylpropyl)-imidazolium chloride (BTMSPIC) under acidic conditions followed by treatment with 3-aminopropyl-trimethoxysilane (Fig. 2) [23–31]. The ILOS-NH₂ was characterized with several techniques such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and energy dispersive X-ray analysis (EDAX).

3.1. Characterization of ILOS-NH₂

DRIFT spectroscopy was used to study the surface functional groups of ILOS-NH₂ (Fig. 3). The broad and strong bands appearing between

3400 and 3430 cm⁻¹ are corresponded to stretching vibration of O—H and N—H bonds of material surface [32,33]. The bands at 1133 cm⁻¹, 1041 cm⁻¹ and 925 cm⁻¹ are respectively assigned to the asymmetric stretching vibration, symmetric stretching vibration and bending vibration of the siloxane (Si—O—Si) groups [34]. Moreover, the absorption peaks of other organic functional groups are observed at 3137 cm⁻¹ (for unsaturated C—H stretching), 3090, 2931 and 2881 cm⁻¹ (aliphatic C—H stretching), 1652 cm⁻¹ (C=N stretching of imidazolium ring), 1557 cm⁻¹ (C=C stretching of imidazolium ring), 1453 cm⁻¹ (C—H deformation vibrations), 773 cm⁻¹ (for C—Si stretching vibrations) and 455 cm⁻¹ (bending vibration of Si—O—Si), respectively [23–29,35–37]. The N—H bending vibration is also observed at 684 cm⁻¹. These data confirm successful incorporation and/or immobilization of ionic liquid and aminopropyl organic groups onto/into material network. The results of energy-dispersive X-ray (EDX) spectroscopy elemental microanalysis of the ILOS-NH₂ before the adsorption of dye showed the presence of carbon, nitrogen, oxygen, silicon and chlorine in nanoparticles of the material (Fig. 4a). After adsorption of CV, the intensity of carbon and nitrogen peaks, corresponding to dye molecule, are increased (Fig. 4b). These observations strongly confirm the successful adsorption of the CV molecules onto/into the ILOS-NH₂ material.

Thermal gravimetric analysis (TGA) of the ILOS-NH₂ was next carried out to investigate thermal stability of the material (Fig. 5). This showed three mass losses in different temperature ranges. The first one (9.70%) observed at temperature below 130 °C, can be attributed to the removal of water and methanol or ethanol solvents retained from synthesis process on the ILOS-NH₂ surface and/or occluded in the micro- or mesopores of the material. The second mass loss (19.23%) observed at the range of 280–360 °C is attributed to propylamine groups and that part of ionic liquid moieties which are located in the surface of the material. The third and main mass loss (36.31%) that took place between 360 and 660 °C is corresponded to the ionic liquid moieties incorporated in the body of the solid network. These data are in good agreement with DRIFT and EDX analyses and significantly confirm the successful supporting of aminopropyl and ionic liquid groups in the solid framework as well as prove high thermal stability of the material. The scanning electron microscopy (SEM) image of the ILOS-NH₂ was taken to study the surface morphology of the material (Fig. 6). This showed the presence of spherical particles with high pores available on the surface and size distribution about 45–75 nm for the ILOS-NH₂. These types of particles and pores make the material as efficient candidate for dye sorption.

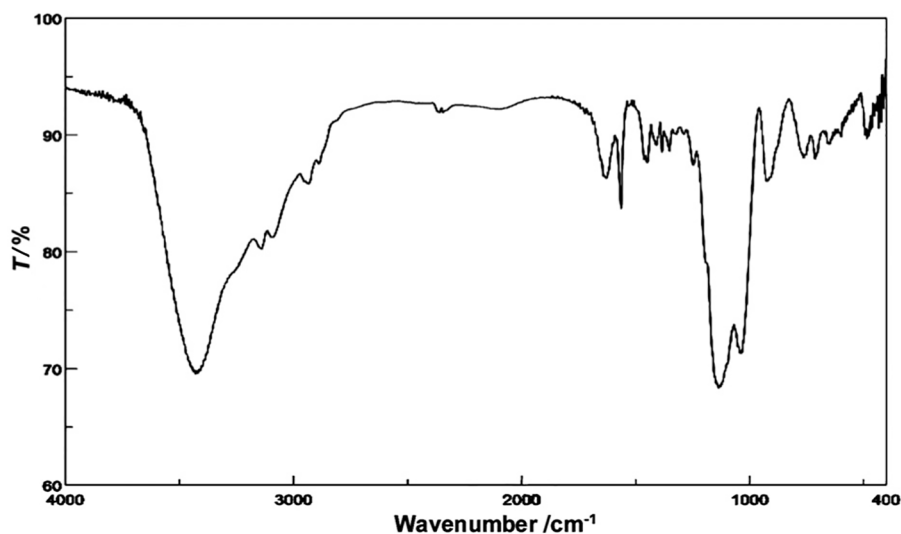


Fig. 3. DRIFT spectrum of ILOS-NH₂.

