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Equilibrium, Isotherm Studies of Dye Adsorption onto Orange Peel Powder

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Abstract Nowadays adsorption is an effective method for removal of dyes from aqueous solution using different sources of low cost agricultural wastes. However, the adsorption characteristics of two basic dyes namely crystal violet (CV) and methylene (MB) from their aqueous solution using treated orange peel (OP) waste were investigated in a batch mode technique. The effect of variations parameters which are affecting factors on the rate of adsorption for both dyes such as initial dye concentration, adsorption time, adsorbent dosage, and reaction volume were studied. According to data obtained during the experimental work the following results were obtained: i) adsorption time of 30 min, initial concentration of both dye 40 mg/l, solution pH 6.5, and 50 ml as working solution have been selected as the optimum conditions by the batch process; ii) the removal percentage and the maximum adsorption capacity of CV and MB onto OP were found to be 97.5% and 99.2%, and 27.17mg/g and 25.87mg/g respectively iii) This study showed that the use of orange-waste peel as adsorbent for the removal of CV and MB from colored water is possible.

Keywords Adsorption, Batch mode, Equilibrium, Isotherm, Low cost, Orange peel

1. Introduction

The textile industry consumes a huge volume of water in its manufacturing processes used mainly in the dyeing and finishing operations of the plants. The wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as the effluent composition [1]. It is reported that, about 200,000 tons of these dyes are lost to the textile industry effluents every year during the dyeing and processing operations [1, 2]. In addition, the increased demand for textile products and the proportional increase in their production, and the use of synthetic dyes have together contributed to dye wastewater becoming one of the substantial sources of severe pollution problems [1]. Organic dyes are harmful to human beings, the need to remove color from textile industry effluents before discharging to the water bodies because environmentally important [3]. From the structures point of view, synthetic dye have mainly aromatic structures, which are biologically non-degradable and difficult to treat their effluents [3]. Adsorption process using agricultural waste materials such represented the major process currently used for the treatment of dye effluents and considered to be relatively superior to other technologies because of its low cost, easy to operate, simplicity of design, availability and eco-friendly technique [3, 4]. Expanding fruit production has naturally resulted in increased amounts of waste, every year [5]. Several million tons of agricultural wastes are disposed every year, around the world. In India alone, more than 400 million tons of agricultural residues are generated annually [5, 6]. One of the agricultural wastes from orange juicing industry is orange peel [7]. It is estimated that up to 68 million tons of global orange are production annually, according to FAO, the generation of these solid wastes is estimated to be in the range of 15 to 25 million

tons; a huge amount of which is still being dumped every year, which causes both economic and environmental problems such as high transportation cost, insufficient dumping sites, and the accumulation of high organic content material [5, 8]. On the other hand, orange peel is largely composed of cellulose, hemicelluloses, lignin, pectin (galacturonic acid), chlorophyll pigments and others [7]. These components contain various functional groups, such as hydroxyl and carboxyl, which make orange peel to be potential adsorbent material for adsorptive and removing many different pollutants like heavy metals and dyes from liquid media [7]. Authors who have used orange peel-based adsorbents for water treatment used them in modified form as reported in a previous review work by Titi and Bello., (2015), and as a precursor for the preparation of adsorbent by chemical treatment [7]. Agricultural wastes could also be sources for the production of low cost activated carbon (AC) which has the advantage of offering and effective, low cost replacement for non-renewable coal-based granular activated carbon provided that they have similar or better adsorption efficiency [4, 8, 9]. However, the current study is undertaken to investigate the adsorptive removal of dyes onto raw orange-waste peel (OP). OP was chemically modified with alkaline solution (NaOH), and then utilized for the adsorptive removal of dyes; CV and MB from their aqueous solution.

2. Methods

2.1. Materials

Crystal violet (CV) and methylene (MB), a cationic dyes purchased from B.D.H Chemicals, Ltd., England were chosen as the model adsorbate. Working solutions were prepared from an aqueous stock solution (1000 mg/l) by diluting the dye stock solution with deionized water to give the needed initial concentrations ranging from10 to 70 mg/L by using the formula (1). The calibration curve was plotted from each dye solution prepared in the concentration range of 0.3-20 mg/L. Standard curve of MB at concentration range from 0.3 to 20 mg/l taken as example and presented later in section 2.3.

$$C_1 V_1 = C_2 V_2 \qquad (1)$$

2.2. Preparation of adsorbent

In this study, waste of orange peel (OP) was selected as a low cost and biosorbent material for the adsorptive removal of basic dye; crystal violet (CV) and methylene blue (MB) from their aqueous solution. The raw orange peel-waste was obtained from a house yard at Tripoli, Libya. Raw materials were collected and put into plastic bags and immediately transported to the laboratory. Then, the material was cut to small pieces and washed completely with warm water. This washing without soap was repeated three times to remove impurities and other undesirable materials. Then, about 100 g of peel were soaked in sodium hydroxide (NaOH) at 75±1.5 ^{o}C for 24 hr. After that washed many times with distilled water and dried once at room temperature for one week. The other was dried in the oven at 100 ^{o}C until constant weight was recorded. Finally, the dried material was crushed using a electric mechanical mill to produce powder adsorbent material of uniform size less than 0.25 mm and stored in plastic bags for adsorption experiments. For elemental analysis, the powdered peel was analyzed by FLASH 2000 CHNS/O Analyzer, USA. A glass cylinder 25 ml was filled to a specified volume with powdered peel and dried in an oven at 70 ^{o}C for 420 min was used to estimate bulk density of dried orange peel. The cylinder was tapped for few minutes to compact the material and the bulk density estimated and presented as g/ml using Equation 2. The procedure was similar to that used by Sugumaran et al. (2012) [8].

$$\text{Bulk density of OP (g/ml)} = \text{weight of dry peel powder (g)} \div \text{final volume (ml)} \qquad (2)$$

