J. Mater. Environ. Sci. 6 (8) (2015) 2045-2052 *Banerjee et al*
ISSN : 2028-2508
CODEN: JMESCN

Adsorption Characteristics of a Low Cost Activated Carbon for the Removal of Victoria Blue from Aqueous Solutions

Sushmita Banerjee[1*], Gopesh C. Sharma[2], Shikha Dubey[3], Yogesh C. Sharma[3*]
[1]*Department of Chemistry, University of Allahabad, Allahabad 211002, India.*
[2]*Department of Applied Science & Humanities , Invertis University , Bareilly 243123 , India*
[3]*Department of Chemistry, Indian Institute of Technology (BHU),Varanasi, Varanasi 221 005, India*

Received 8 Jan 2015, Revised 26 June 2015, Accepted 26 June 2015

Abstract
The adsorption of victoria blue by a low cost activated carbon synthesized from agro waste lemon grass was investigated. Activated carbon was prepared in the atmosphere of nitrogen and then characterized by BET surface area, X-ray Diffraction, Fourier Transformation Infrared (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM) . Removal of the selected dye victoria blue (VB) onto lemon grass activated carbon (LGAC) was conducted. BET surface area of LGAC was found to be ~218 m^2/g. Effect of initial concentration and contact time of dye, pH and temperature on the removal was investigated. Alkaline pH range favoured removal of VB. Maximum removal of the dye was found to be 90% under optimum conditions. Kinetics of removal process has been studied and mass transfer coefficient and intra-particle diffusion constant were also determined for removal of the dye at different temperatures. Value of be rate constant for the removal was found to be 1.40×10^{-2} min^{-1} at dye concentration of $1.53\text{x}10^{-2}$ at 30^oC. Increasing the temperature increased the removal of the dye, indicating the endothermic nature of the process of removal. Langmuir and Freundlich isotherm constants were determined and revealed that LGAC is a proper adsorbent material for the removal of VB from aqueous solution.

Keywords: Activated carbon**,** adsorption, waste material, Victoria blue; isotherms

1. Introduction
Many industries such as, textile, leather, paint etc. use different dyes and colours and generate large volumes of coloured effluents. These dyes have been reported to cause several health problems, affecting both the human and aquatic life [1-3]. About 40,000 dyes and pigments are known and accounted and over 7000 different chemical structures are consisted and over 7×10^5 tonnes effluents are produced annually world-wide [4]. Removal of colour/dyes from industrial effluents is a major challenge for environmental viewpoint. Millions of tons of dyes and colours are produced annually world-wide, and a significant part of it is discharged into water systems polluting them by dyes[4]. This warrants for the removal of the dyes from effluents. Adsorption, precipitation, oxidation, etc are well known methods for removal of dyes from effluents and activated carbon adsorption has been most common. Major drawback of activated carbon is that it is a very expensive material and small industrial units and developing countries cannot afford using activated carbon at large scale. Because of this aspect, search of alternates of activated carbons has come up as an important area of research. . In that series scientists have used a number of waste materials, minerals, etc. as precursors for production of activated carbons in laboratory [5-7]. Lemon grass is a weed prevalent in northen part of India in plenty and is recognised as a nuisance. Animals do not eat this material. In the present study, lemon grass has been used for laboratory scale synthesis of activated carbon by lemon grass. The activated carbon was characterized and effect of various parameters on the removal of VB by LGAC was studied.

2. Materials and methods

2.1Materials

All reagents used in the present experiments were of analytical grade and were obtained from Merck, Mumbai, India. The stock solution of victoria blue was prepared by dissolving the dye in double distilled water. The formula, molecular weight and solubility in water of Victoria Blue R are $C_{29}H_{32}ClN_3$, 457.5 g/mol, and 0.5%, respectively. Its absorption maximum occurs at 615 nm. It has the appearance of a reddish blue powder. It is a photosensitizer also. Molecular structure of the dye is given Fig. 1.