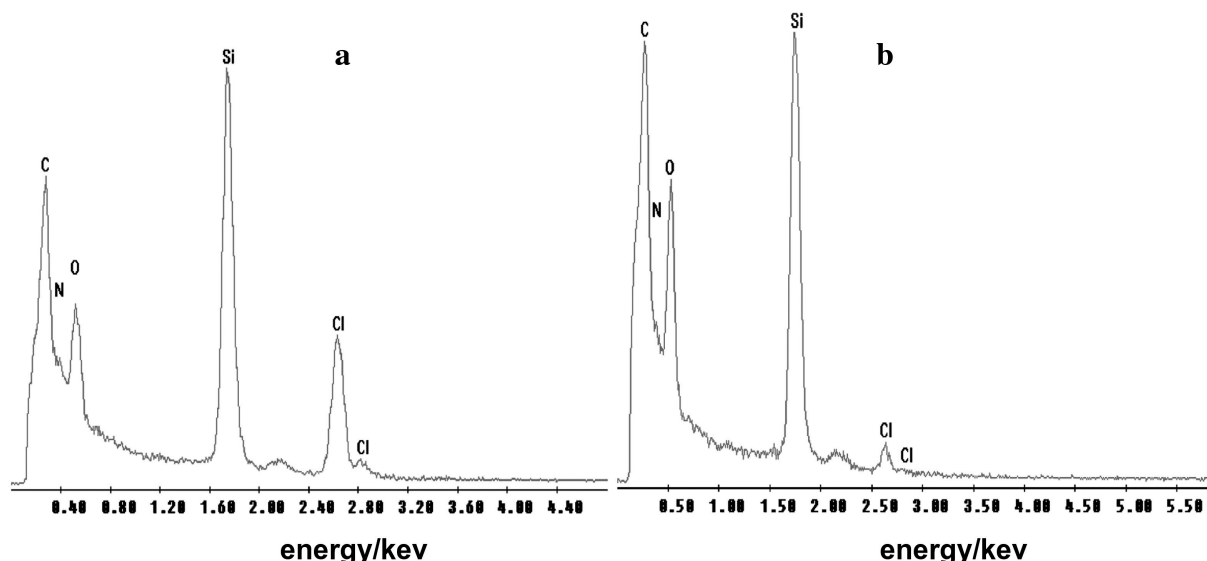


Fig. 4. Energy dispersive X-ray (EDX) spectroscopy of the ILOS-NH₂ (a) before and (b) after the adsorption of CV.

3.2. Effect of pH

The pH value of the dye solution has been recognized as an important factor in adsorption process, which influences not only the surface charge, the dissociation of functional groups on the active sites, the degree of ionization of the adsorbents, but also the dye chemistry [15,46]. Solution pH affects the functional groups present in ILOS-NH₂. Sorption of CV as a function of pH was studied over a pH range of 4–10 with CV concentration of 10 mg·L⁻¹ and adsorbent dose of 0.05 g per 25 ml. The experiments were conducted for 45 min of contact time in temperature of (35 ± 2) °C (308 ± 2)K. Fig. 7a shows the effect of pH on the sorption of CV. As can be seen, the maximum uptake and removal of the CV was obtained at pH 8.0. Therefore, all subsequent studies were carried out at pH 8.0 as optimum pH. It was observed that

the elimination of CV increases with increasing pH. At initial pH lower than 8.0, as a result of protonation of the OH and NH₂ functional groups, the ILOS-NH₂ surface gets positively charged and there would be a strong repulsion forces between the cationic dye molecules and ILOS-NH₂ surface, this would in turn decrease the sorption at lower pH values. On the other hand, high pH leads to deprotonation of the active adsorption sites on the ILOS-NH₂ surface, so the negatively charged sites dominate which results in an increase in the attraction forces and therefore increase the adsorption. Accordingly, it can be concluded that the adsorption of CV molecules is achieved via hydrogen bonding interactions between Si—OH and NH₂ groups of the ILOS-NH₂ with NH₂ groups of CV molecules. The effective π - π interactions between imidazolium ring of sorbent and aromatic rings of CV are additional ways for this successful adsorption (Fig. 8).