2.3. Equilibrium adsorption studies

Adsorption process were carried out at room temperature in a batch mode systems as follows: batch mode experiments were carried out in 250 ml flasks and total volume of the reaction solution, and temperature of reaction were kept at 50 ml, room temperature respectively, with pH of (6 -7). The flasks were agitated at 250 rpm for 30 min until equilibrium was reached on a digital shaker (GFL 3005 model, Germany). The effect of variations parameters which are affecting factors on the rate of adsorption for both dyes were studied. After the termination of the

adsorption experiments, the remaining concentration of CV and MB in each sample was determined by UV spectroscopy after filtering the adsorbent with filter paper (Whatman) to make it solid phase free. From an analytical point of view, each experiment was performed three times under the same conditions and the average results were taken. The amount of dye adsorbed per gram of adsorbent, and percentage removal were calculated using Equation (3) and (4) respectively [5].

$$q_e\ (mg/g) = (V/M)\ x\ (Co - Ce) \qquad (3)$$

$$\%\ \text{Removal} = (Co - Ce) \div (Co)\ \text{x}\ 100 \qquad (4)$$

where C0 and Ce are the initial and equilibrium dye concentrations respectively (mg/l), V is the dye solution volume (L), and M is the mass of the adsorbent (g).

Matrix of the experimental work including, range and levels of independent process variables are given in Table 1.

Table 1: Experimental range and levels of independent process variables involved in this study

Independent variable	**Unit**	**Sample symbol**	**Levels**				
			-2	**-1**	**0**	**1**	**2**
Initial dye concentration	mg/l	A	10	25	40	50	70
Contact time	min	B	5.0	10	20	30	60
Adsorbent doses	g	C	0.05	0.1	0.2	0.3	0.4
Reaction volume	ml	D	50	75	100	150	200
pH	--	E	2.0	4.0	6.0	8.0	9.0
Temperature	Was fixed during the whole adsorption process at 25±1.5^{o}C						

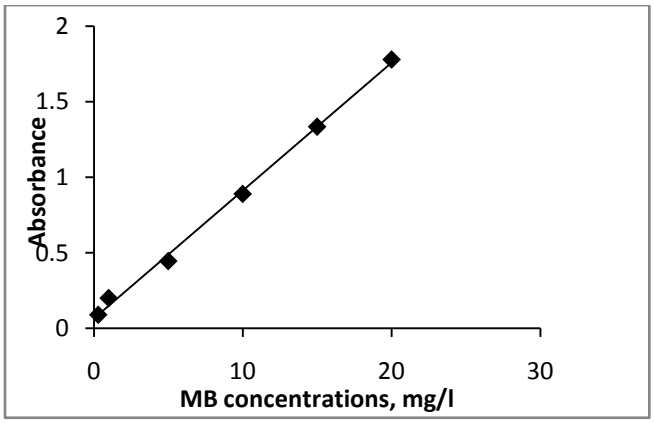

Figure 1: Calibration curve for MB dye

2.3.1. Evaluation of initial concentrations of dyes

The effluents of different industries may have different dye concentrations. The initial dye concentration is also an important factor that affects adsorption kinetics [5]. The effect of initial concentration of both dyes; CV and MB were investigated by agitating 0.1 g of orange peel in 50 ml of 25 mg/l of CV and MB solution at pH (6 -7) for 30 min at a constant agitation speed of 250 rpm. The step was then repeated using 10, 40, 50, 60 and 70 mg/. Finally, the optimum initial concentration was selected for next step.

2.3.2. Evaluation of contact time

Equilibrium time is a very important parameter to study when considering economical wastewater treatment application [5]. The effect of contact time was investigated by agitating 0.1g of adsorbent in 50 ml and initial concentration which is selected from section (2.3.1) and pH 6-7 each in a 250 ml beaker, over time periods ranging from 5 to 90 min at a constant agitation speed of 250 rpm and room temperature. The optimum contact time was selected to use in the next step.

2.3.3. Evaluation of adsorbent dosage

The adsorbent mass is also plays an important parameter role in adsorption studies because it determines the capacity of adsorbent used for a given initial concentration of dye solution [10]. In order to find out optimum

amount of adsorbent at which maximum adsorption takes place, 50 ml of dye solution with an initial dye concentration and reaction time, which have been selected as the best conditions from section (2.3.1 and 2.3.2) respectively at room temperature, speed of agitation rate of 250 rpm and pH of 6-7. The effect of OP amount on dye adsorption was investigated using (0.05, 0.1, 0.2, 0.3, and 0.4g), each experiment was performed three times under the same conditions and the average results were taken. Finally, the best conditions of adsorption process by orange peel were reported.

2.3.4. Evaluation of pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process of syntactic dye (SD). In general, the adsorption of most dyes on adsorbent materials increased with the increase of pH [5, 9]. The effect of pH on both dyes adsorption was studied by agitating 0.1 g of orange peel powder and a series of 50 ml dyes solution with initial concentration which is selected from section (2.3.1) at different pH value, ranging from 2-9. The samples were agitated for 30 min to reach equilibrium, and agitation rate was maintained at 250 rpm. The pH of the solution was varied from 2 – 9 using 0.1 N of hydrochloric acid (HCl) and sodium hydroxide (NaOH) depending upon the required pH, and measured by digital pH meter (740 Inolab WTW model pH meter with a SenTix 20). Finally, the optimum pH was selected.

2.3.5. Evaluation of reaction volume

In order to find out best reaction volume, different five volumes of sample ranging from 50 to 200 ml at the optimum conditions which were selected from the above affecting parameters were studied. And the best working solution of adsorption system was reported.

2.4. Isotherm studies

In order to evaluate the adsorption as an unit operation, one of the important physicochemical aspects was discussed: equilibrium of dyes adsorption by the adsorbents. Equilibrium investigation gives information regarding the maximum adsorption capacity and affinity of the studied adsorbents for the studied pollutant [12]. It is also, very important in view to develop a model equation which can accurately represent the results and could be used for the design purposes [11]. In order to describe the equilibrium between the solid phase (adsorbent) and the liquid phase (dye solution) two models: Langmuir and Freundlich isotherms are widely used for this purpose [12].

