

## Original paper

## Biosorption of crystal violet from aqueous solution by pearl millet powder: Isotherm modelling and kinetic studies

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## ABSTRACT

Environmental pollution caused by industrial effluents is an important issue. Biosorption of crystal violet (CV) from aqueous solution using pearl millet powder (PMP) was investigated in a batch mode. The use of pearl millet powder was as an additional substitution of activated carbon for the adsorption of CV from its aqueous solution. The adsorbent pearl millet powder was productively used for the biosorption of dye from its aqueous solution. The effect of initial concentration for CV, sorption time, dose of adsorbent, pH and temperature on dye removal were studied. The equilibrium sorption isotherms have been analyzed by the Freundlich, Langmuir and Temkin models. Sorption kinetic is quick and the data agree well with pseudo-first order kinetic model. But the kinetics studies were provided with Pseudo second order. The adsorption capacity ( $Q_0$ ) of PMP was found to be 48.535 mg/g. Thermodynamic parameters such as the free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were determined from Van't Hoff plot. The data reported shows the adsorption process is endothermic in nature.

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## 1. Introduction

Recent years, Environmental pollution caused by industrial effluents is an important issue. Different types of dyes are common pollutants usually found with textile effluents in many countries (Carliell et al. 1995). Environmental pollution could be termed as ecological crisis which has posed threat on basic amenities such as air, water, and soil. Among all, the water pollution (Sharma et al. 1994) is one of the major serious problems, which is highly significant. Most of the dyes are toxic and carcinogenic compounds which cause serious problems to human and animal which is not only limited to themselves but may be passed onto further generations (Crini. 2008) Large amounts of dyes are annually produced and consumed by textile, cosmetics, paper, lather, food and other industries (Hocking. 2005). Dyes from the wastewater of those factories must be removed before discharging into water. Even a small amount of dye when discharged into water can affect aquatic life, food webs and also on humans due to the carcinogenic and mutagenic effects of synthetic dyes (Allen et al. 2004). Many treatment processes have been applied for the removal of dyes from wastewater such as photocatalytic degradation, Sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, adsorption/precipitation processes, integrated chemical-biological degradation, and adsorption on activated carbon (Bockris. 1997).

As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal water and wastewater (Rafatullah et al. 2010). Adsorption processes (Forgacs. 2004) provide a feasible treatment especially if the adsorbent is inexpensive and readily available. Earlier works showed that the activated carbon prepared from rice husk (Nawar et al. 1989) and wood of *Ailanthus Altissima* (Bangash et al. 2009) were effectively used as adsorbent for the removal of dyes. The carbons are prepared from locally available cheap materials like, palm nutshells, cashew nut shells and broom sticks (Rajavel et al. 2003) have

been used for the removal of dark green PLS dye from textile industrial waste. The adsorptions of the dye on the carbons were in between 92 and 95 %. The removal of textile dyes from textile dye effluent using TBAB based aqueous biphasic systems has been studied (Meghna et al. 2005). Adsorption of acid dyes from aqueous solution onto the surface activated kammoni leaf powder has been studied (Ubale et al. 2010). Dyeing is the finishing and the important process in the textile, paper and leather industries. Color is a visible pollutant and color pollution caused by the discharge of effluents from pulp, paper, textile and leather industries containing heavy metals, organic and other micro-toxic pollutants may affect and alter the aquatic eco systems, creating un-aesthetic conditions also. Crystal violet base (methylrosanilide, *tris* [4-(dimethylamino) phenyl] methanol,  $C_{25}H_{31}N_3O$ ) is taken as dye for the present study. However, in large quantities, gentian violet may lead to ulceration of a baby's mouth and throat and is linked with mouth cancer (14). Gentian violet has also been linked to cancer in the digestive tract of other animals. Fig. 1 displays chemical structure of Crystal Violet (CV).

A careful literature survey has revealed that no studies have been made on the removal of CV from aqueous solution by *Pearl Millet* powder as an adsorbent. This has prompted us to take this investigation.

