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Thin coated adsorbent layer: characteristics and performance study

S.F. Azha, A.L. Ahmad, S. Ismail*

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Nibong Tebal, Pulau Pinang 14300, Malaysia, emails: syahidafarhan@gmail.com (S.F. Azha), chlatif@usm.my (A.L. Ahmad), Tel. +60 4 5996458; Fax: +60 4 5941013; email: chsuzy@usm.my (S. Ismail)

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ABSTRACT

Adsorption is the most versatile and widely applied method for water and wastewater treatment due to their economic, simple in operation and efficient process. The aim of this study is to introduce a new approach on adsorption application that are tailored to operator's requirement and make full use of the existing facilities. The current work will evaluate the feasibility performance of a thin coated adsorbent layer specifically design for colour removal in wastewater. This laboratory-scale experiments reported on the preparation of adsorbent coating layer named *Paintosorp*. *Paintosorp* coated on the surface of the glass and tested for its adsorption performance using methylene blue (MB) dye in batch scale. The adsorption process was investigated by varying the initial dye concentration, pH and temperature. The percentage removal of MB was found to be 99% for all concentrations of 50, 100, 150 and 200 mg/l upon achieved equilibrium within 4–20 h for the surface area approximately 0.03 m^2 of coated *Paintosorp*. Equilibrium data were simulated using Langmuir, Freundlich and Temkin isotherm models. Kinetic modelling was fitted to the pseudo-first-order and pseudo-second order equation, while adsorption mechanism was determined using the intraparticle diffusion model. The finding revealed the potential of *Paintosorp* as a viable coating adsorbent for future wastewater treatment technology as easily incorporated with plant's existing facilities and can be tailored to the customer's needs.

Keywords: Paintosorp; Adsorbent coating; Colour removal; Adsorption

1. Introduction

In keeping abreast with the country's rapid economic development policy and in a bid to meet the nation's aspiration for improved quality of life, industries in Malaysia are facing challenges to find reliable effluent treatment technology. Specifically to ensure the compliance with Malaysian Environmental Quality Act (1974) on industrial effluent standard discharge limit especially on colour removal. In industrial waste streams, dyes are among the most common pollutants present. The dyes are discharged from sources such as textile, paper, leather and plastic industries [1]. Dyes are compounds with complex aromatic structure which are widespread used to make colour to other substances [2]. Synthetic dyes are widely applied by industries due to their cost-effective and ease of fabrication and formulation compared with natural dyes [3].

Dyes are resistant to light, heat and oxidizing agents and they are usually non-biodegradable [4]. This is very indispensable in the industry as it attributes to colour fastness, but brings drawbacks which

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*Corresponding author.

lead to difficulty in treating their wastewater effluents containing dye [3]. Even though dye effluents which discharge into the environment only create low percentage of water pollution, dyes are brilliances and visible even in small quantities. Moreover, some dyes are known to have carcinogenic and mutagenic properties [3]. The coloured wastewater cannot be discharged without proper treatment since they are toxic to plants and aquatic life. Even if they are non-toxic, such wastewaters interfere light penetration and ultimately lower the efficiency of photosynthesis in aquatic plants, and increase the chemical oxygen demand [3].

Physical, chemical and biological processes are techniques used to treat dyes in effluent wastewater [5]. Among the methods include coagulation–flocculation, electrocoagulation, chemical oxidation, filtration, ozonation, membrane separation, ion-exchange, aerobic and aerobic microbial degradation and advanced oxidation process [6]. However, these methods are expensive and contribute to operational problems such as development of toxic intermediates, lower removal efficiency, higher sludge generation and higher specificity for a group of dyes [7,8]. Hence, adsorption is the most versatile and widely used method of water treatment through various claims that this process is low cost, ease of operation and efficient in treatment [9].

Several adsorption processes have been developed, patented and introduced for application in removing contaminants from waters. Nevertheless, despite the number of published laboratory data and various non-conventional low-cost adsorbents introduced by researchers, very few of these adsorption products and processes have been applied on industrial scale. There are several reasons in difficulty to transfer the research-based findings to industrial-scale applications and one of the obvious reasons is the unwillingness of industries to invest on new equipment which upon their calculation require higher budget allocation continuously.

Recently, researchers have developed techniques for coating an adsorbent onto sand to overcome the problem of using adsorbent powders in waste treatments process. Iron-oxide-coated sand (IOCS) has been tested for removing cations and anions from synthetic and natural wastes [10]. The IOCS was prepared by the impregnation of sand with mixed solution of salt and precipitator and subsequent drying [10,11]. However, the thickness of the coated layer was only several micrometres, which resulted in low adsorption capacity. Furthermore, the coated layer can be easily shredded off, leaving the sand with little adsorption capacity which caused secondary pollution in drinking water [12].

Besides, Chen et al. have done research on coating granulation technology focusing on the spraying of a Fe–Al–Ce nano-adsorbent suspension onto glass beads in a fluidized bed. Acrylic–styrene copolymer latex was used as a binder [12]. The granulated adsorbent was used in a packed bed for fluoride removal from drinking water. This approach was proposed in order to use the immobilizing of a powder adsorbent on an inert support to overcome the large pressure drop when small powder particles are used in a water treatment process [12].

There are a variety of solid adsorbents which have been useful in adsorption including commonly known materials such as activated carbons, activated clays, silica gel, activated alumina and crystalline molecular sieves. Dunne et al. mentioned that it is desirable to have solid adsorbent deposited on a substrate as a coating instead of being contained in particulate form as pellets, beads, powder or other particles. There are several reasons why solid adsorbent coating will be used, for example, to improve the catalytic or adsorption properties of the solid adsorbent by improving the surface area to weight ratio, to reduce the amount of solid adsorbent required, to protect the underlying substrate material from a harmful environment, to achieve a particular strength or form and to perform the particular adsorptive or catalytic function over the entire coated surface of the substrate [13].

Clay has been accepted as one of the appropriate low-cost adsorbents for the removal of dyes from wastewater. Clay's studies have received considerable recognition as an adsorbent because of high adsorption capacity. It is hydrated alumina-silicate clay primarily composed of the smectite-class mineral montmorillonite [14]. It is well known that the negative charge of clays is balanced by exchangeable cations, which are usually Na^+ and Ca^{2+} [15]. The wide application of clay minerals is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties [16].