2.4.1. Langmuir adsorption isotherm

Langmuir isotherm assumes that the adsorption take place only on single layer on the adsorbent, and after the formation of this monolayer no further adsorption take place[13-16]. In other words, the Longmuir presumes a specific homogenous type of the adsorption. The Langmuir adsorption isotherm study has been done by varying the initial concentration of CV and MB from 10 to 70 mg/l, keeping all other conditions constant. A plot of Ce/qe versus Ce, indicates a straight line of slope $1/q_{max}$ and an intercept of $1/b\ q_{max}$, where, Ce is the equilibrium concentration (mg/l), qe is the amount of dye adsorbed (mg/g); q_{max} is the maximum adsorption capacity corresponding to complete monolayer adsorption (mg/g); b is the Langmuir constant (l/mg). The linear form of the Langmuir adsorption is given as:

$$C_e/q_e = 1/q_m\, b + C_e / q_m \qquad (5)$$

2.4.2. Freundlich adsorption isotherm

Freundlich isotherm model is widely used for many years, and this is mainly applied to describe characteristics for the hetrogeneouse surface. The model assumes that adsorption takes place on a heterogeneous surface, and can be used for non-ideal adsorption [16]. The linear form of Freundlich is given as 6:

$$\ln q_e = 1/\mathrm{n} \ln C_e + \ln K_\mathrm{f} \qquad (6)$$

where K_f, is the Freundlich adsorption constant (l/mg) related to the adsorption capacity of the adsorbent; n is the heterogeneity factor of adsorption sites, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent respectively [10].

3. Results and Discussion

3.1. Physical properties and the elemental analysis of orange peel

The chemical character based on elemental analysis of dried orange peel powder included C, H, N, and O was analyzed and are presented in Table 2, while, the bulk density of OP was also estimated regarding to Equation (1) and showed in Table 2 as well. The procedure of bulk density has been shown in Figure 2. From the table it can be seen that orange peel have high proportion of nitrogen. Unlike almost other biomaterials such as rice husk, coconut shell, corn cob and etc., as reported and clarified in an extensive review work by Sulyman et al., (2017) [4].

Table 2: Most elements found as constituents of dried OP; bulk density; and yield of dried OP

Material Properties	**Dried orange peel powder**				
	Content of C	**Content of H**	**Content of N**	**Content of O**	**Bulk density**
Unit	%	%	%	%	g/ml
Value	40.1	6.3	2.6	38.1	0.47

3.2. SEM analysis

The surface area of adsorbent (OP) was studied by Scanning electron microscopy (SEM) and is shown in Figure 3. Several researchers which as reported in a review work by Titi and Bello, 2015 [7], they found that the modified of biomass has clearly difference in the surface morphology of adsorbent and high adsorption capacity compared to the unmodified adsorbents. For instance, Kalavathy and Miranda [17] have investigated the adsorption of copper ion from its aqueous solution by raw saw dust (RSD). The modification was done by using phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH). Their studies observed that surface modification of saw dust contributed positively to the development of microspores. Surface was also more homogeneous in case of saw dust modified with NaOH in comparison to saw dust modified with phosphoric acid and unmodified saw dust which shows a more heterogeneous surface. In another work conducted by Moosa et al., (2016) their results showed that no differences in the maximum adsorption capacity q_{max} (mg/g) of untreated Aloe Vera and activation aloe Vera for the removal of Zinc ions from aqueous solution which was found to be 5.0839 and 5.4113 mg/g respectively [18]. In different work conducted by the same authors [19]. It was reported that the maximum capacity of activation aloe Vera was improved by about 24% for the removal of lead. In another work done by Saiban et al., (2006) [20] found that the use Na_2CO_3 for chemical treatment is less efficient than the use of NaOH when the investigated the efficiency of sawdust in the removal of Cu(II) ion. Also, authors reported that chemical modification with NaOH could enhance the adsorption capacity of saw dust than sawdust modified with phosphoric acid for the removal of copper from aqueous solution. In this study, as can be observed from Figure 3, there is clear pore surface and regular morphology. The regular morphology could be due to the removal of considerable organic by-products and minerals presented in the orange peel by soaking of raw orange peel with alkaline solution (NaOH) at temperature of 75±1.5 ^oC for 24 hr. Chubar et al., (2004) [21] reported that treatment of cork powder obtained from cork oak tree with NaOH at high temperature increased the adsorption capacity for heavy meals by 33%. Similarly, Syuhadah and Rohasliney, (2012) reported that generally chemically modified rice husks exhibit higher adsorption capacities than unmodified rice husks [22].

3.3. Spectral analysis

Fourier transform infrared (FTIR) was used to provide structural and compositional information on the functional groups presented in the solid adsorbent. Figure 4 shows IR spectra of dried raw orange peel, while the major functional groups are presented in Table3. A strong and broad peak at 3269.86 cm^{-1} results due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group of alcohols and phenols. The absorption peaks at 2922.98cm^{-1} could be assigned to –CH stretching vibrations of $–CH_3$ and $–CH_2$ functional groups. The shoulder peak at 1734.4 cm^{-1} can be attributed to carbonyl –CO group from carboxylic acids. The peak at 1604 cm^{-1} indicates the fingerprint region of CO, C–O and O–H groups. The absorption peaks at 1361 cm^{-1} could be attributed to the presence of C–O stretching in carboxyl. The region between 1284 and 1000cm^{-1} is the fingerprint region, OH, and C-H bending vibration and C-O stretching vibration absorption bands. The intense band at 1037cm^{-1}.

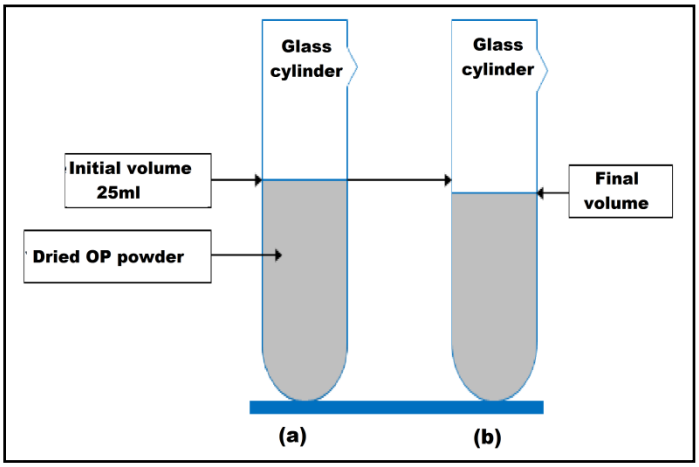

Figure 2: Procedure of bulk density, at the start point (a), after storage verticlly at 70^{o}C for 420 min (b).

