Original Research Paper

Open Access

Adsorption of Methylene Blue Using Chemically Enhanced *Platanus orientalis* Leaf Powder: Kinetics and Mechanisms

Baba Imoro Musah†, Lai Peng and Yifeng Xu

Department of Environmental Science and Engineering, School of Resources and Environmental Engineering, Wuhan University of Technology, Luoshi Road No. 122, Hongshan, Wuhan, Hubei, 430070, PR China
†Corresponding author: Baba Imoro Musah

ABSTRACT

The adsorption of methylene blue in an aqueous medium using two activated carbons AC1 and AC1 + H_3PO_4 was studied. The AC1+ H_3PO_4 adsorbent, which was inoculated with phosphoric acid, had better methylene blue removal capacity compared with AC1 adsorbent which had only thermal treatment. The optimum activation temperature for both adsorbents was 500°C while the suitable activation time was 180 min. The best pH in this investigation was 6. With AC1 + H_3PO_4 adsorbent, 100% removal of methylene blue was recorded for concentrations 20 to 100 mg.L^{-1} and the suitable adsorbent dosage was 3 g.L^{-1}. The effect of temperature showed insignificant effect on the adsorption of methylene blue ions. The SEM results for AC1 + H_3PO_4 adsorbent showed better pores compared with AC1, an indication that, the injection of phosphoric acid into it before the activation played a significant role in enhancing the porosity of the adsorbent surface.

INTRODUCTION

Textile, paper, painting and coating industries are major sources of dye pollutants. Large amount of dye wastewater are emptied into freshwater bodies which have negative consequences on the environment and human health (Oliveira et al. 2008). When exposed to light and water, methylene blue is difficult to fade and hard to be treated in wastewater by simple techniques such as biological treatment and chemical precipitation (Oliveira et al. 2008). In the production chain, it is reported that between the range of 1 to 15% the dye is lost and it is discharged as wastewater (Galindo et al. 2001, El-Sharkawy et al. 2007). Dye wastewater that ends up in fresh water bodies cause havoc to aquatic species by increasing toxicity chemical oxygen demand (COD). It also affects the photosynthetic activities of aquatic plants through the reduction of light penetration (Oliveira et al. 2008). It has been reported that, high COD, biological oxygen demand (BOD5) values, particulate matter (PM) and sediments, grease and oil in effluents lead to the depletion of dissolved oxygen creating serious consequences on aquatic species (Wang et al. 2011).

Methylene blue (MB) wastewater can be treated by photocatalytic degradation (El-Sharkawy et al. 2007). Generally, MB has poor biodegradability or resistance to environmental conditions (Tsai et al. 2001). Research indicates that, there are over 100,000 available commercial dyes and more than 7 × 10^5 t dye-materials are produced yearly (Lee et al. 2006). Methylene blue is used in many industries e.g. dyeing of silks, paper, plastic, leather, but it has wider usage in the synthetic textile fibre industries as the most suitable substrate (Oliveira et al. 2008). There are various classification of dyes such as anionic- direct, acid and reactive dyes; cationic - basic dyes; and non-ionic- disperse dyes (Fu & Viraraghavan 2001). The textile industry emission or discharge standards vary for many countries for different indicators e.g. China is COD 100 mg.L^1, BOD$_5$ 25 mg.L^{-1} and pH 6-9; in Germany, COD 160 mg.L^{-1} and BOD$_5$ 25 mg.L^{-1}; in Jordan COD 160 mg.L^{-1}, BOD$_5$ 60 mg.L^{-1} and pH 6-9; Oman COD 150 mg.L^{-1} and BOD$_5$; Tunisia COD 90 mg.L^{-1}, BOD$_5$ 30 mg.L^{-1} and pH 6.5-8.5 (Wang et al. 2011, WHO 2006, Sawal 1986).

Wastewater from dye-stuff and textile industries have dye concentrations below 1 g/dm^3, high alkalinity, biochemical oxygen demand, chemical oxygen demand and total oxygen dissolved solids (Kaushik & Malik 2009). Methylene blue is a cationic dye widely used in silk, cotton and wool processing as dyes (El-Sharkawy et al. 2007).

There are different treatment techniques that can be employed in the removal of environmental pollutants such as dyes. They include membrane filtration (Abid et al. 2012), electrochemical (Babu et al. 2011), reduction (Wali 2015), oxidation (Murthy et al. 2011), adsorption (Weng & Pan

Fig. 1: (a) leaf, (b) leaf powder inoculated with H_3PO_4 and (c) activated carbon.

2007), electrocoagulation (Akyol 2012), photocatalytic degradation (Sleiman et al. 2007). However, in the case of methylene blue $C_{16}H_{18}ClN_3S.3H_2O$, it is resilient to fading when exposed to water and light making it difficult to be removed from wastewaters through commonly used techniques like biological and chemical precipitation (Franca et al. 2009).

Adsorption as a technique for removing different kinds of pollutants such as heavy metals, dye among others in wastewater is reported to be an efficient method (El-Sharkawy et al. 2007). In this research adsorption technique is employed due the following reasons: environmentally friendly, ease of operation, wide range adsorbent sources among others are reported by some past studies (Saengbutr et al. 2014, Tong et al. 2010, Rashed 2013 and Lupascu & Povar 2016). With regards to industrial wastewater handling, adsorption processes serve as very interesting Alternative, especially when organic substances removal or recovering important chemicals are involved (Worch 2012).

The use of activated carbon as adsorbents are effective given that they have highly developed pore and large surface area with high degree of surface reactivity (Dias et al. 2007).

In recent times, there's rising interest in new techniques regarding the production of cost effective, efficient and eco-friendly adsorbents for large scale utilization. In view of this, agricultural by-products or plant waste materials are of interest to research for utilization as adsorbents; wheat brand (Çiçek et al. 2007), green pea peels (Dod et al. 2012), mango leaves (Kamsonlian et al. 2012), yellow passion fruit waste (Pavan et al. 2008), rice hull ash (Wang & Lin 2008), neem leaves (Saengbutr et al. 2014), hevea brasilliensis seed coat (Hameed & Daud 2008). It is reported that plant leaves contain certain constituents, e.g. polyphenols, lignin, pigments and protein making it suitable to provide active sites for binding dyes (Abadian et al. 2015). This study considers *platanus orientalis* leaf powder as a potential adsorbent for the removal of methylene blue in an aqueous solution.

MATERIALS AND METHODS

Materials and Chemicals

The adsorbent material for this investigation was obtained in December 2015, from Wuhan University of Technology campus, China. It went through systematic processing stages until the final product (AC) was obtained. Sample activated carbons were subsequently stored in a desiccator at room temperature (25°C) to keep it free from moisture contact. Fig. 1a is the leaf sample, 1b is leaf powder inoculated with H_3PO_4 and 1c is activated carbon.

The following chemicals were used in the investigation e.g. methylene blue trihydrate, phosphoric acid (H_3PO_4), sodium hydroxide (NaOH) and hydrochloric acid (HCl). The rest of the chemicals used in the study were: sodium chloride (NaCl), potassium bromide (KBr), ethanol (CH_3CH_2OH), all by China Sinopharm Chemical Reagents Co. Ltd. A 1000 mg/L stock solution methylene blue was prepared using deionized water obtained from Milli-Q Direct 16 distillation machine with Vent Filter MPK01. Different concentrations of methylene blue such as 20, 40, 60, 80, 100, 120 and 140 $mg.L^{-1}$ were subsequently prepared from the stock solution for use in the investigation. All chemicals and reagents used in the investigation were of analytical grade.