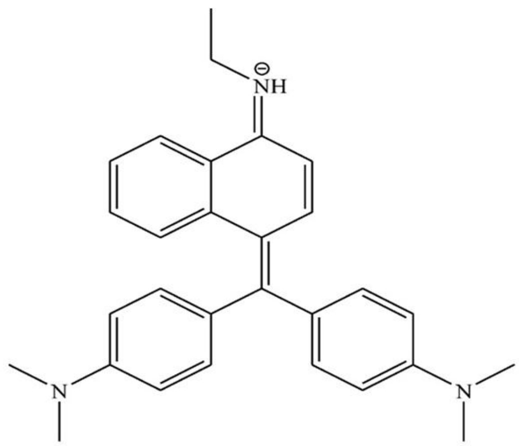

Figure 1. Molecular structure of Victoria blue

2.2 Synthesis and characterization of the adsorbent

Activated carbon synthesized from lemon grass (LGAC) was used as an adsorbent in this study. Details of synthesis method has been reported earlier [8]. After synthesis, adsorbent was characterized by using X-ray diffraction (XRD), Fourier Transform IR (FTIR) and SEM (Scanning Electron Microscopy). The Brunauer Emmett-Teller (BET) surface area, pore volume, and pore size distribution were investigated using a computer controlled automated porosimeter (Micromeritics ASAP 2020, V302G single port).

2.3Batch adsorption experiments

For batch experiments stock solution of victoria blue was prepared by dissolving 1g of dye powder in 1000 ml of distilled water. Stock solution was diluted for getting required concentrations of working solutions. For pH adjustment, 0.1MHCl/0.1M NaOH solutions were used as required. Removal studies were carried out by usual batch mode adsorption experiments by taking 50 ml of dye solution in 125 mL reagent bottles at desired concentration, pH ,agitation speed and dose. Batch adsorption experiments were conducted at 30°C (± 0.5) on a shaking thermostat water bath. After adsorption experiments, adsorbent was separated by centrifugation (Remi 24, New Delhi, India). After the equilibrium time, the adsorbent was separated from the solution by centrifugation at 6,000 rpm for 10 min. The residual concentration of victoria blue and malachite green in the solution was determined by UV-vis spectrophotometry at ~ 615 nm respectively. The amount of dye species adsorbed per unit mass of the adsorbent was determined using the following equation:

$$\%removal = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

$$\text{Amount adsorbed } (q_e) = \left(C_o - C_e\right)\frac{V}{W} \qquad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of MB and MG mgl/L, W the mass of adsorbent(g) and V is the volume of solution (L), q_e is the amount adsorbed(mg/g). All the experiments were carried out in triplicate and average of the three values has been reported in the manuscript.

3. Results and discussion

3.1. Characterization of the adsorbent

XRD analysis of the prepared activated carbon and it revealed the formation of phase of lemon grass activated carbon (figure not shown). XRD analysis was carried out for structural identification of the activated carbon in the 2θ range between $10^o$and 90^o. The X-ray diffraction

Table 1: Characterization of lemon grass activated carbon

Parameters	BET surface area (m^2/g)	Moisture content (%)	Ash (%)	Carbon (%)	Density (g/m^3)	Porosity
Values	172.8	8.40	31.23	11.32	2.71	0.48

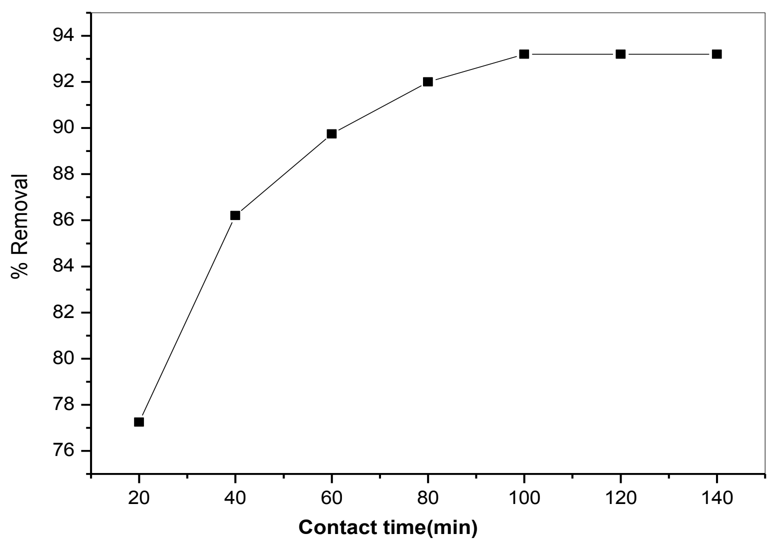

Figure 2: Effect of initial concentration on the removal of VB by adsorption on LGAC, dye concentration of VB $16.04X10^{-2}$ mol/L, Temperature, (303 to 323) K; 100 rpm.