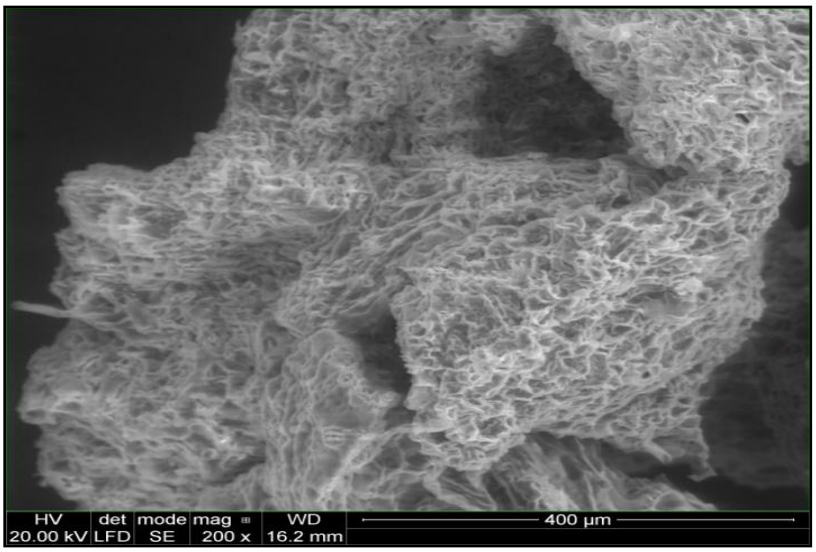

Figure 3: SEM of raw material of dried orange peel in form of pwder.

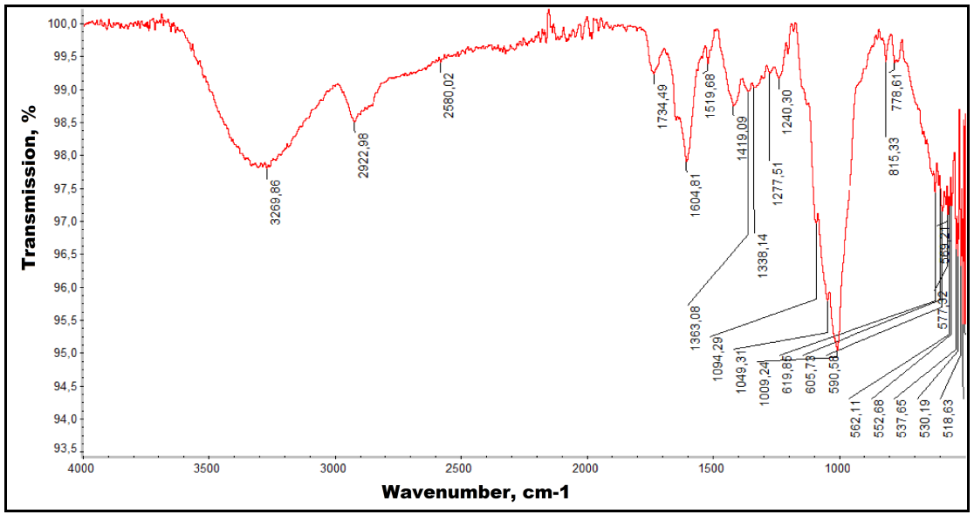

Figure 4: FTIR spectra of dried raw orange peel before adsorption process

Table 3: IR Absorption bands and corresponding possible groups

IR absorption bands, cm^{-1}	Functional groups	IR absorption bands, cm^{-1}	Functional groups
3269.86	(OH) bond / N-H	1235	C-O / C=O / OH
2922.98	C-H / OH	1009.24	C-OH primary alcohol / C-N
1734.49	C=O	815.33	C-H / N-H
1604.81	CO, C–O and O–H	---	---

4. Affecting parameters on the rate of adsorption

4.1. Effect of initial concentration of dye

In general, the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [10]. The effect of initial CV and MB dye concentrations on the rate of adsorptive removal efficiency of orange peel (OP) is shown in Figure 5. Adsorption experiments were carried out at different initial concentrations of both CV and MB ranging from 10 to 70 mg/l respectively at operating conditions (adsorption time of 30 min, adsorbent mass of 0.1 g, agitation rate of 250 rpm, room temperature, and pH (6-7). From the figure it can be seen that, the removal percentage decreased with an increase in initial dye concentration. For, instance decrease from 99.4% to 72% for MB, and from 99% to 67.2% for CV respectively was observed when the initial concentration of both dyes increased from 10 mg/l to 60 mg/l. This behavior can be explained by the limited available number of adsorption sites and the surface area of adsorbent with increasing the initial concentration of liquid phase at constant dosages of adsorbents. Also it can be explained by the saturation of almost adsorption sites on the adsorbents. This is agreement with the literatures [4, 5, 10, 23]. From figure 5, it can also be seen that the adsorptive removal of MB onto orange peel a little higher than of CV, which may be due to the deference in the molecular weight. Initial concentration of 40 mg/l for both dyes; CV and MB has been selected as the best concentration level for the next step.