Sample Activation

A total of 40 g of dried fallen *platanus orientalis* leaf powder (FPOLP) was used for two sets of activations in this investigation involving methylene blue. First, 20 g of FPOLP was thermally treated (pyrolyzed) in an electric furnace for 180 min at temperature 500°C. After that, the activated sample labelled AC1 and it was allowed to cool and the black activated sample obtained was reweighed. It emerged that after subjecting the FPOLP to the above temperature and duration, 63.4% of the sample got lost through the application of heat leaving only 36.6% representing 7.32 g in the process.

Another sample constituting 20 g of FPOLP was impregnated with 30 wt % of H_3PO_4 solution with a ratio of 1:1 (Demiral & Güngör 2015scanning electron microscopy (SEM, Prahas et al. 2008). The sample was thoroughly mixed to ensure uniformity and kept for 12 h, afterward the mixed sample was heated at 80°C to ensure that excess water is evaporated for 4 h in an oven 101-1AB, manufactured by Tianjin Taisite Instrument Co. Ltd. The mixed sample was put into a crucible and then pyrolyze at 500°C for 180 min. Once heating was over, the sample was allowed to cool down. Finally, it was washed repeatedly with deionized water till the pH of the mixture became neutral (7.0). The particulates were separated using Ø12.5 cm filter paper made in Hangzhou (GB/T1914-2007). It was oven dried at 80°C for 12 h, it was reweighed as 10.16 g which represented 50.8% of adsorbent retained after chemical and thermal treatment. It was then labelled AC1 + H_3PO_4 preserved in capped petri dish and stored in desiccator for subsequent use.

Batch Adsorption

The removal efficiency and equilibrium adsorption capacities were determined from batch experiments conducted using isothermal shaker. Different adsorbent dosages were investigated e.g. 1, 2, 3 and 4 g.L^{-1}. At the end of the investigations into the adsorbent dosage, 3 g.L^{-1} was found to be the optimum dosage and it was used for further investigations. To each conical flask, 3 g.L^{-1} adsorbents (AC1 and AC1+ H_3PO_4) were applied to 25 mL of methylene blue solution. The shaking frequencies were maintained for 120 min with agitation speed of 150 rpm.

At the end of the quaking process, Whatman filter papers were used to separate the adsorbent. Fourier transform infrared (FT-IR) thermo-scientific NICOLET (iS10) Spectrometer was employed to identify the functional groups on the surface of the adsorbent. About 0.05 g of potassium bromide (KBr) were mixed with 0.01 g of the adsorbent, compressed into a light tablet shape. The FT-IR spectrometer were allowed to calibrate 32 times to set the background and the spectra were recorded in the band range of 4000 nm to 500 nm for subsequent analysis. The amount of MB absorbed at equilibrium (mg/g) was obtained using Eq. 1

$$q_e = \frac{(C_o - C_e)}{m}V \qquad \ldots(1)$$

Where, C_0 is the initial dye concentration (mg/L), C_t is the concentration of solution at time t, V is the volume of the solution (L) and m is the mass of the adsorbent (g).

The methylene blue removal efficiency (R in %) was calculated using Eq. 2

$$R = \frac{(C_e - C_t)}{C_o} \times 100\% \qquad \ldots(2)$$

Sample Characterization

The effect of dye solution pH was investigated. The initial pH range of methylene blue solutions were varied from 2 to 10. The pH was controlled by adding 0.1 M dilute HCl and 0.1 M NaOH solutions using Cyberscan pH 2100-meter Eutech instruments. The pH of point zero charge (pH$_{pzc}$) of the adsorbent was equally investigated because there is a correlation between the surface behaviour of the adsorbent and adsorbate. The uptake of dye can be explained based on the pH$_{pzc}$ of the adsorbent (Cardenas-Peña et al. 2012). The investigation was done by the solid addition method (Ponnusami et al. 2008).

An amount of 2 g.L^{-1} of AC1+H_3PO_4 adsorbent was added to 50 mL of 0.1M NaCl solution into six 250 mL conical flasks. The pHs were regulated in the range of 2 to 12 using 0.1 M NaOH and 0.1 M HCl solutions respectively. A number of batch absorptions were conducted with the electrolyte solution; the mixtures were allowed to agitate in a shaker for 12 h. The initial pHs were labelled (pH$_i$) and the final pH labelled (pH$_f$). The change in pH (ΔpH) determined by this relationship as follows; (ΔpH = pH$_i$ - pH$_f$), the ΔpH is plotted against the pH$_i$. The pH$_{pzc}$ of the adsorbent is the point on the graph where it is equal to zero (0) (Cardenas-Peña et al. 2012).

Several 250 mL conical flasks each containing 25 mL of methylene blue solution of 100 mg.L^{-1} concentration were prepared. Varied amounts of adsorbent in the range of 1 to 4 g.L^{-1} applied under 25°C temperature condition at pH 6 to each flask containing the methylene blue solution. These flasks were vigorously agitated in shaker at a speed of 150 rpm for 120 min. The mixtures were then filtered after the desired time had elapsed using filter papers. The adsorbate was then used for analysis by employing spectrophotometer calibrated or standardized at 665 nm. The amount of methylene blue absorbed is calculated in each case using origin 8 application software. SEM analysis was done using analytical JSM-IT300, a product by JEOL Ltd. Japan.

RESULTS AND DISCUSSION

Effect of Adsorbent Surface Modification

Inquiries were carried out with AC1 and AC1+H_3PO_4 adsorbents respectively, with constant dosage of 3 g.L^{-1} in 25 mL methylene blue solution. The concentrations of methylene blue were varied in the following order 20, 40, 60, 80, 100, 120 and 140 mg.L^{-1}. Fig. 2 illustrates the results from this investigation, it is evident that AC1 adsorbent has less efficiency in the removal of methylene blue after the concentration increased from 20 mg.L^{-1}. For AC1 + H_3PO_4 adsorbent on the other hand showed high removal efficiency
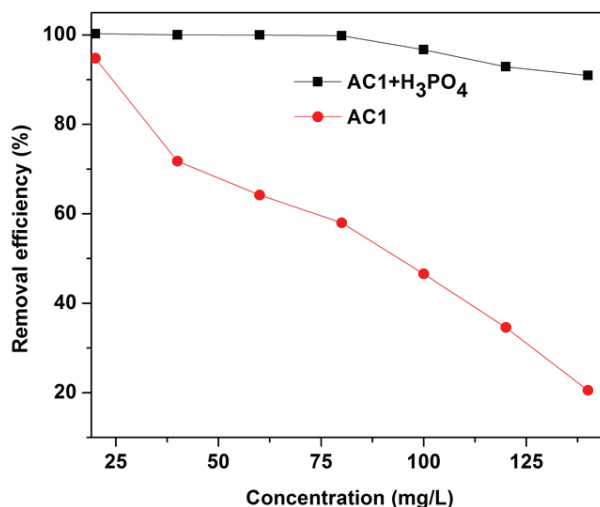
Fig. 2: Effect of adsorbents surface modification. Removal efficiency using AC1 and AC1+H$_3$PO$_4$ with adsorbents dosage of 3 g.L^{-1} at temperature 25°C, time 2 h and neutral pH with agitation speed at 150 rpm.

for all initial methylene blue concentrations studied.