The main objective of this study is to introduce a thin adsorbent layer coated on existing surface with specific function as dye removal. This is an exploratory step in finding new approach in adsorption application which will open up options to industries meeting their requirement by providing fundamental results at different angle of the adsorption concept. This research work is an important building block in giving a new concept for adsorption application and aimed to be economical and easily acceptable by industries. The fundamental studies in evaluating the concept is crucial as it serves as a feeder for another stage of study in developing a pollution prevention system that does not require any new facilities or special equipment but only rely on small modifications of the existing industrial facilities.

2. Materials and methods

2.1. Adsorbate

Methylene blue (MB), supplied by Modern Lab Sdn. Bhd. Malaysia, was used as an adsorbate and used as received without further purification. MB dye was made up in stock solution of concentration 1,000 mg/l and was diluted to the required concentrations (50–200 mg/l). Distilled water was employed for preparing all the solutions and reagents. The characteristic and chemical structure of MB dye is presented in Table 1.

2.2. Preparation of adsorbent coating

The sorbent used in this study was prepared by the combination of clay-based adsorbent and binder with designated ratio. The mineral clay is laboratory grades purchased from Modern Lab Sdn. Bhd. Malaysia and also used as received without any modification. The mineralogical analysis showed that the native crude clay mineral contains preponderantly Montmorillonite. The major chemical composition of clay-based adsorbent from other previous study was given in Table 2 [17].

The binder is basically mixtures of calcium carbonate, PVA, formalin, ammonia and hydrosol. The mixture functioned as a support or binder for the adsorbent particle where this adsorbent will be coated onto surfaces of any inert materials. The solid adsorbent was dispersed homogeneously in the mixture with specific ratios by agitating using magnetic stirrer at 150 rpm until it dispersed completely. For the laboratory-scale testing, the *Paintosorp* was coated onto the glass surfaces as shown in Fig. 1. The coating was dried in an oven for 10 h at 70°C. It is very important to achieve complete dryness in order to prevent any peeled off of the adsorbent coating.

Table 2
XRF analysis for major element in adsorbent sample [17]

Element	Percentage by weight/unit
SiO_2	64.53
Al_2O_3	17.86
TiO_2	0.38
Fe_2O_3	3.23
MgO	3.05
CaO	1.69
Na_2O	1.27
K_2O	1.17

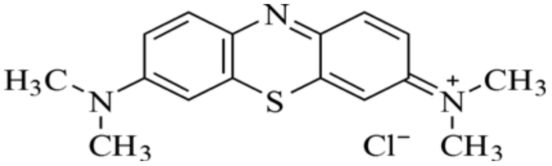
2.3. Characterization analysis

In order to study the dispersion of the clay-based adsorbent particles in the binder, the *Paintosorp* layer was examined by scanning electron microscopy (SEM), (model Crest System (M) Sdn. Bhd, Quanta Feg 450). The observation was carried out on the upper surface of adsorbent coating layer. The morphologies of the spectroscopic changes in adsorbent coating surface before and after adsorption also being observed using Fourier transforms infrared (FTIR) spectroscopy (FTIR-NICOLET iS10) in the region of 4,000–400 cm^{-1}.

2.4. Adsorption performance study

The equilibrium dye concentrations were determined by absorbance measurement using UV–vis

Table 1
Physical properties and molecular structure of MB

Dye name	Methylene blue
Colour index number	52015
Chemical formula	$C_{16}H_{18}N_3SCI$
IUPAC number	3,7-bis (Dimethylamino)-phenothiazin-5-ium chloride
Molecular weight (g/l)	319.85 g/mol
λ_{max}	664 nm
Solubility in water	1 g/25 ml
Molecular structure	

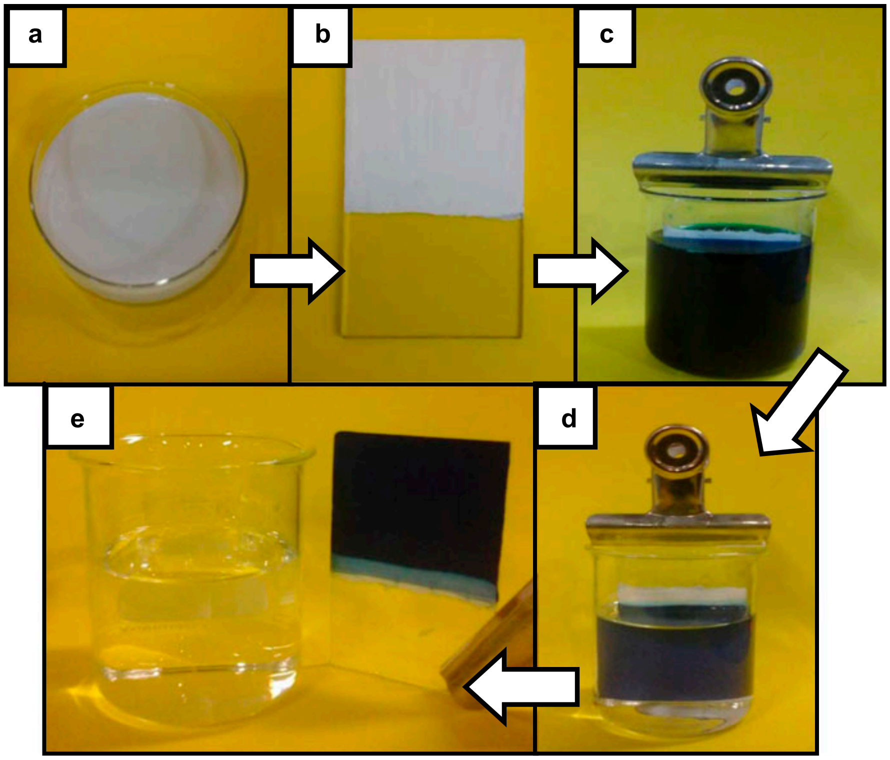


Fig. 1. (a) *Paintosorp* solution, (b) *Paintosorp* coated on glass surface, (c) adsorption test in MB solution, (d) after adsorption test and (e) glass with clear water after adsorption and MB being adsorbed on glass plate.

Spectrophotometer (HASH UV–vis model DR 5000 spectrophotometer) at 664 nm. It was then computed into dye concentration using a standard calibration curve.