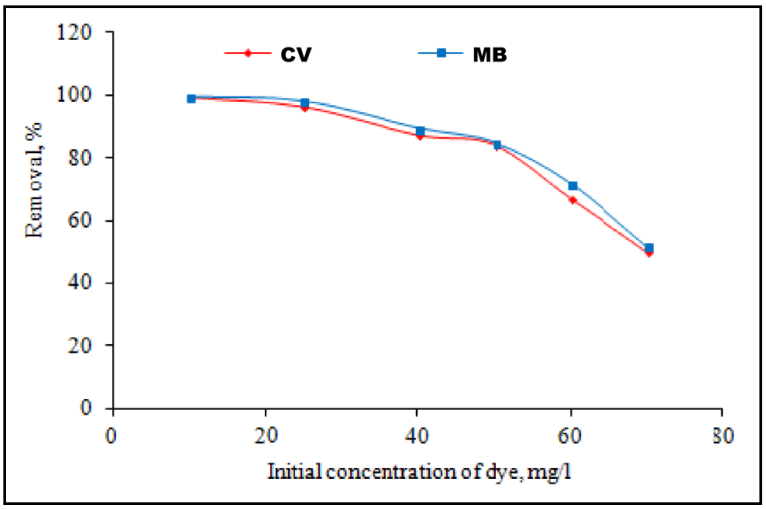

Figure 5: Relationship between initial concentration of dye and adsorptive removal onto orange peel

4.2. Effect of contact time

From figure 6, it can be observed that the percent removal efficiency and adsorption capacity of dyes onto orange peel increased with increase of contact time and reached equilibrium in 30 min. Increase in contact time after 30 min cannot enhance the adsorption of dyes onto adsorbent(OP). In the beginning, the percent of dye was rapidly increased with the increase of adsorption time at first 20 min for both CV and MB. Due to the adsorption more molecules of dye on the unsaturated surface area of OP. The equilibrium time was reached at 30 min at the adsorption conditions of (0.1g of orange peel, 40 mg/l of dye solution, pH (6-7), agitation rate of 250 rpm, and room temperature) with percent removal of 95% and 98% for CV and MB, respectively. Therefore, 30 min was found to be the optimum contact time, while the adsorption capacity was found to be 19 mg/g and 19.6 mg/g for CV and MB, respectively at the optimum contact time. This is agreement with the study of Seidmohammadi *et al.* (2015) [24].

The initial rate of adsorption capacity was rapid in the first stage due to the larger surface area and the availability of the binding active sites of the adsorbent at the first minutes [5, 25] and the driving force provided by the initial concentration at the first stage which overcomes all mass transferred resistance of dyes between the aqueous and solid phases [4, 5, 26, 27]. This is agreement with the literature [5]. Similarly, work [10] reported that more than 80% of MB dye was removed in the first minute of adsorption and increased slowly up to equilibrium was reached at about 20 min.

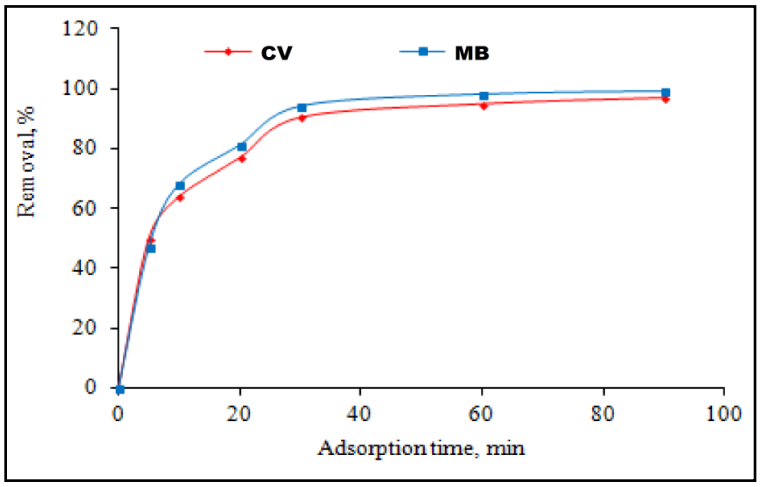

Figure 6: Relationship between adsorption time of dye and the percent removal onto orange peel at room temperature; agitation speed = 250 rpm; initial concentration = 40 mg/l; pH= (6 -7)

4.3. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption CV and MB dyes is showed in Table 4 and Figure 7. The trend revealed a progressive increase in the amount of dye adsorbed as adsorbent dosage increased from 0.05 to 0.3g. The percentage of dye removed increased from 57 to 97.5 % for CV and from 61.4% to 99.2 for MB respectively, and then the value of percentage removal were very close indicating that adsorption was almost finish with 0.3 g of the adsorbent and the equilibrium take place. It is reasonable that increasing the adsorbent dose increased the surface area, thus providing increase in the available active sites for the adsorption. Similar trend was also observed by [10, 28], while adsorption capacity was decreased with increasing amount of orange peel. For instance a decrease from 23 mg/g to 6.50 mg/g % for CV and from 24 mg/g to 6.59 mg/g for MB respectively was recorded when the adsorbent mass increased from 0.05 g to 0.30g. This trend can be explained as a result of overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the day and an increase in the diffusion path length [10]. Etim et al., (2016) have investigated adsorption of methylene blue from aqueous solution by unmodified coconut coir dust. They found that the percentage of dye removal increased from 92.1% to 99.5% when the dosage increased from 0.05 to 0.2g and the equilibrium was reached with 0.1g of the adsorbent [10]. A similar phenomenon was also observed for CV and MB by palm kernel fibers [29]. From the nature point of view, MB and CV are basic dyes. So they are similar results in the removal efficiency from aqueous solution onto orange peel powder has been observed.

Table 4: Influence of adsorbent mass on removal efficiency and adsorption capacity at initial dye concentration of 40mg/l, reaction solution of 50ml, and pH 6 for 30 min.

Adsorbent mass, g	**0.05**		**0.1**		**0.2**		**0.3**		**0.4**	
Type of dye	**CV**	**MB**	**CV**	**MB**	**CV**	**MB**	**CV**	**MB**	**CV**	**MB**
Ce , mg/l	17.2	15.6	4.6	4.1	2.4	0.68	1.0	0.32	0.5	0.31
Removal, %	57.0	61.0	88.4	90.0	94.0	98.3	97.5	99.2	98.4	99.5
Capacity, mg/g	23.0	24.4	17.7	19.5	9.4	9.83	6.5	6.62	6.57	6.59