spectrum of the activated carbon confirms the amorphous nature of the material. The diffractogram was indexed using powder sample by software JCPDS (19-0629). From FTIR spectrum of lemon grass activated carbon the presence of peaks in the (4500 to 500) cm^{-1} region is related to the lattice of water molecules, indicating the presence of moisture in the powder or KBr. By the observation of FTIR peaks suggested that chemical bonding between the dye species and the synthesized activated carbon plays no role in the adsorption and thus confirmed that removal of the dye occurs by physical adsorption. The BET surface area of the prepared lemon grass activated carbon was measured to be 218.67 m^2/g. Other parameters of the adsorbent are also given in Table 1.

pH_{zpc} of adsorbent is used to determine nature of adsorbent at different pH which provide information on selecting best pH for maximum removal. It is determined by plotting the graphs between initial pH and final pH and the point of intersection of the two graphs decides pH_{zpc} of the adsorbent of the material. In present study, the value of pH_{zpc} was found to be 7.66 (Figure not shown).

3.2. Effect of contact time and concentration

The effect of initial concentration on the removal of VB by adsorption on lemon grass activated carbon was studied. The concentration of selected dyes for adsorption studies was dye concentration of VB

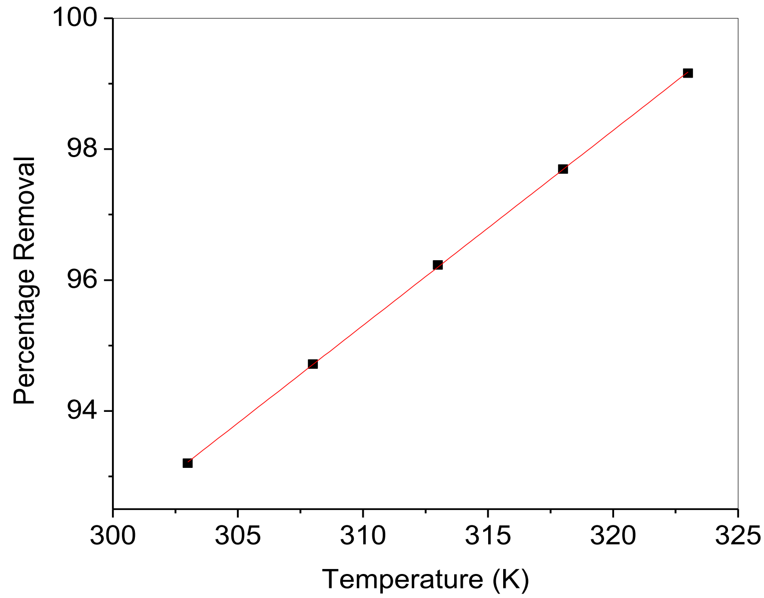

Figure 3: Effect of temperature on removal of VB by adsorption on Plot for transfer of mass for the removal of victoria blue on lemon grass activated carbon (LGAC); dye concentration of VB $16.04 X 10^{-2}$ mol/L, Temperature, (303 to 323) K; 100 rpm.

12.02×10^{-2} and 5.7×0^{-2} mol/L respectively. The results obtained are plotted in Figure 2 as percent removal versus contact time, respectively. It is clear from the figure that increasing the contact time increased the percent removal from ~70 to 90 % for the dye. The initial concentration of the dye plays an important role and affects the adsorption capacity of dye species on the adsorbent. This finding has an industrial importance and can be implemented as base line data [9].

3.3. Effect of dose

Effect of the dose of LGAC on the removal of VB from aqueous solutions was investigated . The dose of the adsorbent was varied in 0.40 -0.60 mg/50 ml in the solutions of VB. Values of all other parameters were kept constant in this case. It was found that the removal of dye varied from 85 to 96%.Also higher removal in initial stages can be attributed to availability of larger number of active sites in initial times of the removal.