2.4.1. Effect of initial dye concentration and contact time

The batch adsorption studies were conducted in a set of 250 ml beakers with glass plate coated with *Paintosorp*. The beaker was filled with 200 ml MB dye solution with various initial dye concentrations (50, 100, 150 and 200 mg/l). The dye solutions in each beaker were stirred using magnetic stirrer at 130 rpm and temperature controlled within 30˚C until equilibrium stage was reached. MB uptake at equilibrium, q_e (mg/g), was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/l) are the liquid-phase concentrations of dye at initial and its equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of adsorbent used.

2.4.2. Effect of temperature

To study the effect of temperature, the experiment was carried out at temperature 30 and 60˚C with similar procedure applied for initial dye concentration effect studies.

2.4.3. Effect of pH solution

The effect of pH on the adsorption process was conducted at adsorption temperature of 60˚C. The pH was adjusted by adding NaOH (0.1 M) or HCl (0.1 M) solutions to obtain pH values in the range of 3–11. The pH measurement was taken using pH meter.

2.5. Batch kinetic study

Kinetic experiment procedure was basically identical with the procedure for equilibrium test. The aqueous samples were taken at different time intervals and the concentrations of dye were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by the following formula:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{2}$$

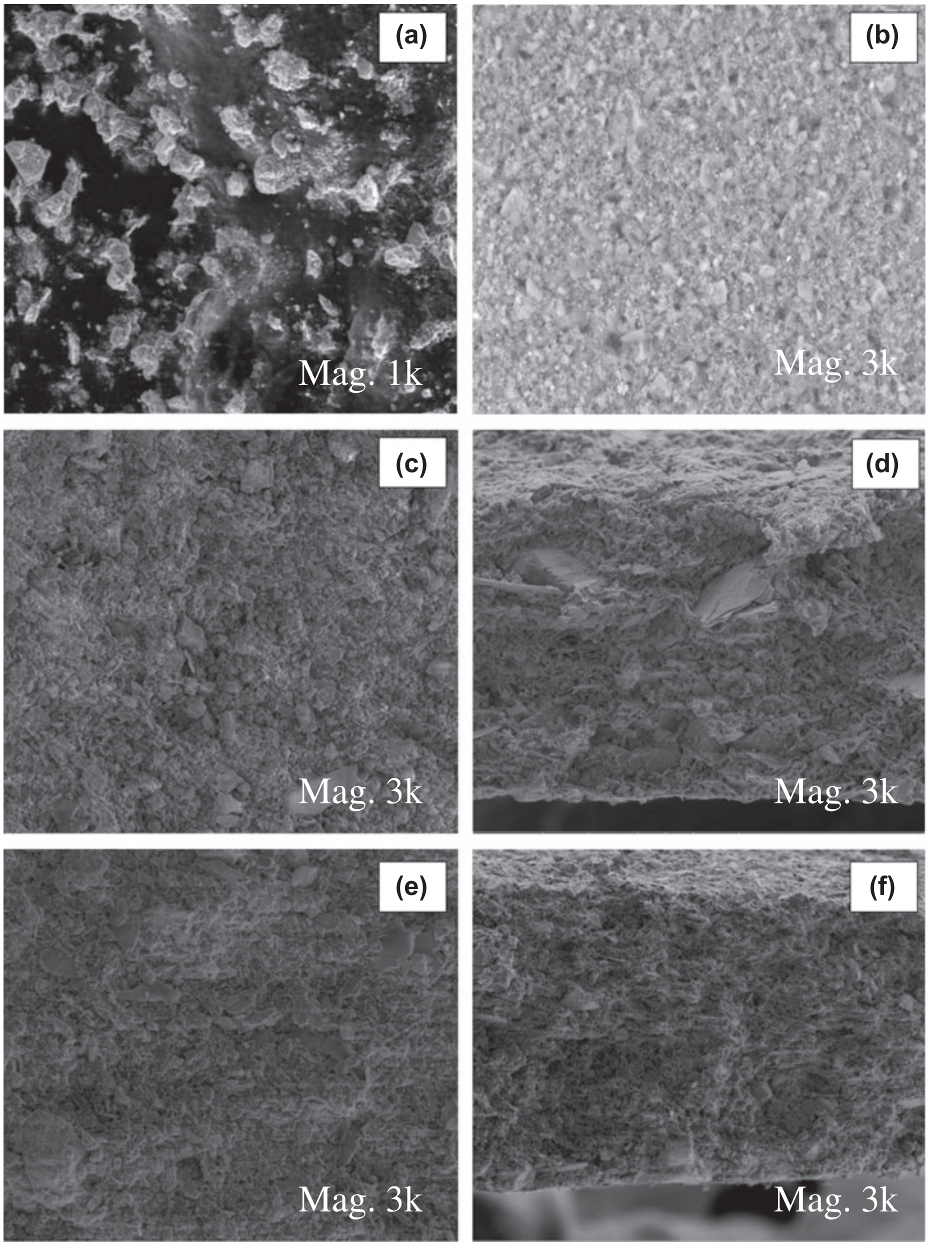


Fig. 2. SEM image of (a) Clay-based adsorbent particle, (b) Binder, (c) *Paintosorp* (surface), (d) *Paintosorp* (cross-sectional), (e) *Paintosorp* after adsorption (surface) and (f) *Paintosorp* after adsorption (cross sectional).

where C_0 and C_t (mg/l) are the liquid-phase concentrations of dye at initial and at any time t (min/h), respectively. V (L) is the volume of the solution and W (g) is the mass of adsorbent used.

3. Result and discussion

3.1. Characterization analysis

The surface structure examination of adsorbent particles can be observed through the SEM images (Fig. 2(a)–(f)). Fig. 2(a) shows the SEM image for the clay-based adsorbent particles which were approximately spherical and had different particle grains size with an average particle size of 20–30 μm. The lamellae show irregular form. The widespread use of clay adsorbent can be attributed to its physical and chemical properties such as small particle size, high porosity, large surface area and high cation-exchange capacity [18]. It has excellent adsorption capacity and its adsorption ability is determined by the chemical structure and pore structure [19]. The porous structure of clay adsorbent was classified into three categories such as micropores, mesopores and macropores. Micropores are smaller than 2 nm, between 2 and 50 nm are mesopores and larger than 50 nm are macropores [20]. Thus, this clay adsorbent used was classified under mesopores.