## 2. Materials and methods

The stock solution (500 ppm) was diluted to the required initial concentration of dye with double distilled water. 50 ml of the dye solution was taken in each 250 ml leak proof corning reagent bottles. Required amount of adsorbent of fixed particle size was exactly weighed and then transferred into each one of these bottles. The bottles were placed in a mechanical shaker and shaken vigorously for a required period of time (15 minutes). After shaking for a certain period, the flask was set aside for the adsorbent to settle out and the sample taken from the flask was centrifuged. The filtrate equilibrium concentration can be obtained from the standard curve as usual.

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The optical density of each solution was measured by using UV-Visible spectrophotometer (Systronic Spectrophotometer, model no: 104) at 582 nm ( $\lambda_{max}$ ). A plot of optical density versus concentration results a straight line for this particular dye. The optical density for dye solution before and after adsorption is obtained using the spectrophotometer. The corresponding relative concentration can be obtained from the standard curve.

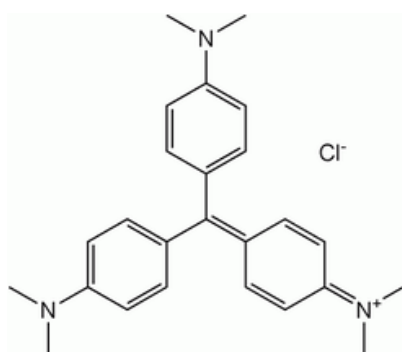


Fig. 1. Chemical structure of CV dye.

### 3. Results and Discussion

#### 3.1. Effect of Initial dye concentration

For PMP of 2 g/L, the percentage removal of dye decreases from 80 to 71 as the dye concentration increases from 15 to 50 mg/L. (Fig. 2). But, the amount of CV adsorbed per unit mass of adsorbent increased with increasing in CV dye concentration. This may be due to all CV there in solution could intermingle with the binding sites at lower concentration and thus the percentage adsorption was higher than those at higher initial dye concentration. At higher concentrations lower adsorption yield is due to the saturation of adsorption sites. At low concentrations, sorption sites took up the available CV molecule more rapidly while at higher concentrations the rate of diffusion became slow (Zafar et al. 2006).

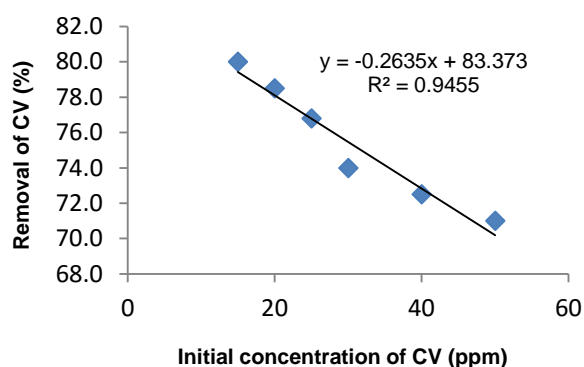


Fig. 2. Effect of Initial CV concentration.

#### 3.2. Effect of adsorbent dosage

The effect of changing adsorbent dosage on the removal of CV was studied by varying the adsorbent dosage from 0.5 to 4 g/L while keeping the other experimental conditions as constant (Fig. 3). An increase in percentage color removal of CV with increasing adsorbent dosage was observed whereas the adsorption capacity for the adsorbents decreased (Garg et al. 2003). This is due to the larger surface area and availability of more surface functional groups at higher concentration of adsorbent. The decrease in adsorption capacity can be explained with the reduction in effective surface area of the adsorbent (Ozer and Dursun. 2007).

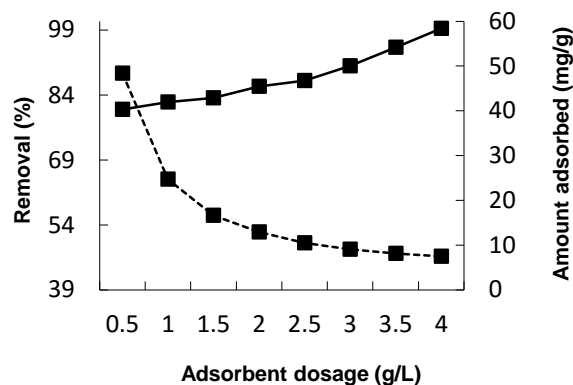


Fig. 3. Effect of adsorbent dosage for the adsorption of CV onto PMP.