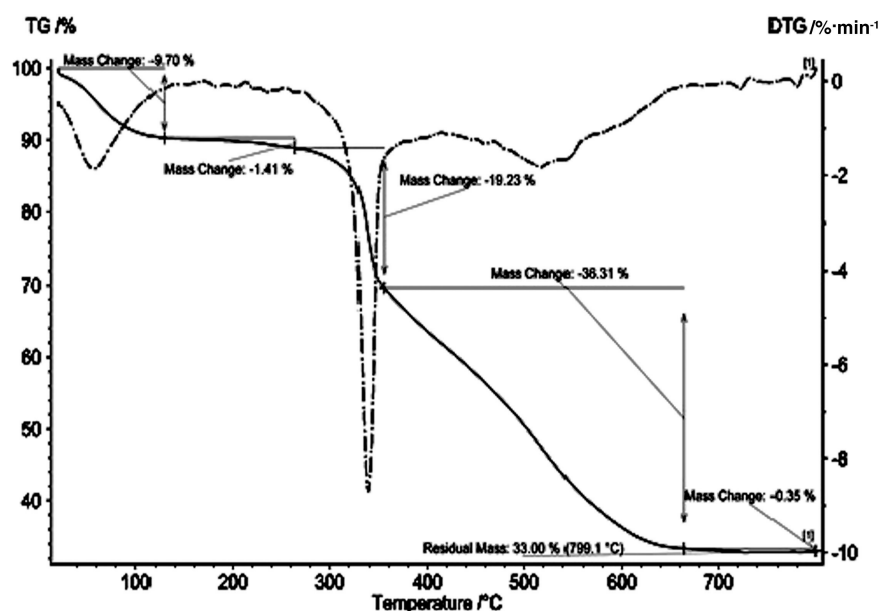


Fig. 5. Thermal gravimetric analysis (TGA) of ILOS-NH₂ material.

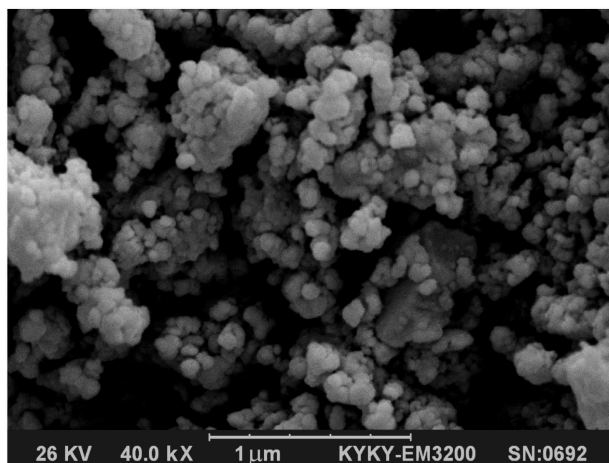


Fig. 6. Scanning electron microscopy (SEM) image of ILOS-NH₂.

3.3. Effect of contact time

The kinetic experiments were performed at $(35 \pm 2)^\circ\text{C}$ to determine the rate of CV removal from the aqueous solutions by the ILOS-NH₂ and SiO₂. The initial CV concentration was $10\text{ mg}\cdot\text{L}^{-1}$ and the pH value of solution was 8.0. In the case of ILOS-NH₂ it can be seen that the initial sorption rate was rapid because of high vacant surface area of adsorbent and the system has reached equilibrium about 45 min. While for SiO₂ the equilibrium time for the adsorption of dye was longer than 45 min. The rapid sorption at the initial contact time can be due to the quite high

accessibility of the empty reactive sites of adsorbent, while at higher times it is difficult to occupy the remaining vacant surface sites due to repulsive interactions between the solute molecules on the solid and bulk phases. Up to 95% of CV removal occurs at 45 min. In addition, the equilibrium time of 45 min and under other optimal conditions, was tested on SiO₂ adsorbent. The result showed that after 45 min, dye uptake was only 64% that is much lower than those of the ILOS-NH₂. The higher efficiency of ILOS-NH₂ in comparison with SiO₂ may be attributed to ionic liquid nature of ILOS-NH₂ which increases the adsorption capacity of the material through π - π interaction with dye molecules.