The morphology of the binder surface was characterized and it can be seen in Fig. 2(b) which was densely and evenly distributed and its structure was close to each other compared with the layer of *Paintosorp*. The scanning electron micrographs of *Paintosorp* layer samples were taken before and after dye adsorption (Fig. 2(c)–(f)). Beside the surface morphology, the *Paintosorp* cross-sectional area was also investigated. The existence of clay adsorbent particles in the *Paintosorp* can be seen clearly in the Fig. 2(c) and (d). The clay type adsorbent such as bentonite will disaggregates in water and take place by swelling effect. Thus, this will make the average clay particle decreasing in size. As a function of decreasing particle size, the number of particles per unit weight of clay increases, and consequently also the available surface area. Fig. 2(e) showed that *Paintosorp* surface was covered with dye molecules and the surface of the samples was much more homogeneous than before adsorption, thus the outstanding lamellar appearance was found less after the adsorption. After dye adsorption, a significant change was observed in the structure of the adsorbent. It can be seen that all adsorbents surface covered with just a thin layer of MB dye molecules.

The energy dispersive X-ray analysis was also carried out on the clay adsorbent (Fig. 3(a)), binder mixtures (Fig. 3(b)), *Paintosorp* before (Fig. 3(c)) and after adsorption (Fig. 3(d)). As seen in Fig. 3(a)–(d) and Table 3, the detected elements in all samples are Carbon (C), Oxygen (O), Calcium (Ca), Magnesium (Mg), Aluminium (Al) and Silicon (Si). From the literature, the SiO_2 and Al_2O_3 are the major constituents of the clay with other oxides present in trace amounts, so it is expected either any of the major oxides present in the adsorbent or their combined influence are responsible for the adsorption of dye [21]. Therefore, the elements of clay adsorbent which are maintained in the *Paintosorp* are C, Ca, O, Fe, Mg, Al and Si. Titanium (Ti) element also gave the effect towards the adsorption of dye since it also contained the binder mixture. In Fig. 3(d), the element of sulphur was found to exist and this was obtained from MB element as an adsorbate in this study. The chemical formula for MB is $C_{16}H_{18}N_3SCl$.

IR techniques have been used by previous researchers for the identification of soil and clay minerals [22]. For the adsorption studies, FTIR results gave an idea about the nature of adsorption between adsorbate and adsorbent. The FTIR spectra of *Paintosorp* before and after dye adsorption are carried out in the range from 4,000 to 400 cm^{-1} and are shown in Fig. 4. The changes in the functional group provide the indication of the changes occurred before and after the adsorption process. It was obvious the presence of C–H stretch for alkanes group in *Paintosorp* before (Fig. 4(c)) and after adsorption process (Fig. 4(d)) at peak 2925.89 cm^{-1}. Paintosorp after adsorption confirmed the vibration of C=O bond for aldehyde which was appear at peak 1731.30 cm^{-1}. The presence of O–H bonds represent bending vibration of alcohol and phenol which originally found in binder mixture at peaks in the range of 1,330–1,430 cm^{-1}. The functional groups of amines and alkenes also found in before and after adsorption performance of *Paintosorp*. The presence of C=C stretch for Arene group was appeared after the adsorption of *Paintosorp* at wavelength 1,600 cm^{-1}. Arene is the substitution of benzenes and polybenzenes. Dyes are aromatic organic compound and are based fundamentally on the structure of benzene [23]. Besides, from the Fig. 4, after *Paintosorp* adsorbed MB dye, the bending of the bond disappeared at wavelength 1,000 cm^{-1}. The stretching vibration showed the bond of amines group which indicated the existence of MB in the *Paintosorp* layer. It can be referred from molecular structure of MB in Table 1.

3.2. Effect of initial dye concentration

To determine the equilibrium time for various MB concentrations, the adsorption were accessed with time until no adsorption of adsorbate onto *Paintosorp* took place. The adsorption data for the uptake of MB dye vs. contact time at different concentrations are presented in Fig. 5. The results indicate that the actual amount of MB adsorbed per unit mass of *Paintosorp* increased with an increase in MB concentration. This is due to the driving force of the concentration gradient, as an increase in the initial dye concentration [24]. The adsorption equilibrium, $q_{e,}$ increases from 18 to 80 mg/g as the MB concentration increased from 50 to 200 mg/l. It is also evidence from Fig. 5 that the contact time needed for MB solution with initial concentrations of 50 and 100 mg/l to reach equilibrium were less than 3 h. However, for MB solutions with higher initial concentrations, longer equilibrium times were required. The result of adsorption process through adsorbent coating can be considered fast because a significant amount of MB was adsorbed onto the sorbent within the first 6 h of adsorption. During adsorption of MB, initially the dye molecules reached the boundary layer, then they had to diffuse into the