#### 3.3. Effect of pH

Fig. 4 shows the effect of pH on the percentage removal of CV by varying the pH of the dye solution from 3.6 to 11. The maximum percentage of dye removal was observed at pH 11. The result indicated that at higher pH the removal of dye was maximum and at low pH the removal of dye was minimum. The hydrogen ion concentration (pH) primarily affects the degree of ionization of the dyes and the surface properties of the adsorbents. The percentage of dye adsorbed increased from 70 to 98 % with increase in pH from 3.6 to 11 at 30 °C. At higher pH, the surface of PMP becomes negative which attract the dye molecules and hence the dye adsorption increases. The adsorbents can also interact with dye molecules via hydrogen bonding and hydrophobic-hydrophilic mechanisms (Al-Degs et al. 2008).

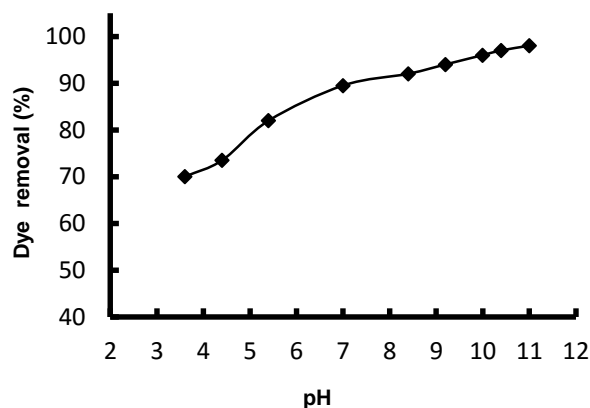


Fig. 4. Effect of pH for the adsorption of CV onto PMP.

#### 3.4. Effect of contact time

The effect of contact time on the removal of CV onto PMP for different concentration of dye is shown in Fig. 5. The results revealed that the rate of CV removal is higher at the beginning by the adsorbent, which was due to the large available surface area. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from exterior to interior sites of the adsorbent. Almost 70 % of the total dye molecule was adsorbed in the initial 10 minutes period and remained almost unchanged after 1 hr, indicating that the adsorption process has reached equilibrium. 3.5.

#### Adsorption Isotherms

Three Langmuir, Freundlich and Temkin isotherm were tested to describe the experimental data for the adsorption of CV onto PMP. Figs. 6a-c show Freundlich, Langmuir and Temkin isotherms respectively. The calculated isotherm constants and their correlation coefficients are given in Table 1.

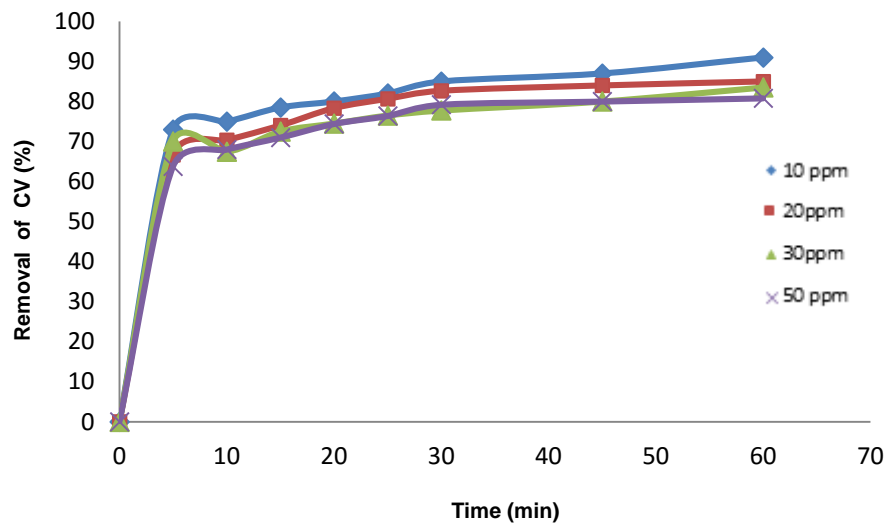


Fig. 5. Effect of contact time for the adsorption of CV onto PMP.