3.4. Effect of adsorbent dose

Influence of adsorbent dosage was studied by contacting initial concentration of CV ($10\text{ mg}\cdot\text{L}^{-1}$) at the pH of 8.0 and stirring period of 45 min using 0.03–0.07 g of ILOS-NH₂ sorbent. The efficacy of sorbent dosage on adsorption of CV dye onto the sorbents was carried out and the actual results are shown in Fig. 7c. As can be seen from this Figure, the percentage of dye uptake was found to increase proportionally with an increase in amount of ILOS-NH₂. As shown the maximum removal percentage was obtained in the presence of 0.05 g of adsorbent. Accordingly, in the future experiments this amount was used under optimum conditions [37].

3.5. Effect of initial dye concentration

The effectiveness of initial CV concentration in the range of 10 – $40\text{ mg}\cdot\text{L}^{-1}$ on its uptake of dye was studied and the results are shown in Fig. 7d. This study showed that with increasing the amount of dye, the uptake percentage and actual amount of adsorbed dye have opposite correlation. At lower CV concentrations, the ratio of

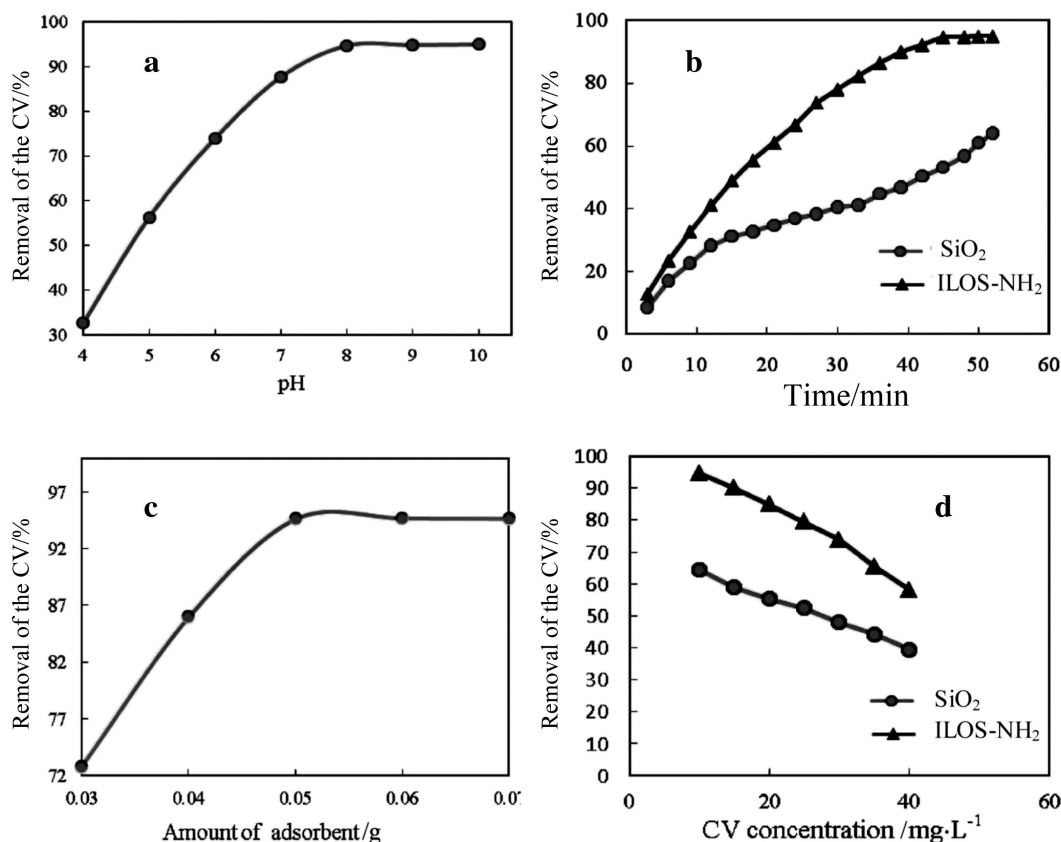


Fig. 7. Effect of (a) pH; dye concentration: $10\text{ mg}\cdot\text{L}^{-1}$, adsorbent dose: 0.05 g per 25 ml, time: 45 min, stirrer speed: $400\text{ r}\cdot\text{min}^{-1}$ and temperature of $(35 \pm 2)^\circ\text{C}$ (b) contact time; dye: $10\text{ mg}\cdot\text{L}^{-1}$, adsorbent dose: 0.05 g per 25 ml, pH: 8.0, stirrer speed: $400\text{ r}\cdot\text{min}^{-1}$ and