Decolourization of aqueous methylene blue solution was 100% for AC1 + H$_3$PO$_4$ at 20, 40, 60 mg.L^{-1}. It declined to 99.8, 96.7, 92.9 and 90.9% at 80, 100,120 and 140 mg.L^{-1} respectively.

When AC1 adsorbent, removal efficiency stood at 94.7, 71.7 and 64.2% with concentration 20, 40 and 60 mg.L^{-1} respectively.

The removal efficiency still reduced significantly to 58.0% with a concentration of 80 mg.L^{-1} and 46.5% with 100 mg.L^{-1}, consequently, an increase in methylene blue concentration to 120 mg.L^{-1} showed a downward trend of 34.5% removal of methylene blue and eventually reduced to 20.5% with a concentration of 140 mg.L^{-1}.

The trends observed could be explained by the fact that, the adsorbent surface becomes saturated with the increase in methylene blue concentration as similarly reported (Xiong et al. 2010).

Effect of pH

The effect of pH on methylene blue adsorption was examined using AC1 and AC1+H$_3$PO$_4$ adsorbents respectively in 100 mg.L^{-1} initial methylene blue concentration with adsorbent dosage 3 g.L^{-1} at temperature 25°C. Initial pH of methylene blue solution was adjusted between 2 to 10 in Fig. 3a. The pH of point zero charge (pHpzc) of the adsorbent was studied in the range of 0 to 12 as shown in Fig. 3b.

When the initial pH was first increased from 2 to 4 in Fig. 3a, the removal efficiency of dye increased from 98.6% to 99.2%. Removal efficiency further increased to 100%

when initial pH was augmented to 6, but both pH 8 and 10 recorded same slight decline in methylene blue removal efficiencies at 99.4% as in Fig. 3a.

In the case of using AC1 adsorbent, when the pH was adjusted from pH 2 to 4, the removal efficiency increased from 49.8 to 70.5%. Additional increase in pH to 6 resulted in a rise in the methylene blue removal percentage to 82.9% in Fig. 3a. Further increase in initial methylene blue pH between 8 and 10, resulted in a minimal reduction in removal efficiency to 81.8 and 79.6% respectively as represented in Fig. 3a.

In Fig. 3b shows the results of pH at point of zero charge (pHP$_{zc}$) of the adsorbent surface. The pHP$_{zc}$ was recorded at pH 1.8 in (Fig. 3b) lower than pH 6 at which maximum adsorption of the dye took place. There is some correlation between solution pH and pHp$_{zc}$. It is reported that if the optimum pH of a solution is great than the pHPzc, the electrostatic force of attraction between positively charge dyes and negatively charged AC1+H$_3$PO$_4$ adsorbent is greatly enhanced and vice versa (El Qada et al. 2008). Since this study revealed pH 6 as optimum, it is clear that, pH had some influence on the adsorption of methylene blue as explained. Similar corroborative report suggests that, hydrogen reduces between pH 6 and 7, this gives rise to enhanced adsorption (Nethaji et al. 2013).

Effect of Adsorbent Dosage

The effect of adsorbent dosage was studied using AC1 and AC1+H$_3$PO$_4$ respectively in Fig. 4.

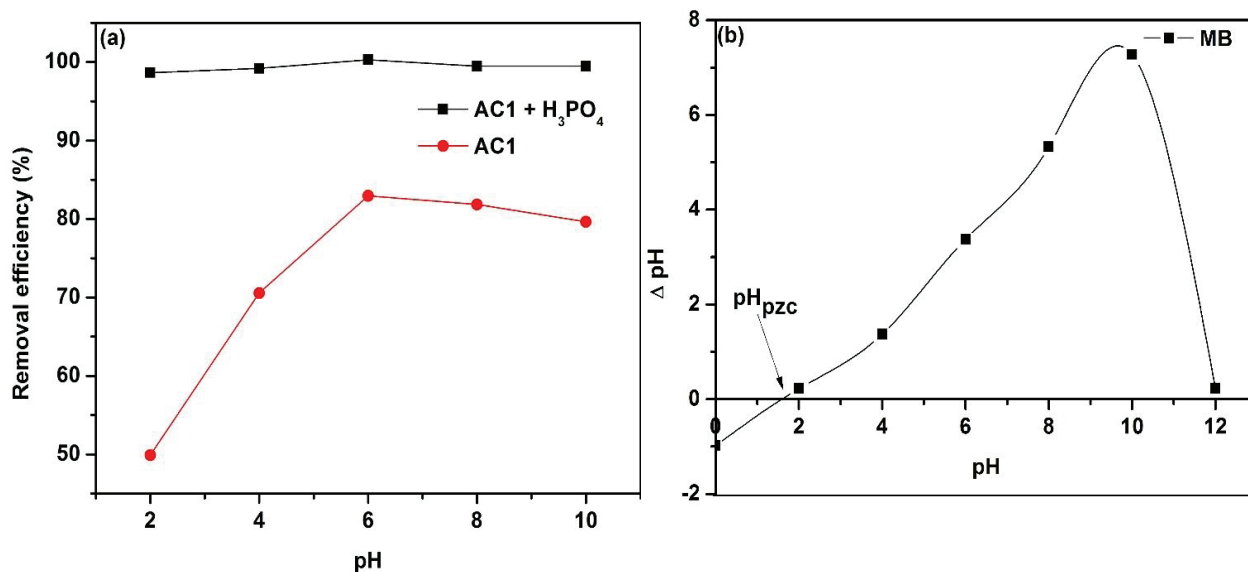In order to determine the suitable quantity of the adsor-

Fig. 3: Effect of pH (a) removal efficiency and (b) pH_{pzc} at temperature 25°C.
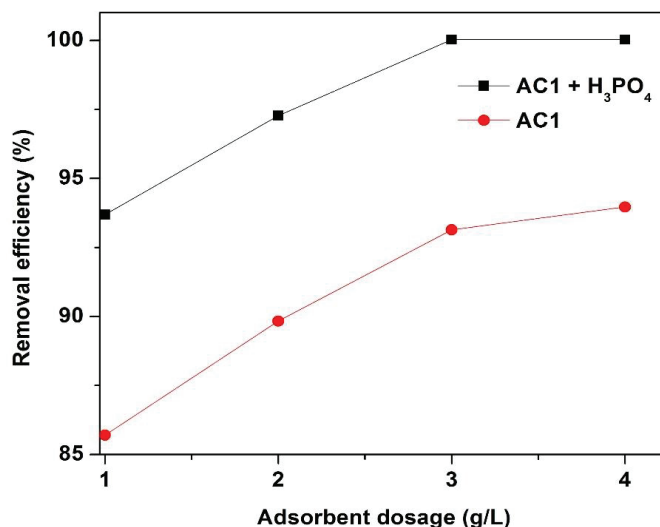

Fig. 4: Effect of adsorbent dosage on methylene blue adsorption, 100 mg.L^{-1}, temperature 25°C, at pH 6 with agitation speed of 150 rpm and time 2 h.

bent to achieve enough removal of dyes, varied dosages in the order 1, 2, 3 and 4 g.L^{-1} per 25 mL solution of methylene blue were applied in each 250 mL conical flask. All other parameters e.g. initial concentration 100 mg.L^{-1}, temperature 25°C, pH 6, shaking speed 150 rpm and contact time with absorbent 2 h were kept constant while varying the adsorbent dosage. The results obtained are presented in Fig. 4. It is clear that, when AC1 adsorbent was increased from 1 g.L^{-1} to 3 g.L^{-1}, the removal efficiency moved from 85.7 to 93.1%. When the adsorbent dosage was further increased

to 4 g.L^{-1}, the depletion of dyes slightly changed to 93.9%. Likewise, with the application of AC1+H$_3$PO$_4$ adsorbent, it was also noticed that, increasing adsorbent dosage resulted in increase in dyes depletion. When the adsorbent dosage was varied from 1 g.L^{-1} to 3 g.L^{-1}, removal of dyes increased from 93.6% to 100%. No further variation in the adsorbent dosage was deemed necessary given the outcome recorded.