From the experimental results, it can be seen that the Langmuir and Freundlich models fitted better than the Temkin model. The constants for all the isotherms studied and their correlation coefficients are given in Table 1. PMP showed the highest adsorption capacity (48.535 mg/g).

The high adsorption capacity of PMP is due to the abundant formation of oxygen-containing functional groups and adequate pore size distribution.

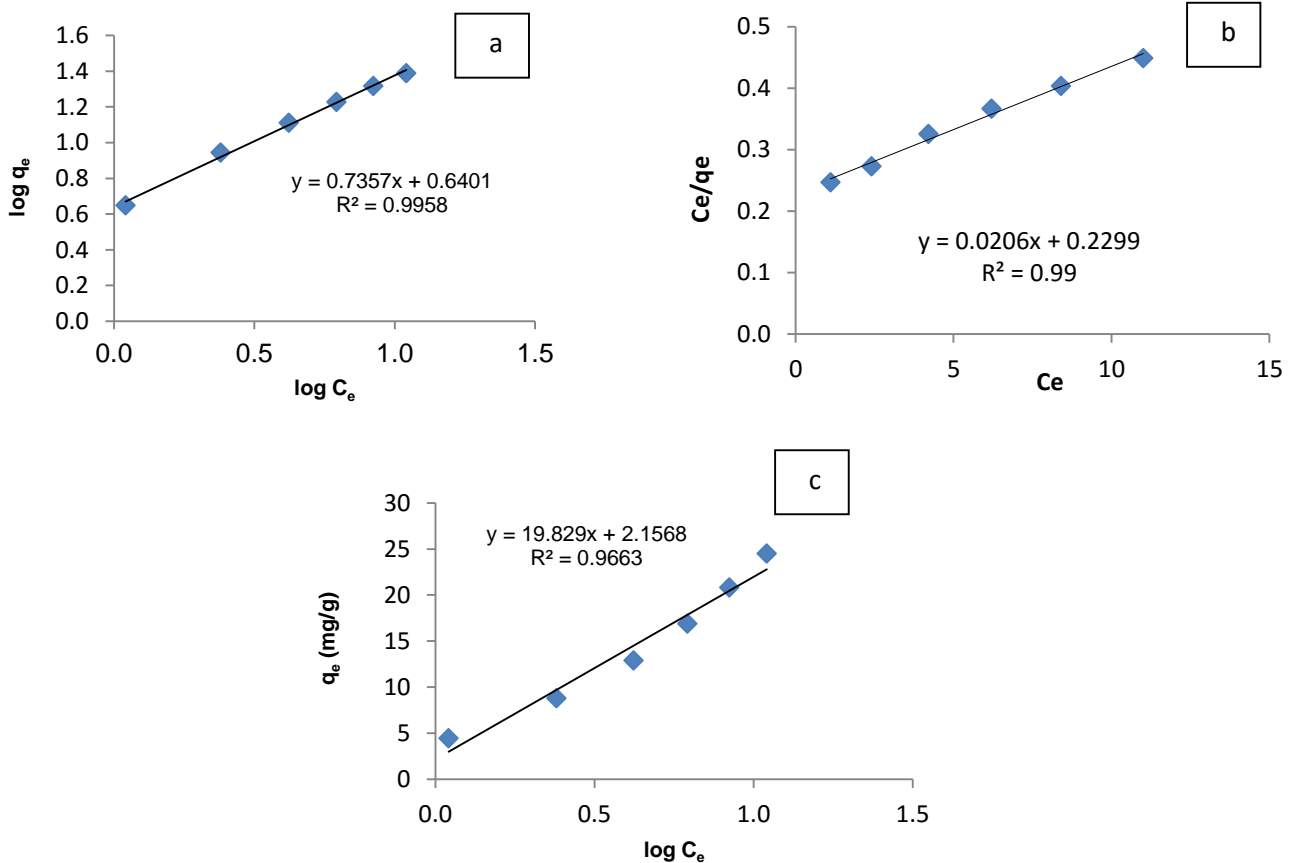


Fig. 6. Isotherm, (a) Freundlich, (b) Langmuir, (c) Temkin.