temperature of $(35 \pm 2)^\circ\text{C}$ (c) adsorbent dosage; dye concentration: $10\text{ mg}\cdot\text{L}^{-1}$, pH: 8.0, time: 45 min, stirrer speed: $400\text{ r}\cdot\text{min}^{-1}$ and temperature of $(35 \pm 2)^\circ\text{C}$ (d) initial dye concentration; adsorbent dose: 0.05 g per 25 ml, pH: 8.0, 45 min agitation time at speed of $400\text{ r}\cdot\text{min}^{-1}$ in temperature of $(35 \pm 2)^\circ\text{C}$ on the removal of CV by ILOS-NH₂ and SiO₂.

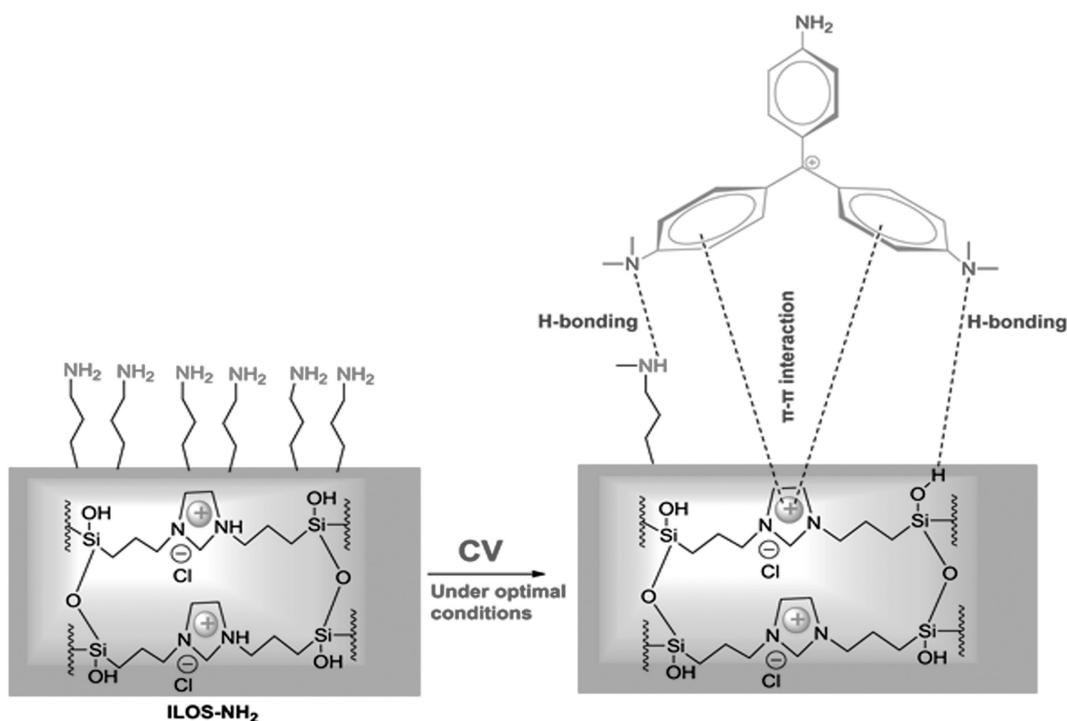


Fig. 8. Proposed hydrogen bonding and π - π interaction for the adsorption of CV on ILOS-NH₂.

adsorbent to the CV molecules is high, which causes an increase in dye uptake and the transfer to the adsorbent surface by migrating and convection. The lower adsorption yield at high concentration of CV may be attributed to saturation of surface active sites as well as possible repulsive interactions between the dye molecules on the solid and bulk phases. The percentage difference of dye removal by ILOS-NH₂ and SiO₂ dose is also shown in Fig. 7d. This figure successfully shows that the removal dye capacity of ILOS-NH₂ is much better than SiO₂.

3.6. Equilibrium isotherms

Adsorption equilibrium isotherm is based on the mathematical relationship between amounts of adsorbed per gram of adsorbent

(q_e , $\text{mg} \cdot \text{g}^{-1}$) and equilibrium solution concentration (C_e , $\text{mg} \cdot \text{L}^{-1}$) at a fixed temperature [38]. The following isotherms are considered for the present study.