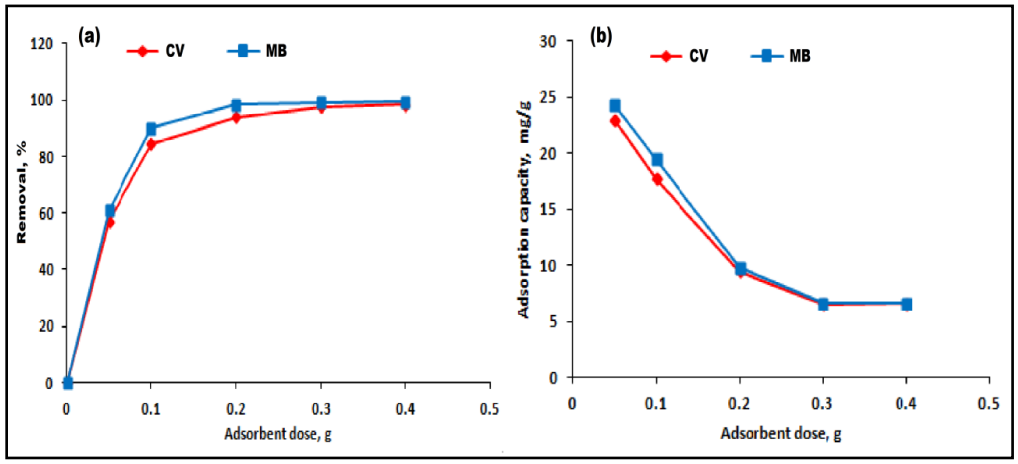

Figure 7: Effect of adsorbent dose on the percent removal of dye (a), and amount of adsorbed dye (b) at room temperature; contact time =30 min; agitation speed = 250 rpm; initial dye concentration = 40 mg/l; pH= 6-7.

4.4. Effect of pH

Figure 8 shows the effect of pH on the adsorption efficiency of orange peel powder. The percent removal of CV and MB onto orange peel increased with increasing pH from 2 to 6, and the maximum uptake of CV and MB was observed at pH 6.5 and found to be 94% and 95.7% for CV and MB respectively. This phenomenon may be ascribed to electrostatic interaction between cationic dyes and the negative surface of adsorbent. Lower adsorption of dyes at highly acidic pH may be due to the presence of excess H^+ ions that complete with the dye cations for adsorption site [30]. As the pH value increased, the number of negatively charged surface sites on the adsorbent increased. At pH above 6.5, no substantial uptake was recorded and this could as a result of saturation of the site or low stability of the dye molecules at higher pH as reported in literature [30]. Similar result was reported for the adsorption of MB dye onto coconut coir dust [10], and onto spent tea leaves [31], for removal of MB and CV by palm kernel fibers [30], for removal of MB from aqueous solution onto untreated palm seeds powder [29], adsorptive removal of CV and MB onto olive-waste cake [5]. On the other hand, as the pH value increased from 7 to 9, the percent removal of dyes is became lesser. At higher solution pH, decrease in the adsorption rate is due to the formation of soluble hydroxyl complex between liquid phase (dyes) and the solid phase (adsorbent) [31]. From the above results we can conclude that basic dyes; CV and MB could greatly be removed from the colored wastewater particularly, the textile industry effluents at pH (6 -7) which is the natural pH for discharging it to the environment, as well as the high-quality treated effluent, which a present a great example of the so-called "Green Chemistry"

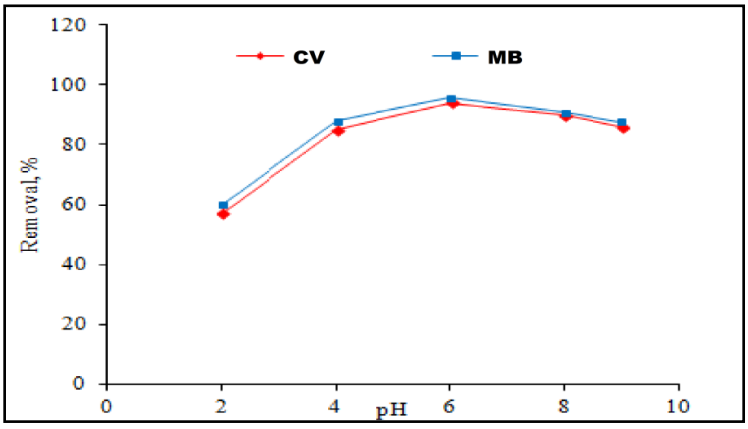

Figure 8: pH effect of dyes adsorption onto orange peel at room temperature; adsorbent dosage = 0.1g; contact time = 30 min; initial dye concentration = 40 mg/l, and agitation speed = 250 rpm.

4.5. Effect of reaction volume

At the optimum conditions of adsorption system the reaction volume of 50 ml achieved the best removal percentage of CV and MB onto orange peel powder. From data obtained, it can be conclude that the percent dye removal decreased with increase volume of reaction from 50 to 200 ml (Figure not shown). Similar trend was also observed for iron uptake using green clover leaves [32]. Investigation of lower volume of reaction effect on the adsorption system is necessary for support this study.

5. Isotherms models

5.1. Langmuir isotherm

Langmuir isotherms of CV and MB obtained are shown in Figures 9 and 10 respectively the slopes and the intercepts of these linear plots were used to calculate the constant parameters in equation of Langmuir isotherm [33, 16, 34]. Considering the values of linear regression coefficients (R^2). Table 5 shows the calculated constants from the obtained results of Langmuir isotherm. From figures 8 and 9 that shows a plot between C_e/q_e and C_e, the Langmuir constants q_m representing the maximum capacity is found to be 27.17mg/g and 25.87mg/g for CV and MB respectively, while b is 0.322 l/mg for CV and 0.938 for MB.