**Table 1.** Isotherm constants for the adsorption of CV onto PMP.

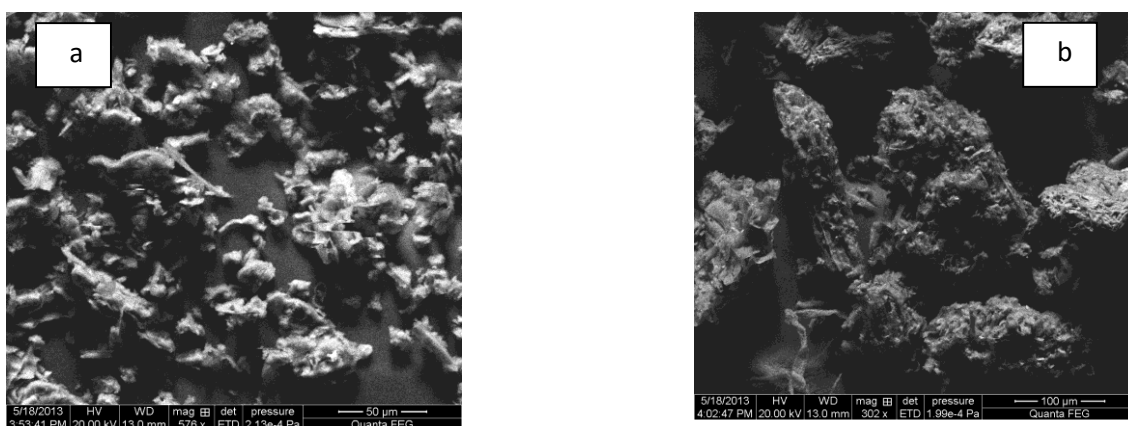
| Adsorbent | Freundlich isotherm |       |         | Langmuir isotherm |                 |       |         | Temkin isotherm |       |         |
|-----------|---------------------|-------|---------|-------------------|-----------------|-------|---------|-----------------|-------|---------|
|           | $K_F$<br>(mg/g)     | n     | $R^2_F$ | $Q_m$<br>(mg/g)   | $K_L$<br>(L/mg) | $R_L$ | $R^2_L$ | $K_T$<br>(L/mg) | $B_1$ | $R^2_E$ |
| PMP       | 4.365               | 0.735 | 0.995   | 48.535            | 0.0857          | 0.286 | 0.9914  | 0.5173          | 19.82 | 0.966   |

**3.6. Characterization of PMP**

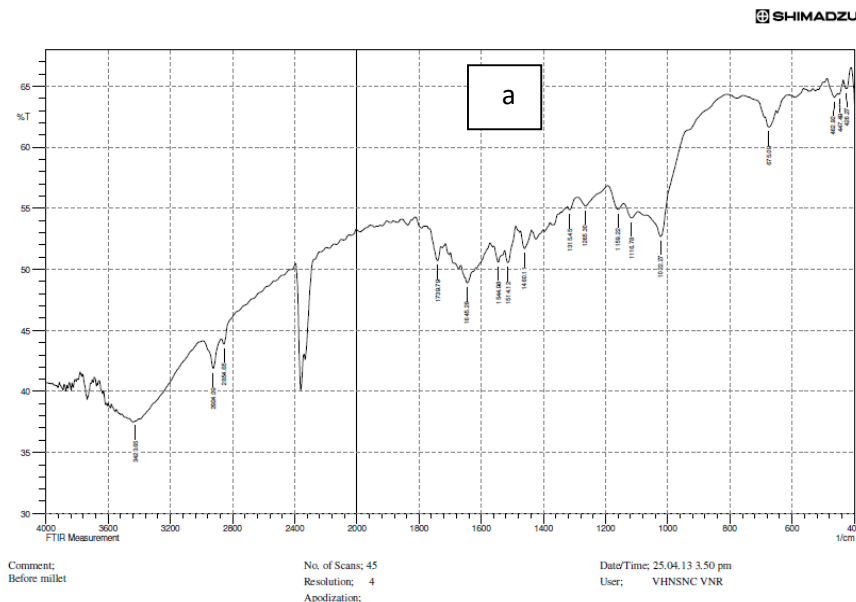
The SEM image of PMP (Fig. 7a) also confirmed the presence of heterogeneous pores on the surface. From the SEM and FT-IR studies (Figs. 7a and b, 8a and b), it is clear that PMP has a considerable number of pores and surface functional groups and therefore there is a good possibility for dye molecule to be adsorbed and trapped into these pores.