3.6.1. Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption of solute from liquid solution without change in the plane of the surface [39]. Based on the linear form of Langmuir isotherm model, the values of K_d (the Langmuir adsorption constant ($\text{L} \cdot \text{mg}^{-1}$)) and Q_m (theoretical maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$)) were obtained from the intercept and slope of the plot of C_e/q_e vs C_e , respectively (Fig. 9 a). The high correlation coefficient with maximum monolayer capacity shows

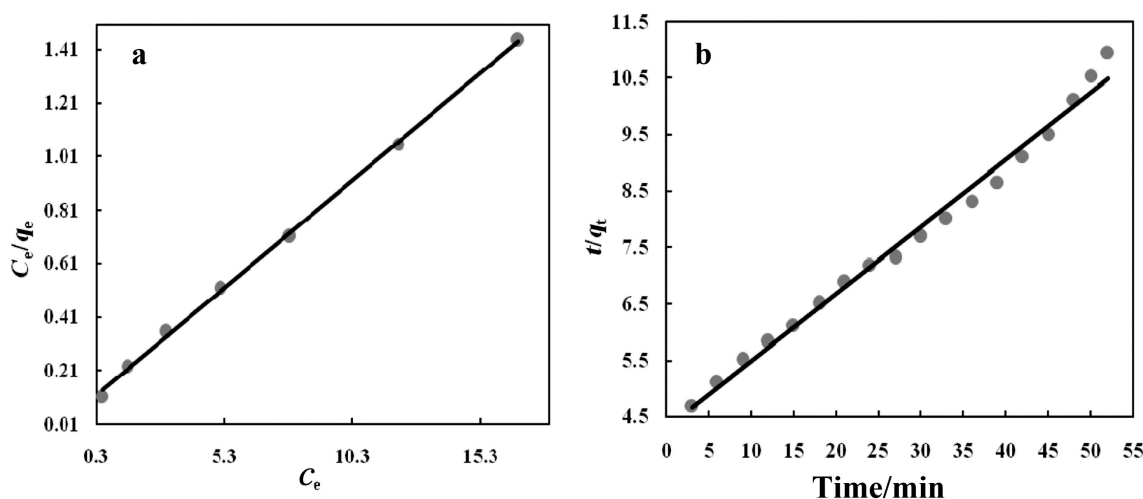


Fig. 9. (a) The Langmuir plot for the adsorption of CV on ILOS-NH₂ (adsorbent dose: 0.05 g per 25 ml, pH: 8.0, 45 min agitation time at speed of $400 \text{ r} \cdot \text{min}^{-1}$ in temperature of $(35 \pm 2)^\circ\text{C}$). (b) pseudo-second order kinetics plot for the adsorption of CV on ILOS-NH₂ (dye concentration: $10 \text{ mg} \cdot \text{L}^{-1}$, adsorbent dose: 0.05 g per 25 ml, pH: 8.0, stirring speed: $400 \text{ r} \cdot \text{min}^{-1}$ and temperature of $(35 \pm 2)^\circ\text{C}$).

strong positive evidence on the fitness of equilibrium data of adsorption of CV using the Langmuir model (Table 1).

Table 1

Isotherm constant parameters and correlation coefficients calculated for the adsorption of CV onto ILOS-NH₂ and SiO₂

Isotherm	Parameters	Adsorbent	
		ILOS-NH ₂	SiO ₂
Langmuir	$Q_m/\text{mg}\cdot\text{g}^{-1}$	20.63	1.28
	$K_a/\text{L}\cdot\text{mg}^{-1}$	0.60	8.50
	R^2	0.999	0.994
Freundlich	$1/n$	0.27	0.48
	$K_F/\text{L}\cdot\text{mg}^{-1}$	5.97	1.83
	R^2	0.962	0.972
Tempkin	B_1	2.14	2.59
	$K_T/\text{L}\cdot\text{mg}^{-1}$	17.11	0.96
	R^2	0.982	0.987

3.6.2. Freundlich isotherm

The Freundlich isotherm model is applicable for non-ideal heterogeneous sorption [40]. The applicability of the Freundlich adsorption isotherm was assessed by plotting $\ln q_e$ versus $\ln C_e$ (Table 1). K_F strongly gives useful information on the bonding energy and/or distribution coefficient and represents the quantity of dye adsorbed onto an adsorbent. $1/n$ shows adsorption intensity (surface heterogeneity) that takes value ranges between 0 and 1. When the value of $1/n$ is equal to unity, the adsorption is linear, while the value of $1/n < 1$ indicates the chemically driven adsorption process and the value of $1/n > 1$ indicates the physically driven process of adsorption [41]. The values of $1/n$ (0.27) give an indication of the favorability of adsorption and high tendency of CV for the adsorption onto ILOS-NH₂.