Effect of Initial Methylene Blue Concentration

Investigation was carried out to evaluate the effect of initial

methylene blue concentration on adsorption. The results of the findings are shown in Fig. 5 using AC1 and AC1+H_3PO_4 adsorbents respectively.

The evaluation was done using constant adsorbent dosage of 3 g.L^{-1} in 25 mL solution of methylene blue at temperature 25°C. The initial concentrations were varied in this order 20, 40, 60, 80, 100, 120 and 140 mg.L^{-1} at pH 6 for 2 h. For AC1 adsorbent, 100% of the dye was removed at initial concentration of 20 mg.L^{-1} but reduced to 84.6% at initial concentration 140 mg.L^{-1}.

The unit adsorption capacity increased from 6.6 to 39.5 mg.g-1 using AC1 adsorbent when initial concentration was varied from 20 mg.L-1 to 140 mg.L-1. This pattern as observed in this investigation has some similarity with other studies involving methylene blue (Elizalde-González et al. 2007, Demirbas et al. 2008).

It was observed that, 100% of the methylene blue was using AC1+ H_3PO_4 adsorbent for initial concentrations from 20 to 100 mg.L^{-1}. However, the removal efficiency steadily declined upon further increase in initial methylene blue concentration between 120 and 140 mg.L^{-1} with corresponding removals at 96.3 and 91.9% respectively.

The adsorption capacity for AC1+ H_3PO_4 adsorbent increased from 6.6 to 42.9 mg.g^{-1} when initial concentration was augmented from 20 mg.L^{-1} to 140 mg.L^{-1}. It is obvious from the above finding that, increasing concentration negatively affected the amount of dyes removed for adsorbents.

This finding is attributed to the saturation of empty sites within the adsorbent (Garg et al. 2004, Hameed et al. 2008).

Effect of Contact Time

This was studied in order to evaluate its impact on methylene blue uptake. This investigation was done using varied intervals of time as indicated in Fig. 6, as a result the equilibrium time was also determined.

Every other parameter in essentially was kept constant while time was adjusted within the intervals 5, 10, 20, 30, 40, 80 and 120 minutes since it was the only factor under evaluation in this case as indicated in Fig. 6. The results showed that, 80 min contact time was enough for the system to reach equilibrium with the given initial concentration. In Fig. 6 above, the adsorption process was a little bit rapid during the initial stages (from 0 to 40 min) with corresponding adsorption capacity from 28.7 to 32.8 mg.g^{-1}. This slow incremental trend continued until the system reached equilibrium with a maximum adsorption capacity of 33.34 mg.g^{-1}. The rapid uptake phenomenon may have occurred due to high presence of unoccupied or relatively vacant sites in the adsorbent at the initial stages. As the vacant sites were being occupied in the process of the adsorption, dye uptake slowed down due to a reduction in active vacant sites on the surface of AC1+H_3PO_4 adsorbent. There is a corroborative finding to what was recorded (Hameed et al. 2008)low-cost, locally available sorbent, pomelo (Citrus grandis).
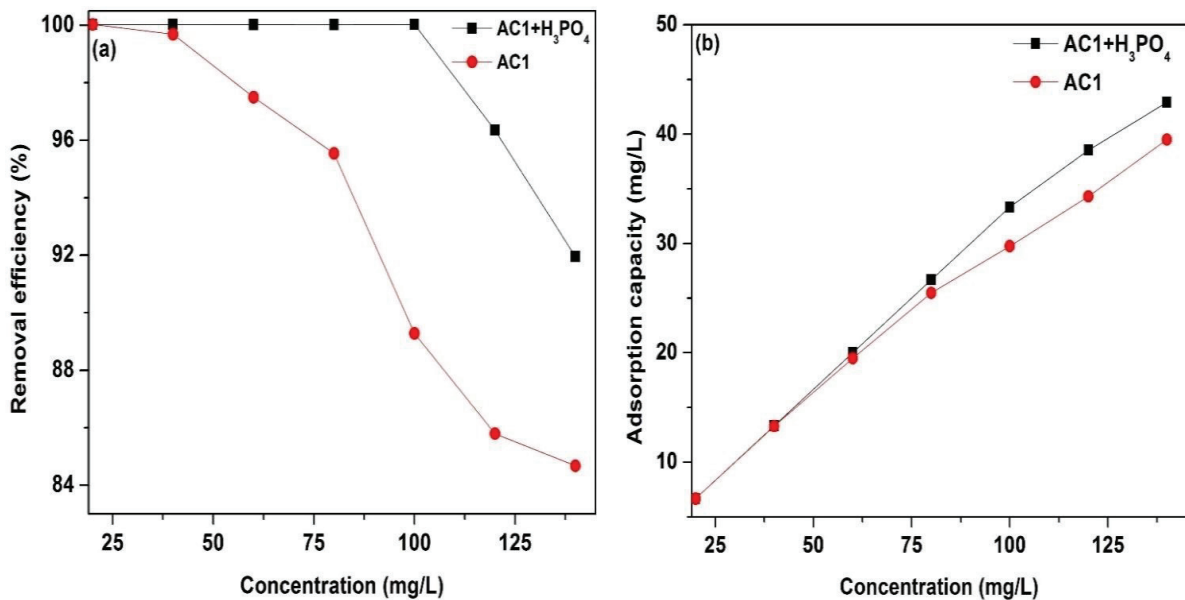

Fig. 5: Effect of initial methylene blue concentration (a) removal efficiency and (b) adsorption capacity, with adsorbent dosage 3 g.L^{-1}, at pH 6, time 2 h at temperature 25°C and agitation speed of 150 rpm.
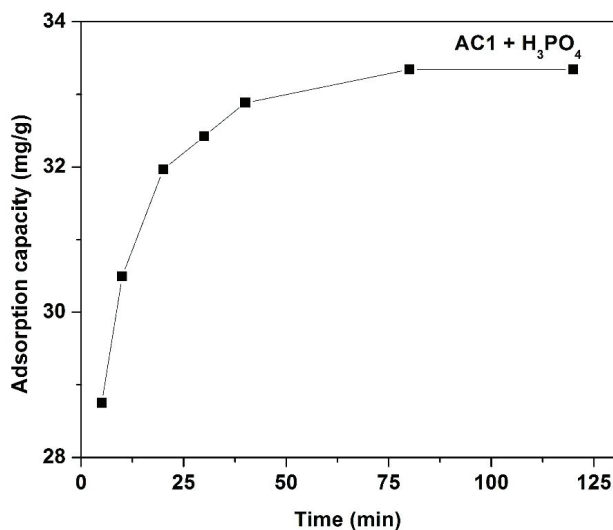
Fig. 6: Effect of contact time on methylene blue adsorption using AC1+H$_3$PO$_4$ adsorbent; initial concentration 100 mg.L^{-1}, pH 6, at temperature 25°C, agitation speed 150 rpm and adsorbent dosage 3 g.L^{-1}.
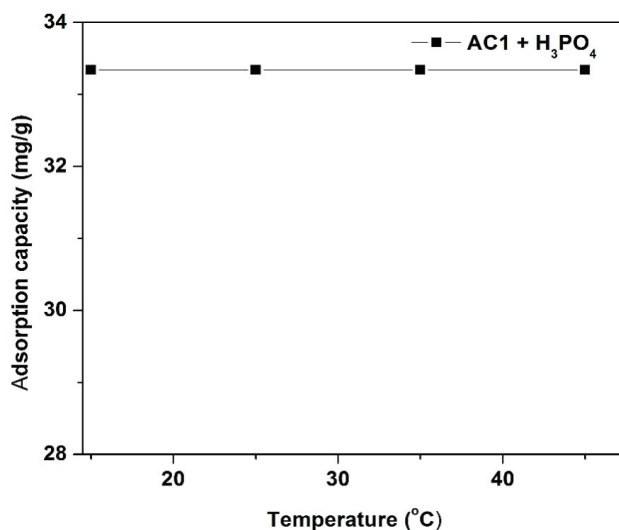