3.4. Effect of temperature

Effect of temperature on the removal of VB by LGAC was plotted in Fig. 3. This figure shows that the removal of the dye increased from ~ 91 to 98% by varying the temperature from 30 to 50°C. This trend seems to be surprising because it hints towards a point that temperature has a feeble role in the present system of VB-LGAC.Our findings are supported by other workers [9].

3.5. Dynamic modeling

Dynamic modeling of the adsorption process is reported by using various first and second order kinetic equations. By replacing the kinetic data in these equations, the data was found to fit better in first order kinetic equation. The first order kinetic model is popularly expressed as Lagergren's model [10]:

$$\log(q_e - q_t) = \log qe - \frac{K_{ad}}{2.303} t \tag{3}$$

where q and qe (both mg/g) are the amounts of dye adsorbed at a particular time and at equilibrium, respectively, and K_{ad} (min^{-1}) is the rate constant for adsorption. The straight line plots of log [(qe - q)] versus t (Figure not shown) confirmed that the process of removal is governed by first-order kinetics. The linear plots also demonstrate the applicability of Lagergren's model for this study. The values of adsorption constant (K_{ad}) were determined by the slopes of the graphs and its value was found to be 1.40×10^{-2} min^{-1} at dye concentration of $1.53\text{x}10^{-2}$ at 30^{o}C for adsorption of Victoria blue by adsorption on LGAC.

3.6 Mass transfer studies of VB

In all adsorption processes it is an important aspect to study the transfer of dye from bulk to the surface and interface of adsorbent and the dye. It decides whether speed of transfer of dye onto the surface is rapid or is slow. This aspect is clarified by analysis of the data by various mass-transfer models. For the present studies, the following mass transfer model was used [11-12]:

$$\ln\left(\frac{C_t}{C_0}-\frac{1}{(1+mk)}\right)=\ln\left(\frac{mk}{1+mk}\right)-\left(\frac{1+mk}{mk}\right)\beta_L S_s t \quad (4)$$

where 'k' is Langmuir's constant, S_s is the specific surface area ,β_L, (cm /s) is coefficient of mass transfer, m is the mass (per unit volume) of the adsorbent. Following relations were used for determination of 'm' and 'S_s' [11-12]:

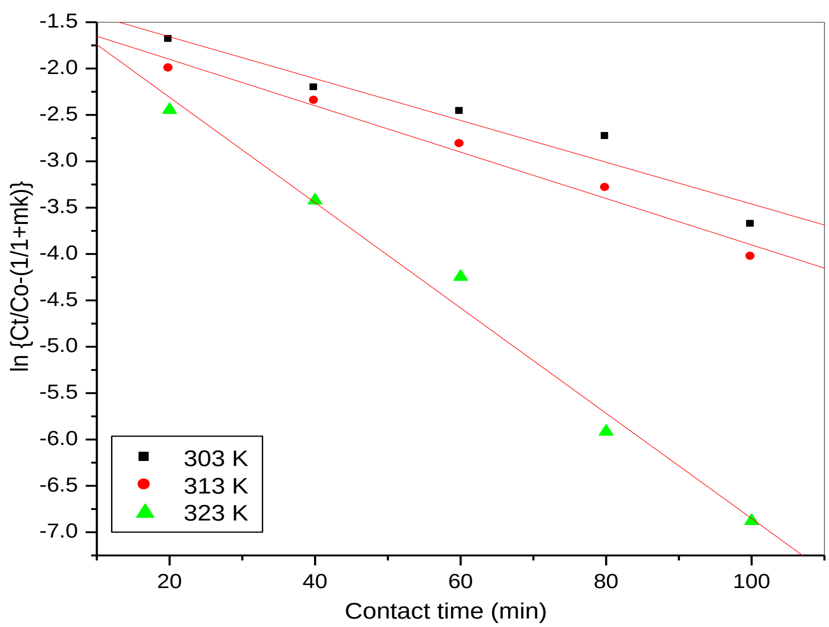

Figure 4: Plot for transfer of mass for the removal of victoria blue on lemon grass activated carbon (LGAC); dye concentration of VB $16.04\text{X}10^{-2}$ mol/L, Temperature, (303 to 323) K; 100 rpm.

$$m=\frac{W}{V} \quad (5)$$

$$S_s=\frac{6m}{d_p\delta_p(1-\varepsilon_p)} \quad (6)$$

where d_p is the diameter of adsorbent ε_p is porosity of the adsorbent, and δ_p is the density of adsorbent. Values of β_L, the coefficient of mass transfer, were calculated at different values of temperature by the slopes and intercepts of the plots of ' $\ln\left(\frac{C_t}{C_0} - \frac{1}{(1+mk)}\right)$ vs. t' (Fig.4).