3.6.3. Tempkin isotherm

The heat of the adsorption and the adsorbent-adsorbate interaction were evaluated by using Temkin isotherm model. In this model, B is the Temkin constant related to heat of the adsorption ($\text{J}\cdot\text{mol}^{-1}$), T is the absolute temperature (K), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and K_T is the equilibrium binding constant ($\text{L}\cdot\text{mg}^{-1}$). Values of B_1 and K_T were calculated from the plot of q_e against $\ln C_e$ [42]. The value of the correlation coefficient (0.982) of this model is lower than those of the Langmuir model (Table 1). Therefore, the Temkin isotherm represents a worse fit of experimental data than Langmuir isotherms.

3.7. Kinetics evaluation

In order to study the kinetic process that controls the adsorption mechanism, the experimental data presented in Table 2 were

Table 2

Kinetic parameters for the adsorption of CV onto ILOS-NH₂ and SiO₂

Model	Parameters	Adsorbent	
		ILOS-NH ₂	SiO ₂
First-order kinetic	k_1	0.10	0.03
	q_e (calc)	11.22	3.16
	R^2	0.651	0.729
Second-order kinetic	k_2	0.003	0.007
	q_e (calc)	8.47	4.44
	R^2	0.988	0.905
Intraparticle diffusion	K_{id}	0.80	0.44
	C	-0.66	-0.26
	R^2	0.985	0.968
Elovich	β	0.60	1.11
	α	0.57	0.35
	R^2	0.971	0.919

investigated using the Lagergren pseudo first and second order, Elovich and intraparticle diffusion models [43–48]. The pseudo-first-order model can be expressed as:

$$dq_t/dt = k_1 (q_e - q_t) \quad (2)$$

Where q_e is amount of CV adsorbed onto ILOS-NH₂ ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium time and q_t is at any time, t (min); and k_1 is the equilibrium rate constant (min^{-1}). By plotting $\ln (q_e - q_t)$ versus time one can obtain the values of k_1 and q_e from the slope and intercept, respectively. Pseudo-second-order kinetics can be expressed as:

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (3)$$

Where k_2 is the rate constant for pseudo-second-order kinetics ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$). For dye concentrations of $10 \text{ (mg}\cdot\text{L}^{-1})$ and the optimized pH (8.0) it's obvious that the kinetics data fitted very well with the pseudo-second-order model with the correlation coefficient values, $R^2 \approx 1.0$ and show good agreement with experimental data (Fig. 9b).

The Elovich equation is as follow:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (4)$$

Where q_t is the sorption capacity at time t ($\text{mg}\cdot\text{g}^{-1}$), α and β are the initial sorption rate ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and desorption constant ($\text{g}\cdot\text{mg}^{-1}$), respectively. Thus, the constants can be obtained from the slope and the intercept, plotting of q_t against $\ln t$. Adsorption is a multi-step procedure included transport of the adsorbate from the aqueous phase to the surface of adsorbent then followed by diffusion of the adsorbate into the pore interiors. If the experiment is a batch system, there is the chance that the transportation of adsorbate from solution into pores of the adsorbent is the rate-controlling step. This eventuality was examined in terms of a relationship between the quantity of dye adsorbed and the square root of time. Whereas the dye is perhaps transported from its aqueous solution to the sorbent by intraparticle diffusion, so the intraparticle diffusion is other kinetic pattern should be used to investigate the rate-limiting step for dye sorption onto adsorbent. The intra-particle diffusion is generally expressed by the following equation:

$$q_t = k_{id} t^{0.5} + C \quad (5)$$

where k_{id} is the intraparticle diffusion constant ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$) and C is a constant related to the thickness of the boundary layer ($\text{mg}\cdot\text{g}^{-1}$). The values of K_{id} were calculated from the slopes of q_t versus $t^{0.5}$ while C was obtained from its intercept. The kinetics parameters obtained from this study are listed in Table 2.