The FT-IR spectra of PMP before and after biosorption were recorded in the range of 400-4000  $cm^{-1}$ . Figs. 7a-b show the FTIR spectra of the PMP before the adsorption and after loaded with the CV dye. The intense absorption bands at 3423  $cm^{-1}$  is assigned to O-H bond stretching. The two  $CH_2$  stretching bands at 2924 and 2856  $cm^{-1}$  are assigned to asymmetric and symmetric stretching of  $CH_2$  groups which present the same wave numbers before and after the adsorption,

indicating that these groups did not participate in the adsorption process. Sharp intense peaks observed at 1645  $cm^{-1}$ , before and after absorption are assigned to the aromatic C—C ring stretching. The wave numbers of these bands were not different before and after the adsorption of CV. Bands ranging from 1116 to 1022 and 1122 to 1024  $cm^{-1}$  before and after adsorption, respectively, are assigned to C—O stretching vibrations. Comparing Figs. 8 and 9, we can conclude that some of these peaks are shifted or disappeared and new peaks are also detected. These changes observed in the spectrum, indicated the possible involvement of those functional groups on the surface of the PMP in adsorption process. Surface morphology of CV loaded adsorbent (Fig. 7b) shows that the surface of PMP is covered with dye molecules.



**Fig. 7.** (a) SEM Image of PMP before adsorption of CV, (b) After adsorption of CV.



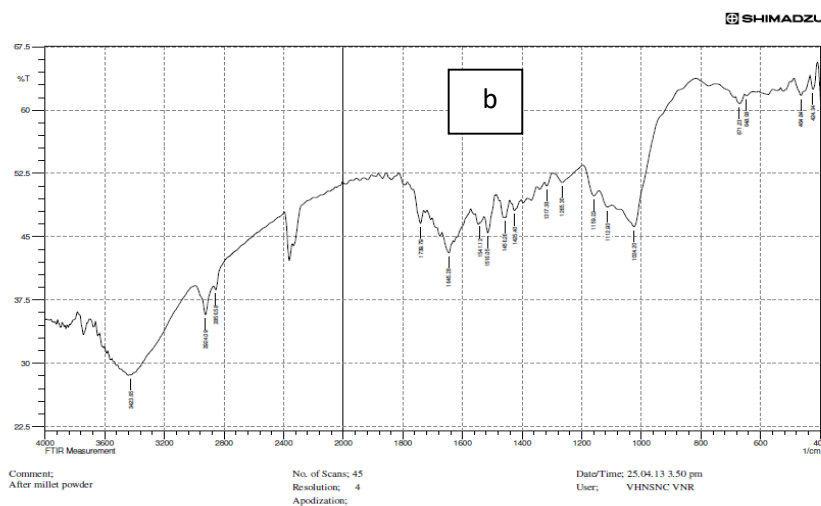


Fig. 8. (a) FTIR spectra of the PMP before the adsorption of CV, (b) FTIR spectra of the PMP after the adsorption of CV.

### 3.7. Adsorption Kinetics

The experimental kinetic data were analyzed to four kinetic models like pseudo-first order, pseudo-second order, and intra-particle diffusion to evaluate the adsorption mechanism. Figs. 9a-b and 10 represent the pseudo-first order, pseudo-second order and intra-particle diffusion model respectively, for the adsorption of CV onto PMP. The constants

associated with these kinetic models are given in Table 2. The correlation coefficients values are greater than 0.99 in the linear plot of pseudo-second order model. The value of equilibrium capacity is found to be 25.64 mg/g which is close to the experimental value of 24.85 mg/g for the initial dye concentration of 50ppm, indicating pseudo-second order nature.