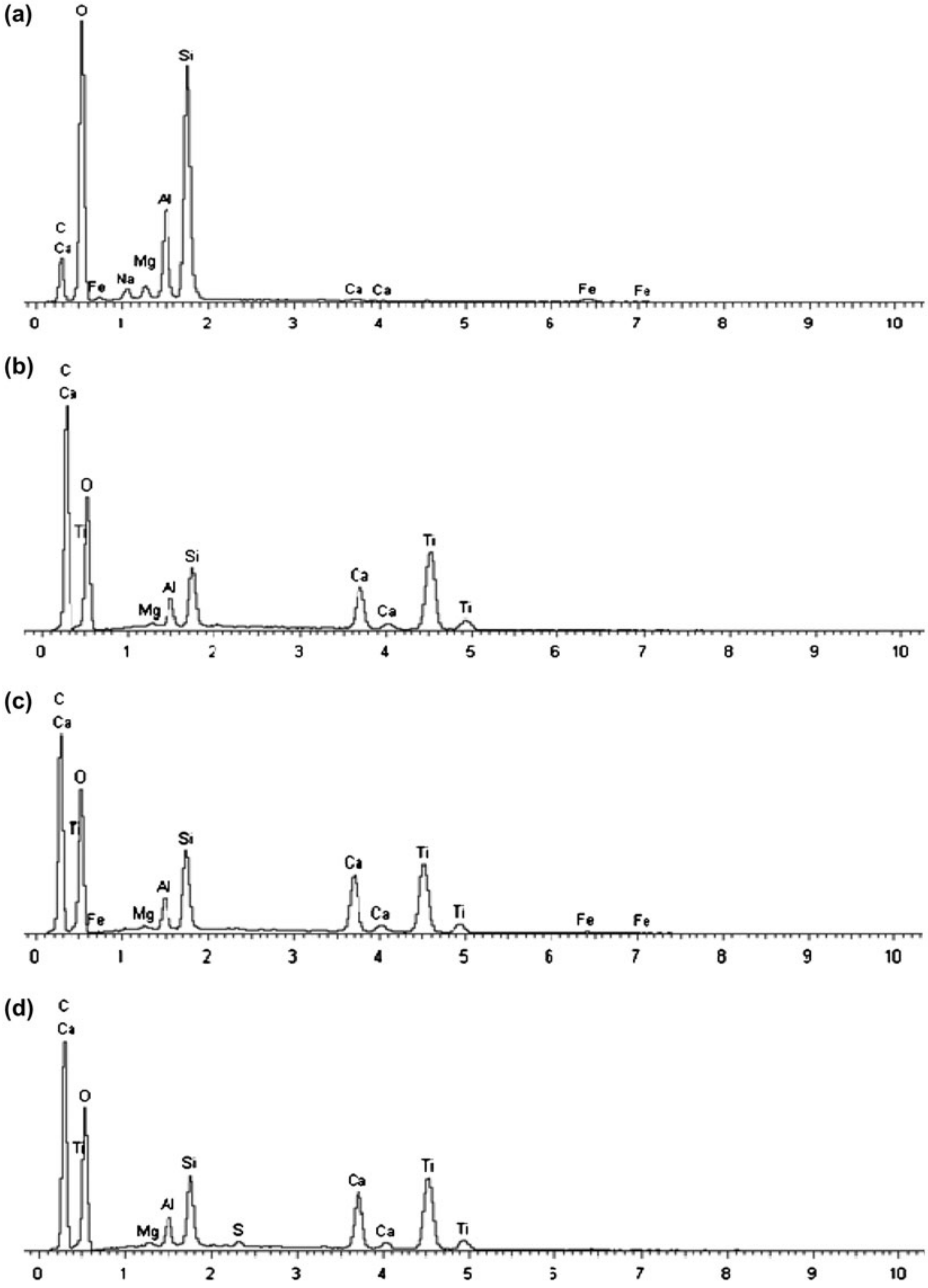


Fig. 3. EDX graph for every major element in (a) clay-based adsorbent, (b) binder, (c) *Paintosorp* and (d) *Paintosorp* after adsorption.

adsorbent surface and, finally, they had to diffuse into the porous structure of adsorbent. Hence, this phenomenon will take a relatively longer contact time especially for higher initial concentration of dye [24].

Fig. 6 shows the effect of the initial dye concentration on the percentage removal of MB. The amount of MB adsorbed decreases with the increase in initial MB concentration. However, in this study, the percentage

Table 3
Result of the elements distribution image of EDX analysis

Element determined with EDX analysis	Bentonite	Paint	Bento-paint	Bento-paint after adsorption
Carbon (C)	/	/	/	/
Oxygen (O)	/	/	/	/
Sodium (Na)	/	–	–	–
Aluminium (Al)	/	/	/	/
Magnesium (Mg)	/	/	/	/
Silicon (Si)	/	/	/	/
Calcium (Ca)	/	/	/	/
Ferum (Fe)	/	–	/	/
Titanium (Ti)	–	/	/	/
Sulphur (S)	–	–	–	/

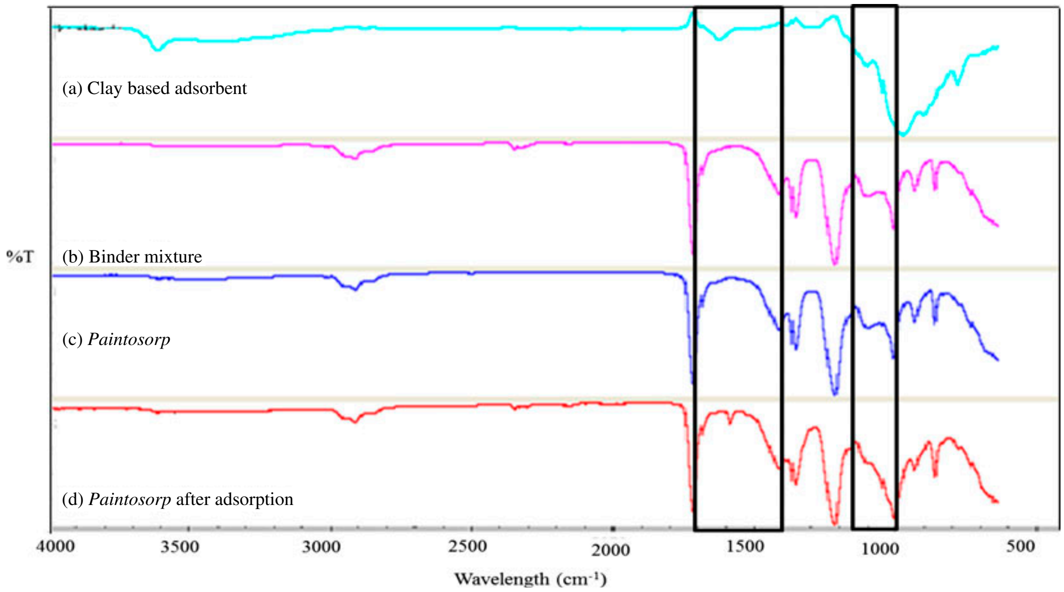


Fig. 4. FTIR of *Paintosorp* before and after adsorption.