3.8. Thermodynamic studies

The temperature has two major effects on the adsorption process. On one hand, increasing the temperature can enhance the diffusion of the adsorbate molecules. On the other hand, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [49]. The effect of temperature on the adsorption of CV on ILOS-NH₂ adsorbent was investigated at 293–333 K. When the solution temperature increased from 20 °C to 35 °C, the adsorption capacity of CV increased to $10.63 \text{ mg}\cdot\text{g}^{-1}$. At temperature greater than 35 °C, the adsorption capacity did not change with variations in temperature. There are three thermodynamic parameters that must be considered to characterize the adsorption process which include the standard enthalpy (ΔH^0), standard free energy (ΔG^0) and standard entropy (ΔS^0). The relationships among these parameters are described by the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

$$\Delta G^0 = -RT \ln K_c \quad (7)$$

where K_c is called the adsorption affinity and is obtained from q_e/C_e equation, q_e is the amount of dye adsorbed per unit mass of adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium concentration ($\text{mg} \cdot \text{L}^{-1}$) and T is temperature in kelvin. Combination of Eqs. (6) and (7) gives;

$$\lg(q_e/C_e) = (\Delta S^0/2.303R) + (-\Delta H^0/2.303RT) \quad (8)$$

The plots of $\ln K_c$ against $1/T$ and the values of ΔH^0 and ΔS^0 can be estimated from the slope and intercept. The values of ΔG^0 were negative indicating that the adsorption of CV on the ILOS-NH₂ is feasible and spontaneous. The value of ΔH^0 was observed to be positive ($11.38 \text{ kJ} \cdot \text{mol}^{-1}$) for the adsorption of CV corresponding to an endothermic process. The positive value of ΔS^0 suggests that the adsorbed CV molecules remain more randomly over the adsorbent surface [50]. The thermodynamic parameters obtained from this study are listed in Table 3.

Table 3
Thermodynamic parameters for the adsorption of CV dye on adsorbent

T/K	$\Delta G^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^0/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
293.15	−5.87	11.38	59.84
303.15	−6.50		
308.15	−7.22		
313.15	−7.44		
323.15	−7.87		
333.15	−8.17		

3.9. Various adsorbent for CV removal

The maximum adsorption capacity of the ILOS-NH₂ for removal of CV was compared with those reported in previous literatures for different adsorbents, as shown in Table 4. The result showed that the present adsorbent is much more efficient than other adsorbents and can remove CV dye from wastewater in nearly short time and quite low dosage of sorbent (0.05 g per 25 ml of sorbent). The high adsorption capacity of ILOS-NH₂ may be attributed to its excellent porous structure as well as the presence of ionic liquid and amine functional groups in the material framework.

Table 4
Comparison of adsorption results of previously reported CV removal with the proposed adsorbent

Dye	Adsorbent	$q_m/\text{mg} \cdot \text{g}^{-1}$	Reference
CV	Bottom ash (BA)	4.00	[50]
	Activated carbon	19.80	[51]
	ZFA	19.60	[52]
	ZBA	17.60	[52]
	Bottom ash	12.10	[53]
	Al-saturated sepiolite	20.40	[54]
	SiO ₂	1.28	Present work
	ILOS-NH ₂	20.63	Present work

4. Conclusions

In conclusion, for the first time a novel aminopropyl-containing ionic liquid based organosilica (ILOS-NH₂) was prepared, characterized and successfully applied as effective sorbent in the removal of CV dye. The DRIFT spectrum confirmed well incorporation and immobilization of

ionic liquid and propyl-amine functional groups into/onto material framework. The TGA also proved high thermal stability of the material. The experimental data showed that the ILOS-NH₂ had a great capacity absorbance for removing CV dye from wastewater in almost short time and low dosage of sorbent (0.05 g per 25 ml of adsorbent). Comparative study also showed that the efficiency of ILOS-NH₂ was much better than those of SiO₂ attributing to the ionic liquid nature of the ILOS-NH₂. The achievement of adsorption process was attributed to the π - π interactions and hydrogen bonding between sorbent and dye molecules. The isotherm models such as Langmuir, Freundlich and Temkin were also evaluated and the equilibrium data were best described by the Langmuir model. The process kinetics was successfully fitted to the pseudo-second-order kinetic model. The temperature effect was also used to calculate the change in activation enthalpy (ΔH^0), free energy of adsorption (ΔG^0), and entropy (ΔS^0). This fundamental study will be helpful for the technology of removing dyes from wastewater.

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