Fig. 7: Effect of temperature on methylene blue adsorption with initial concentration 100 mg.L^{-1}, time 2 h, adsorbent dosage 3 g.L^{-1} (AC1+H$_3$PO$_4$), agitation speed 150 rpm at pH 6.

Effect of Temperature

The effect of temperature on methylene blue uptake was investigate studied with different temperatures ranging from 15 to 45°C. Since the evaluation here was relating to heat variation, the other parameters such as initial methylene blue concentration 100 mg.L^{-1}, adsorbent dosage 3 g.L^{-1} (AC1+ H$_3$PO$_4$), pH 6, contact time 2 h and agitation speed at 150 rpm were maintained. Fig. 7, showed that, temperature variation had little or no effect on the removal percentage of methylene blue when temperature was increased from 15°C to 45°C. This outcome means temperature changes did not influence the adsorption process. The adsorption capacity recorded 33.34 mg.g^{-1}.

Adsorption Kinetics

Kinetics relates directly to thermodynamic equilibrium rate pertaining to a system that is not in an equilibrium state, thus the process of adsorption would linger on until equilibrium is established. However, in the case of desorption, the process is the reverse till the attainment of equilibrium.

The adsorption rates can effectively be evaluated using Lagergren (Ho 2004) pseudo-first-order model for kinetics

together with Ho & McKay modified formula (Ho & McKay 1999). The equation (Eq. 3) is modelled as:

$$\frac{d_{qt}}{d_t} = k_1 (q_e - q_t) \qquad \ldots(3)$$

Where q_e and q_t are the amount of dye absorbed (mg.g^{-1}) at equilibrium and at time, t (min) respectively and k_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}).

The variables in equation (Eq. 3) are defined as: q_e is the adsorbed quantity of ions or molecules at equilibrium point (mg.g^{-1}), q_t is the quantum of molecules uptaken at a given period in the adsorption process while k_1 represents the rate constant for pseudo-first-order kinetic model (1/h). But, in order to determine the rate constant, equation (Eq. 3) was standardized into a linear form to allow a plotting of ln(q_e-q_t) against period. The intercept and slope of the plot were determined from the relationship. Equation 4 can be rearranged in this order taking into account the boundary conditions (Ho & Mckay 1998), t = 0 to t and q_t = 0 to q_t as:

$$\log (q_e - q_t) = \log (q_e) - \frac{d_{qt}}{dt} \qquad \ldots(4)$$

The plot of log (q_e - q_t) versus t was made and the slope and intercept from this relationship was used to determine the first-order rate constant, k_1 in Fig 8a.

For the evaluation of adsorption kinetics data, essentially not every data may fit well in pseudo-first-order equation, thus to overcome this limitation, pseudo-first-order model was additionally employed due to its general flexibility for the data analysis (Ho & McKay 1999). The new equation was reorganized into equation (Eq.5) as follows:

$$\frac{d_{qt}}{dt} = k_2 (q_e - q_t)^2 \qquad \ldots(5)$$

Where, k_2 represents the equilibrium rate constant of pseudo-second-order adsorption (g/mg min).

In equation (Eq. 5), k_2 is defined as pseudo-second-order kinetic rate constant (g/mg min). But for determination of the dynamics relating to rate and other variables, pseudo-second-order equation (Eq. 5) was rearranged. The suitability of this model is verified after getting linear graph from the plot of $\frac{t}{q}$ against t. The value of k_2 was determined from the intercept and the slope respectively. The rearranged equation (Eq. 10) is below and $k_2 q_e^2$ is equal to initial rate of adsorption h (mg/g.min). Equation (5) taking into consideration the boundary condition (Ho 2004) t = 0 to t and q_t = 0 to q_t gives rise to the following:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} k_2 t \qquad \ldots(6)$$

The above equation (6) is the integrated rate law for pseudo-second-order interaction and it can be rearranged in a linearized form as:

$$\frac{t}{q_t} = \frac{1}{k_{2q^2 e}} + \frac{1}{q_e} t \qquad \ldots(7)$$

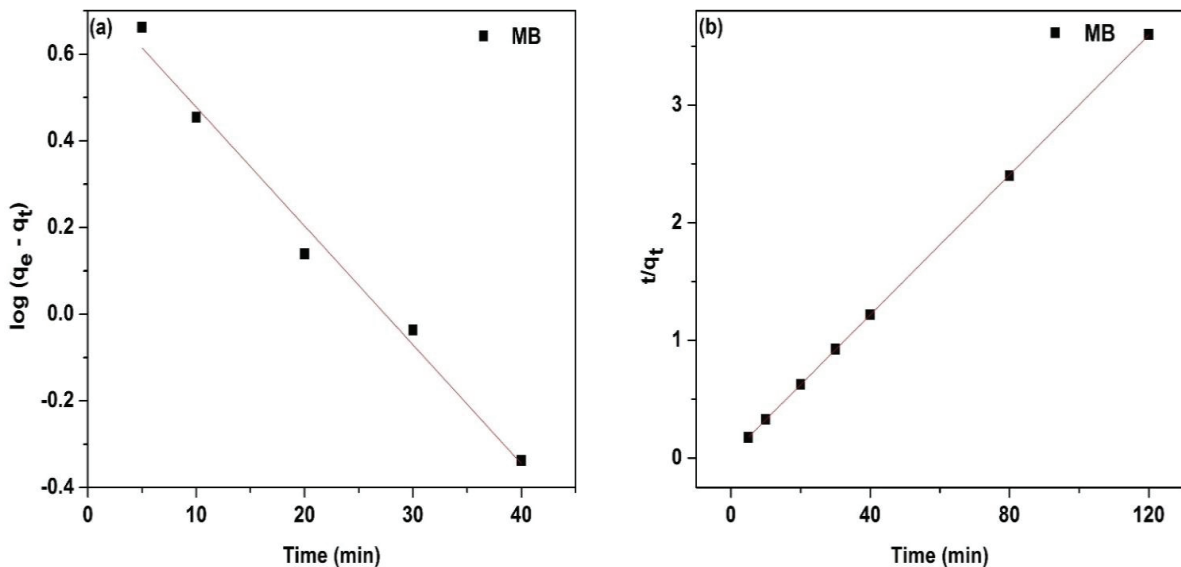The second-order rate constant, k_2 was determined from

Fig. 8: (a) Pseudo-first-order kinetic and (b) Pseudo-second-order kinetic; on methylene, blue adsorption with initial concentration 100 mg.L^{-1}, adsorbent dosage 3 g.L^{-1} (AC1+H$_3$PO$_4$), agitation speed 150 rpm at pH 6.