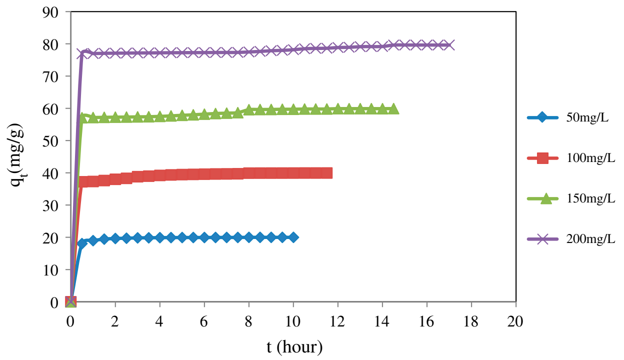


Fig. 5. Effect of initial dye concentration on the adsorption of MB onto the *Paintosorp* adsorbent coating.

removal of MB adsorbed for all initial concentration (50, 100, 150 and 200 mg/l) achieved 100% at different equilibrium time. The saturation of the adsorption sites at higher MB concentrations was the reason why it takes longer time to achieved equilibrium.

3.3. *Adsorption isotherm*

The adsorption isotherm represents the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of the adsorbate [25]. Isotherm results were analysed using Langmuir, Freundlich and Temkin isotherms. Langmuir isotherm model assumes that the adsorption occurs at homogeneous sites of

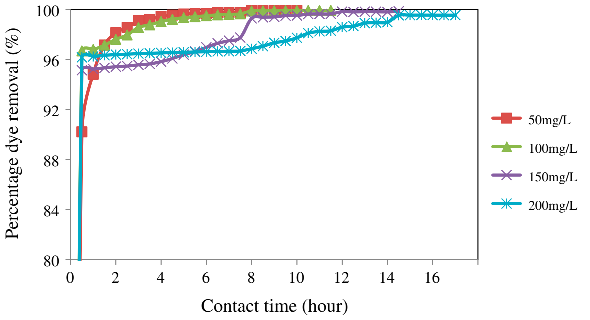


Fig. 6. Effect of initial dye concentration and contact time on percentage removal for MB adsorption onto adsorbent coating (clay-based adsorbent dosage = 0.5 g, temperature, 30˚C, rpm = 130).

adsorbent surface while saturation takes place when the dyes molecules fill the sites where no more adsorption can occur at that site. The constant (K_L and $q_{\max}$) values can be evaluated from the intercept and the slope of the linear plot from the experimental data of Langmuir (C_e/q_e) vs. (C_e). The essential feature of Langmuir isotherm can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using the following equation [26]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{3}$$

The constants and R_L values are listed in Table 3. The values of R_L were found to be at 30˚C and confirmed that was favourable uptake of the MB dye.

The Freundlich isotherm can be used for adsorption on a heterogeneous surface energy system where the binding sites are not equivalent. The constant K_F and n can be evaluated from the intercept and the slope of the linear plot of experimental data with ln q_e vs. ln C_e (Fig. 7(b)). The constant values K_F and n are listed in Table 4. If the value of the exponent n is greater than 1 ($n > 1$), then the adsorption represents favourable adsorption condition. Thus, this research study showed favourable adsorption condition with n value greater than 1.

Temkin and Pyzhev [27] studied the heat of adsorption and the adsorbate–adsorbent interaction on adsorption isotherms. They assumed that because of the adsorbate–adsorbent interactions, the energy of the molecule adsorption will decrease linearly with coverage. The constant A_t and B can be determined from the intercept and the slop of the linear plot of experimental data with q_e vs. ln C_e (Fig. 7(c)). The constant A_t is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B is related to the heat of adsorption [28]. The values of constant A_t and B are listed in Table 4.

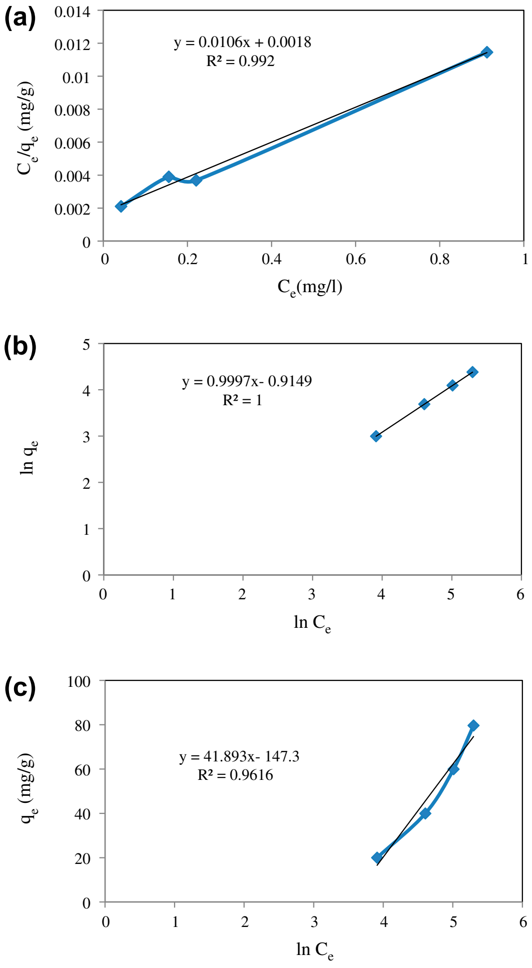


Fig. 7. (a) Linearized Langmuir isotherm for dye removal by *Paintosorp*. (b) Linearized Freundlich isotherm for dye removal of *Paintosorp*. (c) Linearized Temkin isotherm for dye removal of *Paintosorp*.

From Table 4, the Freundlich isotherm model yielded the highest values of the correlation coefficient (R^2) which means the Freundlich model was fitted well with the data R^2 equal to 1 compared with Temkin and Langmuir models. The Freundlich isotherm model describes that adsorption is in heterogenous surface and in multilayer adsorption rules [24]. The homogeneity appears from the presence of different functional groups on the surface. While the K_F values calculated were 2.4965 mg/g $(\mathrm{L/mg})^{1/n}$ which describe the quantity of MB adsorption onto Paintosorp for unit equilibrium.

The fundamental feature of Langmuir isotherm can be expressed in terms separation factor (R_L). The R_L

Table 4
Langmuir, Freundlich and Temkin models constant and correlation coefficients for sorption of MB onto *Paintosorp* adsorbent at 30˚C

Isotherm	Parameters			R^2
Langmuir	Q_0 (mg/g)	K_L (L/mg)	R_L	
	94.34	0.1698	0.0286	0.992
Freundlich	K_F (mg/g) (L/mg)$^{1/n}$	n		
	2.4965	1.0003		1
Temkin	A_T (L/g)	B		
	0.0297	41.893		0.9616

indicates isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [29]. As shown, the R_L value was ranged between 0 and 1, which indicated that the adsorption was favourable at the concentration range being studied.