Values of the parameters d_p, ε_p and δ_p of the adsorbent were determined as reported by Sharma et al.[11]. The value of β_L was determined from the slope and intercept of Fig 3 and was found to be 2.25×10^{-5} cm/s which is rapid enough for the process. The values of β_L at 313 and 323 K were found to be 2.50×10^{-5} and 2.67×10^{-5} cms^{-1} respectively.

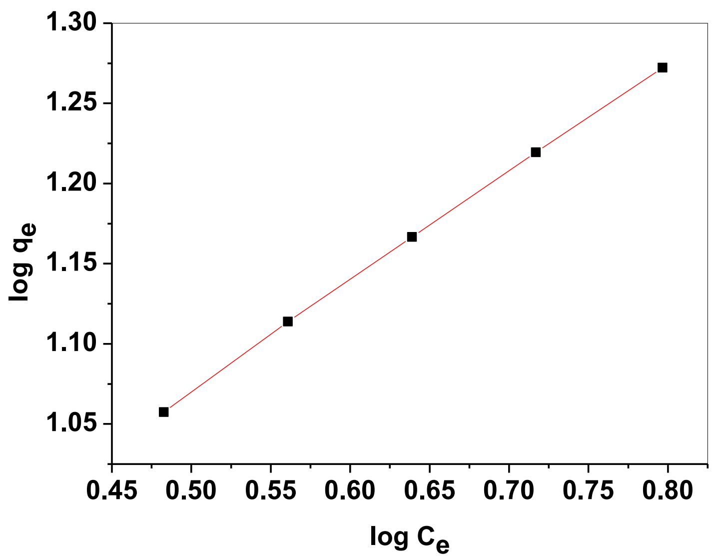

Figure 5: Freundlich plot for the removal of VB by adsorption on lemon grass activated carbon (LGAC);dye concentration of VB 16.04×10^{-2}mol/L, Temperature, (303 to 323) K; 100 rpm.

3.7. Equilibrium Study

The equilibrium data was substituted in the two most known isotherm models namely Freundlich and Langmuir adsorption models but the data fitted better in Freundlich adsorption model.

3.7.1. Freundlich adsorption isotherm

Equilibrium modeling for the removal of VB from aqueous solutions by adsorption on LGAC was carried out by using Freundlich isotherm modeling. Freundlich model is based on the fact that the adsorption occurs on a heterogenous surface. It can be expressed as follows [5]:

$$\log qe = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

where q_e is the amount adsorbed (mg/g), Ce is the equilibrium concentration (mg/l), and K_f and $1/n$ are related to the adsorbent capacity and sorption intensity of the adsorbent, respectively. The values of the Freundlich constants K_f and $1/n$ were determined from the intercepts and slopes, respectively, of the plots shown in Figure 4. The values of K_f for removal of VB for the present system were 0.874 mg/g, and that of n were (0.311 l/g respectively at 303 K(Table 2). The R^2 values for the parameters the isotherm model were calculated, and these values suggest that Freundlich isotherm model fit the equilibrium data.

Table 3: Values of Freundlich constants for the removal of VB by adsorption on LGAC at different temperatures and the corresponding correlation coefficients as (R^2)

T(K)	Freundlich parameters		
	K_f (mg/g)	1/n (l/g)	R^2
303	0.49	0.198	0.998
313	0.53	0.274	0.990
323	0.59	0.314	0.999