Table 1: Pseudo-first and second-order adsorption rate constants for 100 mg L initial methylene blue concentration.

Experiment	Pseudo-first-order			Pseudo-second-order		
Exq_e (mg g^{-1})	k_1 (min^{-1})	cal q_e, (mg.g^{-1})	R^2	k_2 (g.mg^{-1} min^{-1})	cal q_e (mg.g^{-1})	R^2
42.90	0.083	27.44	0.982	0.029	38.40	0.999

a calculation using the slope and intercept of the plot $\frac{t}{q_t}$ versus t.

The Pseudo-first and second-order adsorption rate constants for 100 mg L initial methylene blue concentration are given in Table 1.

Adsorption Mechanisms

The surface morphology, and pores of an adsorbent is dependent on the adsorbent type. In this study, two different methods (Nowicki et al. 2010); physical and chemical activation were employed in the preparation of the adsorbent for the adsorption. Physical activation involves the subjection of a raw material or waste to higher degree of heating either in an oxygen, steam or carbon monoxide condition in a temperature regime such as 300-1200°C (Nowicki & Pietrzak 2010). While in the chemical activation process, the dried leaf powder was largely inoculated with 1:1 phosphoric acid (H_3PO_3) solution (Yakout & Sharaf El-Deen 2016), air-dried and subsequently subjected to thermal treated at 500°C for 3 h. The adsorbents (FPOLP, AC1 and AC1 + H_3PO_4) were spectrally (FTIR) examined with the aid of a spectrometer as shown in Fig. 9. The thermal treatments of AC1 and AC1 + H_3PO_4 adsorbents respectively, could be responsible for the shift of peaks for AC1 graph labelled (B) and for AC1 + H_3PO_4 graph labelled (A) all in Fig. 9. Again, the subsequent chemical injection (H_3PO_4) on AC1 + H_3PO_4 adsorbent effectively changed its morphology, making it more porous as observed in the SEM in Fig. 10b. Apart from acids, other chemicals such as salts, e.g. $ZnCl_2$ (Hu et al. 2009) or base, e.g. KOH (Evbuomwan et al. 2012) could have been used to enhance the porosity of surface area of the adsorbent. The main objective of the activation is essentially to optimize the surface area (micro and mesoporous) availability on the FPOLP for efficient adsorption. From the results, firmed by the SEM analysis, the chemical activation had proven to be more effective compared to the physical activation alone. Similar study has been sighted by Mohammad & Rahbar-kelishami (2014) has been sighted, however, it is important to stress that, the explanation given about the adsorbent preparation is quite ambiguous.

FTIR Spectra Analysis

The spectra analysis of three different samples (a) AC1 + H_3PO_4, (b) AC1 and (c) FPOLP are presented in Fig. 9. In Fig. 9a, the peak 1081 cm^{-1} may be assigned to strong C-O stretching, this functional group is associated with primary alcohol (Pradhan 2011).

Peak 1161 cm^{-1} is generated due to robust C-O stretching and it may be the effect of aliphatic ether. The peak at 1384 cm^{-1} is intermediate bending due to O-H and its functionality could most likely be phenol. However, the strong C=C stretching effect likely generated the peak at 1613 cm^{-1} (Kundu et al. 2008).

The peaks between 3400 and 3550 cm^{-1} on spectra Fig. 9c (FPOLP) could be allotted to great dominance O-H functional group, thus representing free hydroxyl fundamentals located in the FPOLP. The peaks at 2850 and 2925 cm^{-1} may be assigned to aromatic elements, however after being subjected to higher temperature (500°C) in an oxidized environment for 180 min, led to the disappearance of the two peaks in Fig. 9a and 9b.

The peaks between 1626 and 1629 cm^{-1} have the characteristics of carbonyl functionality due to the effect of -COOH (Jokar et al. 2016). However, band 1318 cm^{-1} and 1400 cm^{-1} could be associated with aromatic nitriles which play a significant role in obtaining amines in hydrogenation process (Thusnavis et al. 2011, Wu et al. 2008). After subjection to different modifications in an oxidized condition, peak 1318 and 1048 cm^{-1} in Fig. 9c varnished in Fig. 9a and Fig. 9b, which are attributable to primary alcohol which could easily be oxidized to aldehydes or carboxylic acid depending on the reaction condition. Peak shift occurred at 1081 cm^{-1} (Fig. 9a) compared to the peak at 1048 cm^{-1} in Fig. 9c, this could possibly be the result of the modification effect. From the investigation conducted, the multiple modification had significant reflection in the adsorption attributes on adsorbent AC1 + H_3PO_4. It is reported that, the activation of carbon materials with oxidizing agents help generate oxygen-related functionalities that enhances the adsorption capabilities of the adsorbent during adsorption (Li et al. 2002, Do 1998).

SEM Analysis

Investigations were conducted on samples AC1 and AC1+ H_3PO_4 adsorbents respectively, employing scanning electron microscopic techniques. The results revealed very porous morphological features after it was treated with phosphoric acid (1:1) for 4 h prior to thermal treatment for 3 h for AC1 + H_3PO_4 adsorbent. Fig. 10a (AC1) adsorbent showed cell-
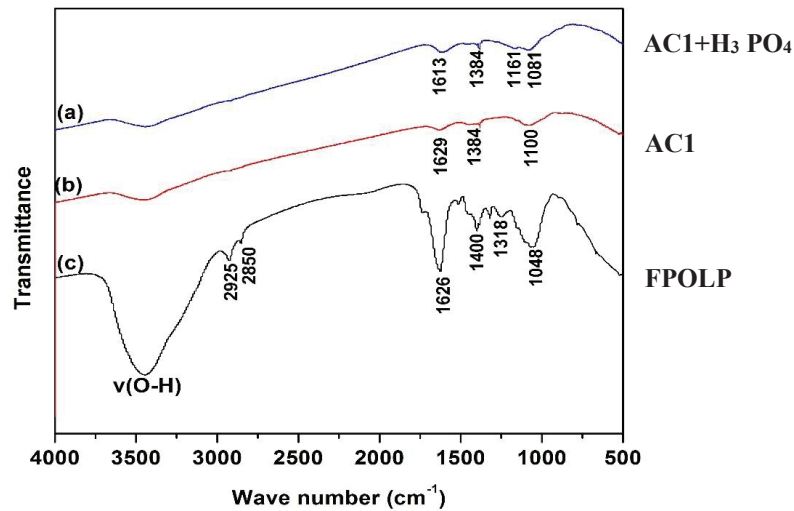
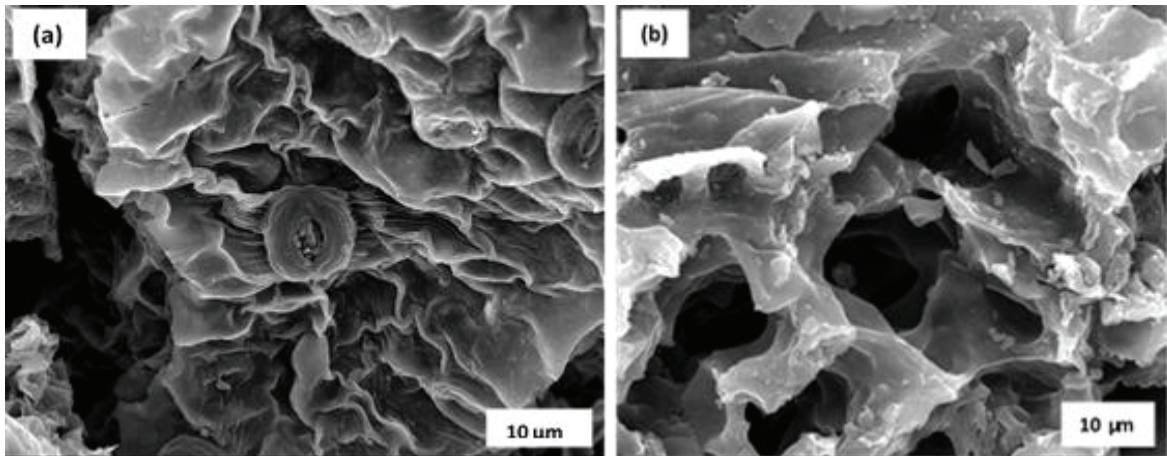Fig. 9: FTIR Spectra graph (a) AC1 + H_3PO_4 (b) AC1 and (c) FPOLP adsorbents respectively.