3.4. Adsorption kinetics

Adsorption kinetic provides a valuable insight into the controlling mechanism of adsorption process which, in turn, governs mass transfer and the residence time [30]. In order to analyse the sorption kinetics of MB onto *Paintosorp*, the pseudo-first-order and pseudo-second-order models were applied to the experimental data. The linear form of the pseudo-first-order model was described by Lagergren [31]. The values of k_1 and q_e were obtained from the slope and intercept, respectively, of plots of log $(q_e - q_t)$ vs. t. It is obvious from Table 5 that the calculated q_e values did not agree with experimental q_e values, thus, the pseudo-first-order model did not fit well.

The pseudo-second-order model [32] also used to study the adsorption kinetics. The values of k_2 and q_e can be determined experimentally from the slope and the intercept of a plot of t/q_t vs. t. It is evidence from Table 5 that the correlation coefficient R^2 for the linear plots of the pseudo-second-order model has high value > 0.999 which is higher than the correlation coefficient R^2 for the pseudo-first-order and the calculated q_e value are in agreement with experimental q_e values. This indicates that the adsorption kinetic is better represented by the pseudo-second-order model [33]. These facts suggest that the pseudo-second-order adsorption mechanism is predominant and, therefore, the overall rate of the dye adsorption process appears to be controlled by the chemisorption process.

The intraparticle diffusion model [34] was proposed to identify the adsorption mechanism and to predict the rate controlling step, where C is the intercept and k_{diff} (mg/g min^{½}) is the intraparticle diffusion rate constant which can be evaluated from the intercept and slope of the plot of q_t vs. $t^{1/2}$. The intraparticle diffusion plots for the adsorption of MB onto *Paintosorp* for the concentration of 50–200 mg/l were presented in Fig. 8. The intraparticle model usually includes three steps. Sharper region completed within the first 45–60 min was instantaneous adsorption representing the mass transfer of adsorbate molecules from the bulk solution to the adsorbent surface. The second region was the gradual adsorption stage where intraparticle diffusion was the rate limiting step. The third region, which existed in some cases, was the final equilibrium stage where intraparticle diffusion started to slow down due to the extremely low adsorbate concentrations left in the solutions [35,36].

From Fig. 8, the linear plot did not pass through the origin indicated that the intraparticle diffusion was not the only rate controlling step, the boundary layer diffusion controlled the adsorption to some

Table 5
Pseudo-first-order, pseudo-second-order constants and correlation coefficients for adsorption of MB on *Paintosorp* at 30˚C

		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Initial dye concentration (mg/l)	$Q_{e\ \text{exp}}$ (mg/g)	$Q_{e\ \text{cal}}$ (mg/g)	K_1 (1/min)	R^2	$Q_{e\ \text{cal}}$ (mg/g)	K_2 (1/min)	R^2
50	19.983	2.6977	0.7347	0.8699	20.0803	0.0908	1
100	39.937	9.1580	0.8817	0.9618	40.3226	0.041	1
150	59.912	12.4108	0.4403	0.8817	60.6060	0.0108	0.9998
200	79.635	7.6103	0.2190	0.8811	79.365	0.0204	0.9998

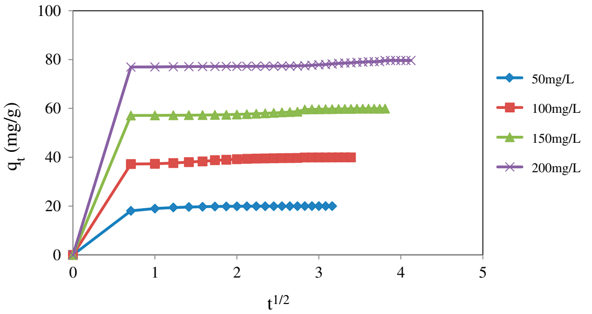


Fig. 8. Plot of Intraparticle diffusion model for MB adsorption onto *Paintosorp*.

degree [36]. This deviation may be due to the differences in mass transfer rate at the initial and final stages of adsorption. The values of C and k_{diff} are given in Table 6. The values of the intercept C increased with an increase in initial dye concentration (50–200 mg/l), where C gives an idea of the thickness of the boundary layer, which indicated an increase in boundary layer effect [35].

3.5. Effect of temperature

Temperature has a pronounced effect on the adsorption process since any changes in temperature will cause changes in the equilibrium capacity of the adsorbent for adsorption of particular adsorbate [36]. The effect of temperature on the adsorption of MB was studied at 30 and 60˚C. The adsorption capacity increases with the increase in temperature if the adsorption process is endothermic. On the other hand, adsorption capacity decreases with the increase in temperature if the adsorption is exothermic [37,38].

In the effect of temperature study, the observation based on temperature varies against contact time. Fig. 9 showed the time needed for each temperature to achieve 99% dye removal. Time consume for adsorption of dye was shorter for 60˚C. Shorter time for dye adsorption with an increase in temperature is mainly due to the increase in mobility of large dye cations. It may also due to higher affinity of sites for the dye and an increase in binding sites on the adsorbent [39]. Moreover, an increase in temperature may produce a swelling effect within the internal structure of the adsorbent enabling large dyes to penetrate further [40].

Table 6
Intraparticle diffusion models for MB adsorption onto *Paintosorp*

Initial dye concentration (mg/l)	Intraparticle diffusion model		
	C	K_{diff} (mg/g min^{½})	R^2
50	18.624	0.5122	0.6212
100	36.635	1.1016	0.9104
150	55.519	1.2241	0.9031
200	75.451	0.9499	0.8295

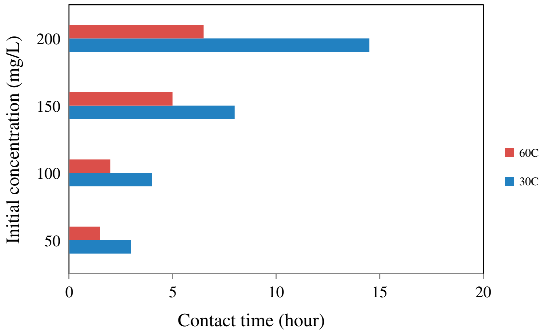


Fig. 9. Plot of Initial dye concentration (mg/l) against contact time (h) for MB adsorption onto *Paintosorp*.