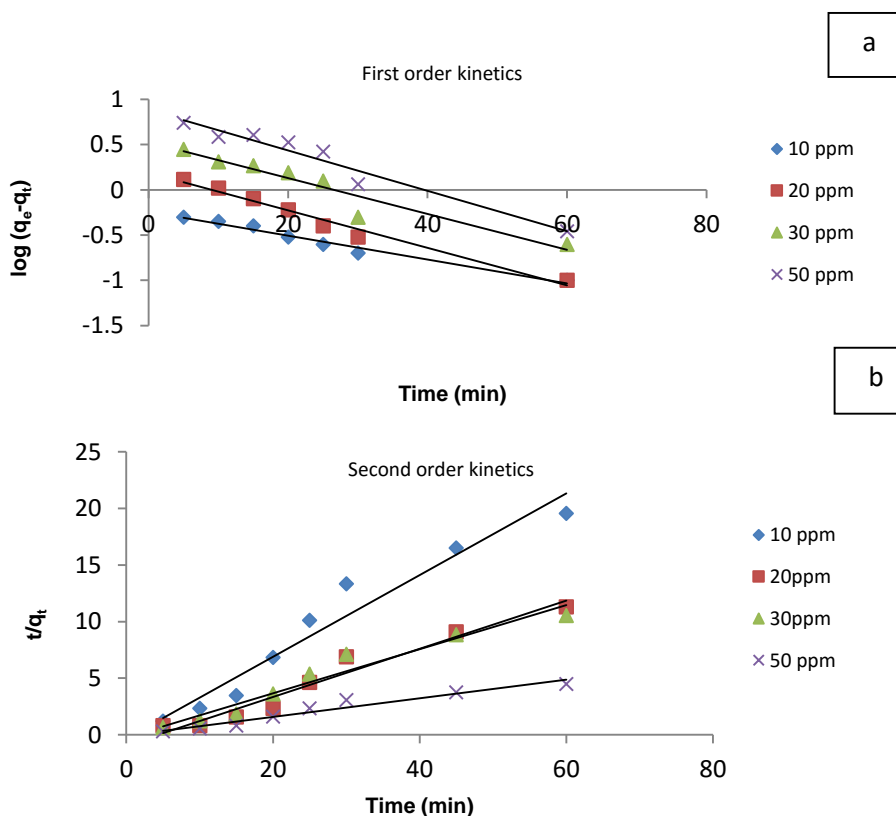


Fig. 9. (a) The pseudo-first order kinetic model for the adsorption of CV onto PMP, (b) The pseudo-second order kinetic model for the adsorption of CV onto PMP.

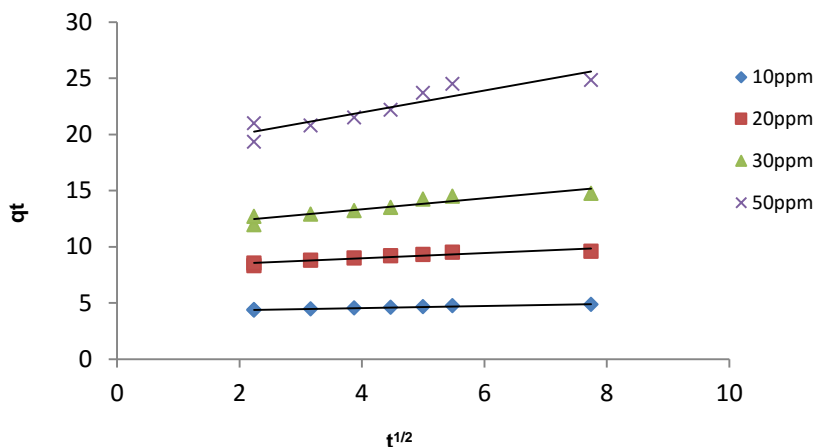


Fig. 10. Intra-particle diffusion model for the adsorption of CV onto PMP.