Fig. 10: SEM results (a) AC1 and (b) AC1+H_3PO_4 adsorbents respectively.

like pores on the surface of the adsorbent while Fig. 10b (AC1 + H_3PO_4) adsorbent revealed the inner pores present in the adsorbent.

The presence of both surface and inner pores on the adsorbent may have contributed significantly to the overwhelming adsorption of the dye molecules. The injection of oxygenated compounds into carbonaceous materials may have increased the level of porosity on the adsorbent which effectively enhance the adsorption capabilities as the adsorption investigation showed a remarkable removal, in some cases as earlier reported (Yakout & Sharaf 2016, Prahas et al. 2008, Altenor et al. 2009, Dias et al. 2007). The effectiveness of an adsorbent may be influenced by

varied parameters such as the porosity and high surface area. In addition, the solubility as well as the affinity that exist between the particulates and the adsorbent could result in a hydrophobic and hydrophilic interaction.

CONCLUSION

This study involved the investigation of Methylene blue using two different absorbents prepared from fallen P. *orientalis* leaves powder. For AC1 adsorbent, it was thermally treated at 500°C for 2 h, while AC1+H_3PO_4 adsorbent was injected with phosphoric acid 1:1 solution followed by thermal treatment at same temperature and time as AC1. The removal efficiency reduced from 100% to 84.6% when MB concentration was

varied from 20 to 140 mg.L^{-1} for AC1 adsorbent, whereas for AC1+H$_3$PO$_4$, removal efficiency decreased from 100% to 91.6% when MB concentration increased from 20 to 140 mg.L^{-1}. The effect of solution pH revealed pH 6 as the optimum condition for maximum adsorption, from the range of 2 to10. The optimum adsorbent dosage was 3 g.L^{-1} at equilibrium time of 80 min and maximum adsorption was 42.9 mg.g^{-1}. The surface morphology of AC1+H$_3$PO$_4$ after an SEM examination confirms earlier reports which suggest that phosphoric acid injection could enhance the surface characteristics of adsorbents, hence a fulfilment of one of the objectives of this study which was to ascertain the veracity of potential of phosphoric acid as activation agent for adsorbents. FPOLP has proven to be a cheap source of activated carbon with good potential for adsorbing methylene blue.

ACKNOWLEDGEMENT

REFERENCES

Abadian, S., Rahbar-Kelishami, A., Norouzbeigi, R. and Peydayesh, M. 2015. Cu(II) adsorption onto *Platanus orientalis* leaf powder: Kinetic, isotherm, and thermodynamic studies. Res. Chem. Intermed., 41: 7669-7681.

Abid, M.F., Zablouk, M.A. and Abid-Alameer, A.M. 2012. Experimental study of dye removal from industrial wastewater by membrane technologies of reverse osmosis and nanofiltration. Iranian J. Environ. Health Sci. Eng., 9: 17.

Akyol, A. 2012. Treatment of paint manufacturing wastewater by electrocoagulation. Desalination, 285: 91-99.

Altenor, S., Carene, B., Emmanuel, E., Lambert, J., Ehrhardt, J.J. and Gaspard, S. 2009. Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation. J. Hazard. Mater., 165: 1029-1039.

Babu, B.R., Parande, A.K. and Kumar, S.A. 2011. Treatment of dye effluent by electrochemical and biological processes. Open J. Saf. Sci. Technol., 1: 12-18.

Cardenas-Peña, A.M., Ibanez, J.G. and Vasquez-Medrano, R. 2012. Determination of the point of zero charge for electrocoagulation precipitates from an iron anode. Int. J. Electrochem. Sci., 7: 6142-6153.

Çiçek, F., Özer, D., Özer, A. and Özer, A. 2007. Low cost removal of reactive dyes using wheat brand. J. Hazard. Mater., 146: 408-416.

Demiral, H. and Güngör, C. 2015. Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse. J. Clean. Prod., 124: 103-113.

Demirbas, E., Kobya, M. and Sulak, M.T. 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. Bioresour. Technol., 99: 5368-5373.

Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J. and Sánchez-Polo, M. 2007. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J. Environ. Manage., 85: 833-846.

Do, D.D. 1998. Adsorption Analysis: Equilibria and Kinetics. Vol. 2, Imperial College Press, London.

Dod, R., Banerjee, G. and Saini, S. 2012. Adsorption of methylene blue using green pea peels (Pisum sativum): a cost-effective option for dye-based wastewater treatment. Biotechnol. Bioprocess Eng., 17: 862-874.

El Qada, E.N., Allen, S.J. and Walker, G.M. 2008. Adsorption of basic dyes from aqueous solution onto activated carbons. Chem. Eng. J., 135: 174-184.

Elizalde-González, M.P., Mattusch, J., Peláez-Cid, A.A. and Wennrich, R. 2007. Characterization of adsorbent materials prepared from avocado kernel seeds: Natural, activated and carbonized forms. J. Anal. Appl. Pyrolysis, 78: 185-193.

El-Sharkawy, E.A., Soliman, A.Y. and Al-Amer, K.M. 2007. Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation. J. Colloid Interface Sci., 310: 498-508.

Evbuomwan, B.O., Abutu, A.S and Ezeh, C.P. 2012. The effects of carbonization temperature on some physicochemical properties of bamboo based activated carbon by potassium hydroxide (KOH) activation. Greener J. Phys. Sci., 3: 187-191.

Franca, A.S., Oliveira, L.S. and Ferreira, M.E. 2009. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. Desalination 249: 267-272.

Fu, Y. and Viraraghavan, T. 2001. Fungal decolorization of dye wastewaters: A review. Bioresour. Technol., 79: 251-262.

Galindo, C., Jacques, P. and Kalt, A. 2001. Photooxidation of the phenylazonaphthol AO20 on TIO2: Kinetic and mechanistic investigations. Chemosphere, 45: 997-1005.

Garg, V.K, Amita, M., Kumar, R. and Gupta, R. 2004. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust: a timber industry waste. Dye Pigment, 63: 243-250.