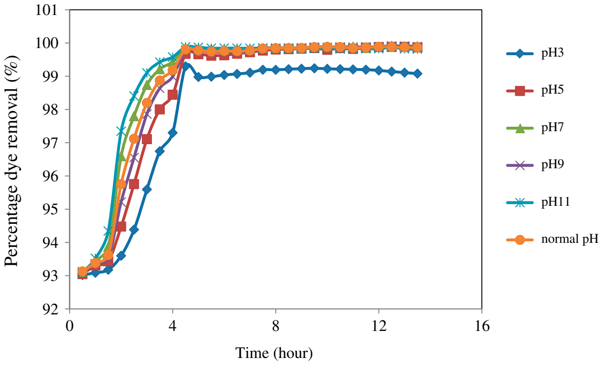


Fig. 10. Plot of percentage dye removal (%) against time (h) for MB adsorption onto *Paintosorp*.

3.6. Effect of solution pH

The pH factor has an important effect on dye adsorption since the pH of the medium controlling the magnitude of electrostatic charges that are imparted by ionized dye molecules. As a result, the rate of adsorption will vary with pH of an aqueous medium [41]. The effect of pH on the removal of MB by *Paintosorp* was studied and it was found that the percentage dye removal achieving 100% for every pH start at 3rd hour till equilibrium time. The study was performed to prove that even at different pH, the result slightly similar and all were achieving 100% removal. This happened due to the adsorbent coating has stabilized the MB solution into the normal pH

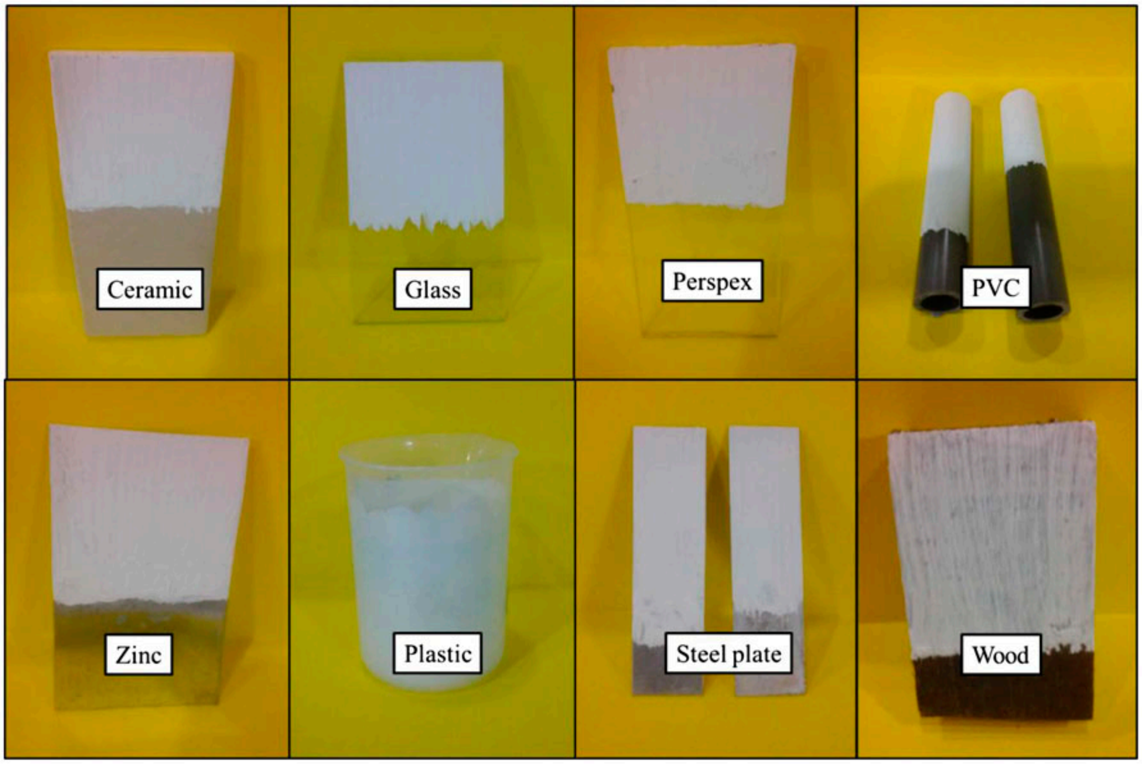


Fig. 11. *Paintosorp* application on surfaces; ceramic, glass, Perspex, PVC, Zinc, Plastic, steel plate and wood.

along the process of adsorption. It is reciprocate with scenario in actual conditions which pH in effluent may vary (Fig. 10).

3.7. Surface coating study

The *Paintosorp* is a new concept for adsorption application and aimed to be economic and easily accepted by industries. *Paintosorp* application as a pollution prevention in colour removal that does not require any new facilities or special equipment, however, only relies on small modifications of the existing facilities in industries. It is aimed to be coatable to any surfaces and there are few types of surfaces being tested by *Paintosorp* such as plastic beaker, PVC pipe, steel plate, zinc plate, glass plate, wooden block, perspex plate and ceramic plate. Observation in Fig. 11 showed that, after drying in oven, all the materials can be coated by *Paintosorp* and give acceptable strength.

4. Conclusion

This study highlighted the potential of *Paintosorp* as an effective adsorbent coating to be used in adsorption technique for dye removal. *Paintosorp* led to a new paradigm in adsorption application which will open up option to industries meeting their requirement. The current work provides feasibility results for different angle of the adsorption concept by using thin coated adsorbent layer. The adsorption of MB was found to be dependent on the initial dye concentration, contact time and temperature. The maximum removal obtained at >99% removal for every initial dye concentration up to its equilibrium time. The equilibrium adsorption data was best presented by the Freundlich isotherm, indicating the adsorption is heterogeneous surface and in a multilayer adsorption rules. The adsorption kinetic that was described well by the pseudo-second-order with intraparticle diffusion was not the only rate controlling step of the adsorption process. The adsorption is more spontaneous at higher temperature. The finding revealed the potential of *Paintosorp* as a viable adsorbent coating for future coloured wastewater treatment technology.

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