Table 2. Kinetic parameters for the adsorption of CV onto PMP.

| C <sub>0</sub><br>(mg/L) | Pseudo-first order |                          |                                     |                             | Pseudo-second order      |   |                             | Intra-particle diffusion                      |        |                              |
|--------------------------|--------------------|--------------------------|-------------------------------------|-----------------------------|--------------------------|---|-----------------------------|---|--------|------------------------------|
|                          | q <sub>e</sub>     | q <sub>f</sub><br>(mg/g) | k <sub>f</sub> (min <sup>-1</sup> ) | R <sup>2</sup> <sub>f</sub> | q <sub>s</sub><br>(mg/g) | k <sub>s</sub> × 10 <sup>-2</sup><br>(g/mg/min) | R <sup>2</sup> <sub>s</sub> | k <sub>id</sub><br>(mg/g/min <sup>1/2</sup> ) | I      | R <sup>2</sup> <sub>id</sub> |
| 10                       | 4.85               | 1.74                     | 0.0299                              | 0.988                       | 4.901                    | 1.12  | 0.999                       | 0.071   | 4.208  | 0.980                        |
| 20                       | 9.6                | 1.54                     | 0.0483                              | 0.989                       | 16.12                    | 11.42   | 0.941                       | 0.232   | 8.041  | 0.933                        |
| 30                       | 14.75              | 3.341                    | 0.046                               | 0.959                       | 15.15                    | 623.03  | 0.999                       | 0.382   | 11.491 | 0.941                        |
| 50                       | 24.85              | 7.62                     | 0.0506                              | 0.975                       | 25.64                    | 165.80  | 0.999                       | 0.769   | 18.755 | 0.945                        |

3.8. Thermodynamic Studies

Fig. 11 shows the relationship between K<sub>c</sub> and T for the adsorption of CV onto PMP. The calculated thermodynamic constants are given in Table 3. The negative value of ΔG° indicates the spontaneous nature of CV adsorption onto PMP. However, the value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature (Bulut and Tez. 2007). The positive values of ΔH° show that the adsorption is endothermic nature. The adsorption process in the solid-liquid system is a combination of two processes: i) desorption of the molecules of

solvent (water) previously adsorbed, and ii) the adsorption of adsorbate species. The CV ions have to displace more than one water molecule for their adsorption and thus results in the endothermicity of the adsorption process.

The positive value of ΔS° suggests increased randomness at the solid /solution interface during the adsorption of CV onto PMP. The enhancement of adsorption at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface (Gaballah and Kilbertus. 1998).

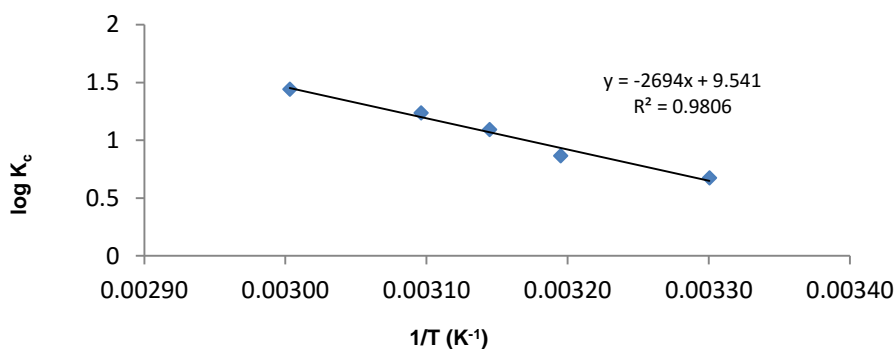


Fig. 11. Plot of log K<sub>c</sub> versus 1/T for the adsorption of CV onto PMP.

Table 3. Thermodynamic parameters for the adsorption of CV onto PMP.

| Adsorbents | ΔG°(kJ/mol) at 313 K | ΔH° (kJ/mol) | ΔS° (kJ/mol) |
|------------|----------------------|--------------|--------------|
| PMP        | -5.6031              | 51.582       | 0.1827       |

4. Conclusion

We have introduced an appropriate new adsorbent in the place of activated carbon. The current investigation shows that PMP is an effective adsorbent for the removal of CV from aqueous solution. From the studies it is observed that:

- The adsorption capacity ( $Q_0$ ) of PMP was found to be 48.535mg/g
- Langmuir and Freundlich models fitted better than the Temkin model.
- Sorption kinetic is quick and the data agree well with pseudo-second order kinetic model.
- The data reported shows the adsorption process is endothermic in nature.

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