Table 5: Langmuir isotherm for CV and MB adsorption onto orange peel

CV			MB		
Q_{max}	b	R^2	Q_{max}	b	R^2
27.17	0.322	0.9754	25.87	0.938	0.999

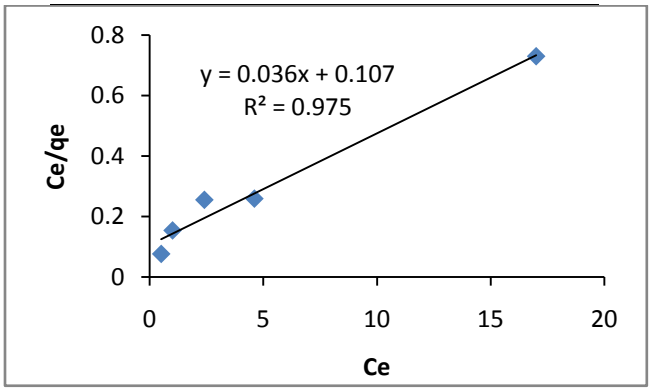

Figure 9: Langumar isotherm plot fot the adsorption of CV dye onto orange peel

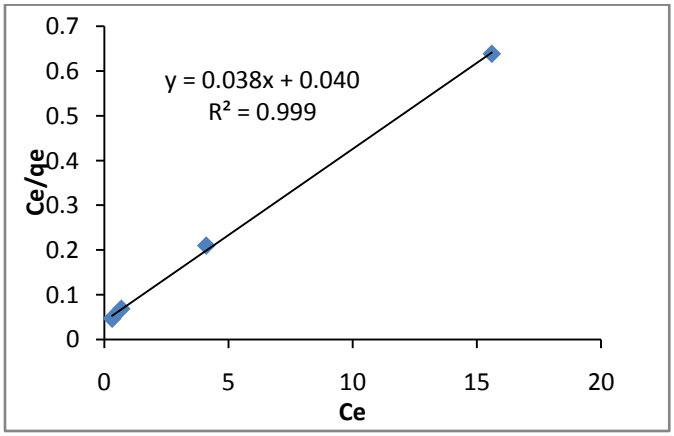

Figure 10: Langumar isotherm plot fot the adsorption of MB dye onto orange peel

The affinity between liquid phase (dyes) and solid phase (adsorbent) can be predicted using the Langmuir parameter b from the dimensionless separation factor R_L [11]

$$R_L = 1 \div 1 + bC_o \qquad (7)$$

where Co is the initial dye concentration, b is Langmuir isotherm constant. The adsorption process as a function of R_L may be described as follows [11]:

$R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable, and $R_L = 0$ irreversible.

The calculated R_L values for the adsorption of CV and MB onto orange peel are shown in Table 5. The R_L values were found to be in the range of 0.25 to 0.043 for CV, and 0.096 to 0.015 for MB at initial dye concentration of (10 to 70 mg/l) as presented in Figure 11. Similar results were reported for the adsorption of MB onto spent tea leaves [31]. In removal of mercury Hg (II) aqueous solution using Adulsa (*Justicia adhatoda*) leaves powder [35]. In a related study conducted by Jemimah and Bheeter (2017), observed similar phenomenon for the removal of procion blue from aqueous solution by water clover plant [36].

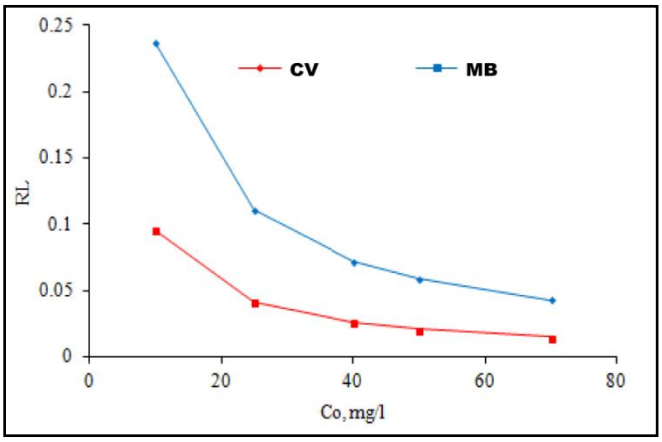

Figure 11: R_L as function of initial concentration of dye onto orange peel powder

5.2. Frenundlich isotherm

Freundlich isotherms of CV and MB obtained are shown in Figures 12 and 13 respectively the slopes and the intercepts of these linear plots were used to calculate the constant parameters in equation of Freundlich isotherms [30, 16, 31]. Considering the values of linear regression coefficients (R^2). Table 6 shows the calculated constants from the obtained results of Langmuir and Freundlich isotherm equations. From figures 12 and 13 that shows a plot between $\ln C_e$ and $\ln q_e$, the Freundlich constants K_f and n are used to represent the adsorption capacity and the adsorption intensity respectively.

Table 6: Frenundlich isotherm for CV and MB adsorption onto orange peel

CV			MB		
lnk	**1/n**	**R^2**	**lnk**	**1/n**	**R^2**
2.0397	0.3996	0.9093	2.3148	0.332	0.9889

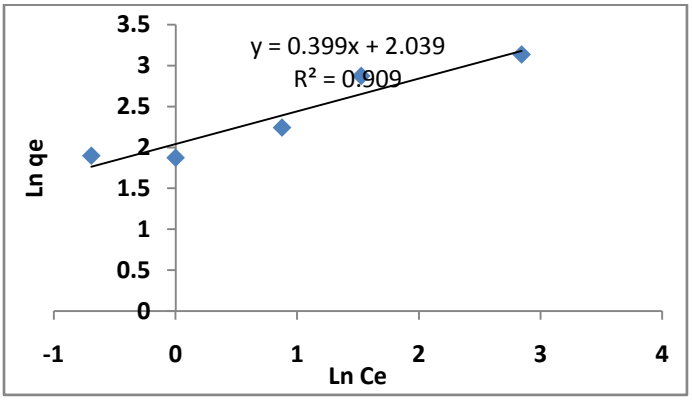

Figure 12: Frenundlich isotherm plot fot the adsorption of CV dye onto orange peel