Hameed, B.H. and Daud, F.B.M. 2008. Adsorption studies of basic dye on activated carbon derived from agricultural waste: *Hevea brasiliensis* seed coat. Chem. Eng. J., 139: 48-55.

Hameed, B.H., Mahmoud, D.K and Ahmad, Al. 2008. Sorption of basic dye from aqueous solution by pomelo (*Citrus grandis*) peel in a batch system. Colloids Surfaces A: Physicochem. Eng. Asp., 316: 78-84.

Ho, Y.S. 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics 59: 171-177.

Ho, Y.S. and Mckay, G. 1999. Pseudo-second order model for sorption processes. Process Biochem., 34: 451-465.

Ho, Y.S. and Mckay, G. 1998. Sorption of dyes from aqueous solution by peat. Chem. Eng. J., 70: 115-124.

Hu, C., Zhou, J., He, S., Luo, Z. and Cen, K. 2009. Effect of chemical activation of an activated carbon using zinc chloride on elemental mercury adsorption. Fuel Process. Technol., 90: 812-817.

Jokar, M., Farahani, T.S. and Ramezanzadeh, B. 2016. Electrochemical and surface characterizations of *Morus alba* pendula leaves extract (MAPLE) as a green corrosion inhibitor for steel in 1M HCl. J. Taiwan Inst. Chem. Eng., 63: 436-452.

Kamsonlian, S., Suresh, S., Ramanaiah, V., Majumder, C.B., Chand, S. and Kumar, A. 2012. Biosorptive behaviour of mango leaf powder and rice husk for arsenic(III) from aqueous solutions. Int. J. Environ. Sci. Technol., 9: 565-578.

Kaushik, P. and Malik, A. 2009. Fungal dye decolourization: recent advances and future potential. Environ. Int., 35: 127-141.

Kundu, S., Wang, Y., Xia, W. and Muhler, M. 2008. Thermal stability and reducibility of oxygen-containing functional groups on multiwalled carbon nanotube surfaces: A quantitative high-resolution XPS and TPD/TPR study. J. Phys. Chem. C., 112: 16869-16878.

Lee, J.W. and Choi, S.P., Thiruvenkatachari, R., Shim, W.G. and Moon, H. 2006. Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes. Dye Pigment, 69: 196-203.

Li, L., Quinlivan, P.A. and Knappe, D.R.U. 2002. Effects of activated car-

bon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. Carbon N. Y., 40: 2085-2100.

Lupascu, T. and Povar, I. 2016. Analysis of adsorption technologies of water and wastewater treatment used in the republic of Moldova. American Journal of Chemical Engineering, 4(6): 147-153.

Murthy, U.N., Rekha, H.B. and Bhavya, J.G. 2011. Performance of electrochemical oxidation in treating textile dye wastewater by stainless steel anode. International Journal of Environmental Science and Development, 2(6): 483.

Nethaji, S., Sivasamy, A. and Mandal, A.B. 2013. Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from *Juglans regia* shell biomass. Int. J. Environ. Sci. Technol., 10: 231-242.

Nowicki, P. and Pietrzak, R. 2010. Carbonaceous adsorbents prepared by physical activation of pine sawdust and their application for removal of NO_2 in dry and wet conditions. Bioresour. Technol., 101: 5802-5807

Nowicki, P., Skrzypczak, M. and Pietrzak, R. 2010. Effect of activation method on the physicochemical properties and NO_2 removal abilities of sorbents obtained from plum stones (*Prunus domestica*). Chem. Eng. J., 162: 723-729.

Oliveira, L.S., Franca, A.S., Alves, T.M. and Rocha, S.D.F. 2008. Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters. J. Hazard. Mater., 155: 507-512.

Pavan, F.A., Lima, E.C., Dias, S.L.P. and Mazzocato, A.C. 2008. Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. J. Hazard. Mater., 150: 703-712.

Ponnusami, V., Vikram, S. and Srivastava, S.N. 2008. Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. J. Hazard. Mater., 152: 276-286.

Pradhan, S. 2011. Production and characterization of activated carbon produced from a suitable Industrial sludge. Doctoral Thesis.

Prahas, D., Kartika, Y., Indraswati, N. and Ismadji, S. 2008. Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. Chem. Eng. J., 140: 32-42.

Rashed, M.N. 2013. Adsorption technique for the removal of organic pollutants from water and wastewater. In: Organic Pollutants-Monitoring, Risk and Treatment. Intech Open.

Saengbutr, K., Wangphon, N. and Wanchanthuek, R. 2014. The investigation of experimental condition and kinetic study of methylene blue adsorption onto neem (*Azadirachta indica*) leaf powder. International Journal of Scientific and Research Publications, 4(10): 2250-3153.

Sawal, M. 1986. General standards for discharge of environmental pollutants. Environ. Rules., 2: 545-560.

Sleiman, M., Vildozo, D., Ferronato, C. and Chovelon, J.M. 2007. Photocatalytic degradation of azo dye Metanil yellow: Optimization and kinetic modeling using a chemometric approach. Appl. Catal. B Environ., 77: 1-11.

Thusnavis, K.P., Vinod Kumar, M. and Sankara Narayana Pillai, G.R. 2011. Seed extract of *Psidium guajava* as ecofriendly corrosion inhibitor for carbon steel in hydrochloric acid medium. J. Mater. Sci. Technol., 27: 1143-1149.

Tong, D.S., Hui, C., Zhou, C., Lu, Y., Yu, H., Zhang, G.F. and Yu, W.H. 2010. Applied clay science adsorption of acid red G dye on octadecyl trimethylammonium montmorillonite. Appl. Clay Sci., 50: 427-431.

Tsai, W.T., Chang, C.Y., Lin, M.C., Chien, S.F., Sun, H.F. and Hsieh, M.F. 2001. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation. Chemosphere, 45: 51-58.

Wali, K.M.F. 2015. Color removal and cod reduction of dyeing bath wastewater by Fenton reaction. Int. J. Waste Resour., 5: 1-6.

Wang, L.H. and Lin, C.I. 2008. Adsorption of lead(II) ion from aqueous solution using rice hull ash. Ind. Eng. Chem. Res., 47: 4891-4897.

Wang, Z., Xue, M., Huang, K. and Liu, Z., 2011. Textile dyeing wastewater treatment. Advances in treating textile effluent, 5: 91-116.

Weng, C.H. and Pan, Y.F. 2007. Adsorption of a cationic dye (methylene blue) onto spent activated clay. J. Hazard. Mater., 144: 355-362.

Worch, Eckhard 2012. Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling. Walter de Gruyter.

World Health Organization 2006. A Compendium of Standards for Wastewater Reuse in The Eastern Mediterranean Region. WHO-EM/CEH/142/E. 19.

Wu, B., Zhang, J., Yang, M., Yue, Y., Ma, L.J. and Yu, X.Q. 2008. Raney Ni/KBH4: An efficient and mild system for the reduction of nitriles to amines. Arkivoc., 95-102.

Xiong, L., Yang, Y., Mai, J., Sun, W., Zhang, C., Wei, D., Chen, Q. and Ni, J. 2010. Adsorption behavior of methylene blue onto titanate nanotubes. Chem. Eng. J., 156: 313-320.

Yakout, S.M. and Sharaf EL-Deen, G. 2016. Characterization of activated carbon prepared by phosphoric acid activation of olive stones. Arab. J. Chem., 9: S1155-S1162.