Thermodynamic behavior of adsorption of Victoria blue on LGAC was evaluated by the thermodynamic parameters – Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o). These parameters were calculated using the following equations [10-18]:

$$K_c = \frac{C_{ac}}{C_e} \quad (15)$$

$$\Delta G^o = -RT \ln K \quad (16)$$

$$\Delta H^o = R\left(\frac{T_2 T_1}{T_2 - T_1}\right) - \ln\left(\frac{K_2}{K_1}\right) \quad (17)$$

$$\Delta S^o = \left(\frac{\Delta H^o - \Delta G^o}{T}\right) \quad (18)$$

Table 4: Thermodynamic parameters for removal of VB by adsorption on LGAC

Temperature (K)	ΔG^o (kcal mol^{-1})	ΔH^o (kcal mol^{-1})	ΔS^o(calmol^{-1}K^{-1})
303	-0.182	-2.76	-8.51
313	-0.108	-1.89	
323	-0.091		

where K_c is the distribution coefficient for adsorption, C_{ae} is the equilibrium dye concentration on the adsorbent (mg L^{-1}) and C_e is the equilibrium dye concentration in solution (mg L^{-1}).

4. Application of activated carbons derived from economically viable sources for dye removal

Adsorption has been recognized as one of the most widely used method for removal of pollutant species from aqueous solutions and ultimately from industrial effluents. A number of materials like nano materials [13-14], waste materials [15], minerals [16], and activated carbons derived from economically viable sources [17-18] have been used for the removal of variety of species from effluents. It has been found that activated carbons are most effective materials but because of their high cost, there have been studies where activated carbons have been derived from cheaper precursors. Nano adsorbents have also been successfully used for the purpose but the acceptability of any of these materials as alternate of activated carbons is yet to be accepted by scientific community.

Conclusions

On the basis of present study it was found that lemon grass which is a waste can act as a potential feedstock for synthesis of activated carbon. The activated carbon was characterized by different methods. Effect of parameters on the removal of selected dye was carried out and the parameters were optimized. The results indicate that the synthesized activated carbon is a suitable material for removal of VB in particular and the study can be extended for discoloration of industrial effluents.

Acknowledgements-The authors thank Defense Research Development Organization (DRDO) for financial assistance (project P 31/46).

References

1. Abdel-El-Haleem D. *Afr. J. Biotechnol.* 2 (2003) 71.
2. Chatterjee S., Lee, D.S., Lee, M.W., Woo, S.H. *Biores. Technol*. 100 (2009) 3862.
3. Retailliau H.F.,Hightower,A.W.,Dixon,R.E., Allen, J.R., *J. Infect. Dis.*,139 (1979) 371.
4. McKay G.; Otterburn, M.S.; Aga, D.A.*Water, Air, Soil Pollut*. 24 (1985.) 307.
5. Chen C.Y. , Kuo, J.T., Cheng, C.Y. , Huang, Y.T., Ho, I.H., Chung, Y.C. *J. Hazard. Mater*. 172 (2009) 143.
6. Sani R.K., Banerjee, U.C. *Enzyme Microb. Technol*., 24 (1999) 433.
7. Dawood S., Sen, T.K. *Water Res*. 46 (2012) 1933.
8. Sharma Y.C., Uma, Sinha A.S.K, Upadhyay S.N., *J. Chem Engg. Data* 54 (2010) 2662.
9. Jaikumar V., Ramamurthi, V. *Int. J. Chem.* 1 (2009) 2.
10. Zhang, J. , Zhang, Y., Li, C., Jing, Y. *J. Hazard. Mater*., 150 (2008) 774.
11. Lua A.C., Yang, T. *J. Colloid Interface Sci.*, 274 (2004) 594.
12. Srivastava V., Weng C.H., Singh V.K., Sharma, Y.C., *J. Chem Engg. Data* 56 (2011) 1414.
13. Srivastava V., Y.C. Sharma, *Water, Air and Soil Pollut*., 225 (2014) Article no 1776.
14. Sharma Y.C., Srivastava, V., Mukherjee, A.K., *J. Chem. Engg. Data* 55 (2010) 2390-2398.
15. Weng C.H., Lin, Y.T., Chen, Y.J., Sharma, Y.C., *Colouration Tech.*,129 (2013) 298.
16. Yadav S., Srivastava, V., Banerjww, S., Weng, C.H., Sharma, Y.C., *Catena*, 100 (2013) 120.
17. Sharma Y.C., Uma , *J. Chem Engg. Data* 55 (2010) 435.
18. Sharma Y.C., Uma, Upadhyay, S.N., *Energy and Fuels*, 23 (2009) 2983.