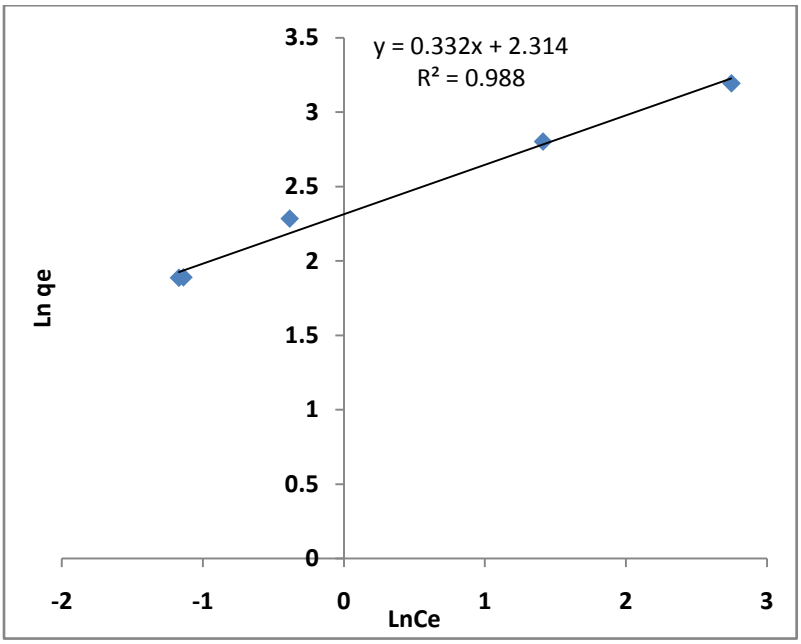

Figure 13: Frenundlich isotherm plot fot the adsorption of MB dye onto orange peel.

6. Thermodynamic studies

In this study only Gibbs free energy (ΔG) which is imply the spontaneous nature of the adsorption process was estimated only for 25±1.5°C because the effect of temperature on adsorption was not studied. But fixed constant during the whole process at 25±1.5°C. The value of Gibbs free energy and the equilibrium constant K_D were calculated using the Equation 8 and 9 respectively [10, 37].

$$\Delta G = - RT \ln K_D \quad (8)$$

$$K_D = qe/Ce \quad (9)$$

The equilibrium constant K_D of the adsorption process, expressed in L/g, and can be obtained for each temperature. R is the molar gas constant (8.314 j/mol k); T is the absolute temperature in Kelvin. From the experimental data, the Gibbs free energy ΔG for CV and Mb onto orange peel was found to be -2.98 kJ/mol and -3.59 KJ/mol respectively at initial dye concentration of 40 mg/l and reaction temperature of 298K. The negative value of ΔG indicates the adsorption is favorable and spontaneous. Similar results were reported by Baccar et al., (2010) for the adsorption of Lanaset Grey G dye onto activated carbon derived from olive-waste cakes [37], adsorption of crystal violet by *Citrullus Lanatus Rind* [16], and adsorptive removal of methylene blue onto coconut coir dust [10].

7. Final Remarks

The study concerns the use of raw orange peel (OP) for the removal of basic dye from the environment. The result obtained showed that raw orange peel modified with NaOH was an effective low cost adsorbent for the adsorptive removal of dyes; CV and MB from aqueous solution. OP had also good adsorption capacity for both dyes. Adsorption parameters obtained from Langmuir and Freundlich isotherms are useful for the explanation of the mechanisms of the adsorption system as indicator by the high correlation coefficient value ranging from 0.9754 to 0.9992. The maximum adsorption capacity for CV and MB onto OP was found to be 27.17 and 25.87 mg/g respectively, while the percent removal was reported as 97.5% and 99.2% for CV and MB respectively at adsorption conditions of 0.3g adsorbent dose, 40 mg/l initial dye concentration, pH 6 and 50 ml of reaction solution. The time to reach equilibrium was reported in 30 min. Dried orange peel after and before adsorption process for CV and MB dyes are shown in Figure 14 using initial dye concentration of 40 mg/l.

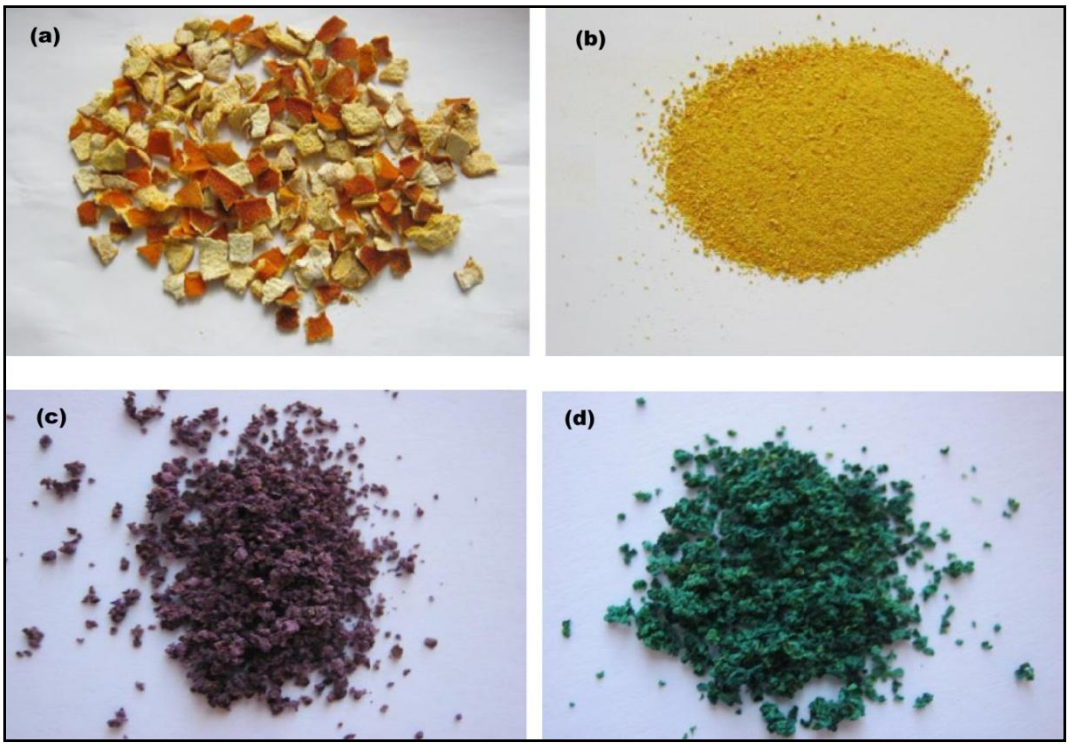

Figure 14: Dried OP alone (a), OP after grinding (b) OP after adsorbed CV (c), and OP after adsorbed MB (d)

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