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Research Article

APPLICATION POTENTIAL OF NUTRACEUTICAL INDUSTRIAL TURMERIC ROOT SPENT AS ADSORBENT FOR THE REMOVAL OF TOXIC CRYSTAL VIOLET DYE

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ABSTRACT

First-ever study on the use of nutraceutical industrial turmeric root spent (NITRS) as biosorbent for the removal of Crystal violet (CV) from aqueous media was tried. The effects of initial dye concentration, adsorbent dosage, contact time between adsorbent and adsorbate, speed of agitation and pH on adsorption were studied. The experimental equilibrium data were analyzed by using isotherm models of Langmuir, Freundlich and Tempkin. The pseudo-first order and pseudo-second order models were applied for adsorption kinetic studies. Kinetic data fitted well to pseudo-second order model. Thermodynamic analysis showed that adsorption is favorable (negative values for ΔG°) and endothermic ($\Delta H^\circ = 12-20$ kJ mol⁻¹) at the initial dye concentrations of 50, 100 and 150 ppm. The low ΔH° value is the indication for the physical process of adsorption involving weak chemical interactions like hydrogen bonds and Van der Waals interactions. SEM images of NITRS show highly fibrous matrix with hierarchical porous structure. FTIR analysis of the spent confirmed the presence of cellulosic and ligno-cellulosic materials imparting hydrophilic and hydrophobic properties. The investigation proved that NITRS is a cost-effective and efficient biosorbent for the remediation of toxic CV dye.

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INTRODUCTION

Indian Textile Industry contributes about 4 per cent to India's GDP and 14 per cent to overall Index of Industrial Production. The textile sector in India is the second largest provider of employment after agriculture. According to India Brand Equity Foundation Report 2017 (<https://www.ibef.org/industry/textiles.aspx>) the Indian textile industry is expected to reach US\$ 230 billion by 2020. Thus, the growth and all round development of this industry has a direct bearing on India's economy. Textile industry is put under chemical industry and dyes and pigments occupy a major portion amongst all the chemicals used by the industry. Dyes are dangerous as their metabolites are toxic, mutagenic and/or carcinogenic (Hamdaoui and Chiha 2007).

Crystal violet (CV) belongs to triphenylmethane class of dyes and is the brightest class of soluble dyes whose tinctorial values are very high since less than 1 mg L⁻¹ of the dye produces an obvious coloration. CV most widely used for dyeing fabrics of cotton, wool, silk, nylon, paper, leather etc., among all other dyes of its category (Tahir & Rauf 2006). CV also finds place in industries, such as, batteries (Takemura *et al.*, 2008), detergents (Sadlowski *et al.*, 2006), inks (Aoyama *et al.*, 2005),

lithographic printing plates (Sabnis 2008; Takemura and Hirai 2008), photoresistors (Toshimitsu 2006), printed circuit boards (Murao 2006) and thin film transistors (Takemura and Hirai 2008; Takemura *et al.*, 2008).

CV is also used in animal and veterinary medicines as a biological stain for detecting microorganisms (Martin *et al.*, 2008), treating atopic dermatitis (Rosenberg & Skinner 2008), dermatological diseases (Stumpp 2008; Pellet 2007), skin wounds (Kuhns 2007), lesions (Kuhns 2007) hemorrhoids (Sabnis 2008; Carroll 2006), multiple myeloma (Tiedemann & Stewart 2008), non-Hodgkin's lymphoma (Tiedemann & Stewart 2008), breast cancer (Tiedemann & Stewart 2008) neurodegenerative diseases (Stockwell 2007), onychomycosis (Rolf 2006), wound dressing (Svetlik 2007), drug delivery system (Sabnis 2008; Nadkarni *et al.*, 2007), dosage form (Nadkarni *et al.*, 2007a), antimicrobial agent (Sabnis 2008; Wilson *et al.*, 2008), antifungal agent (Sabnis 2008; Carr *et al.*, 2008), antimalarial agent (Sabnis 2008; Chong *et al.*, 2006). Besides, it finds application in staining, β -Amyloid plaques (Honson *et al.*, 2007), α -synuclein bacteria (Kataoka 2006), cells (Vujanovic 2007), liposomes (Liu *et al.*, 2008), nucleic acids (Sun *et al.*, 2008), proteins (Szent-Gyorgyi *et al.*, 2008),

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skin (Arndt 2008; Magallon *et al.*, 2007), thrombocytes (Lindberg 2008), vaginal smears (Liu & Fan 2007), hairs (Sabnis 2008; Trigg & Jones 2008; Hoeffkes & Gross 2006).

CV exhibits acute oral toxicity (Sabnis 2008; Hodge *et al.*, 1972), carcinogenicity (Sabnis 2008; Gold *et al.*, 1993; Littlefield *et al.*, 1989; Littlefield *et al.*, 1985), chronic toxicity (Sabnis 2008; Littlefield *et al.*, 1989; Littlefield *et al.*, 1985), cytotoxicity (Sabnis 2008; Huang *et al.*, 2008), chromosome damage (Krishnaja and Sharma 1995), DNA damage (McCarroll *et al.*, 1981), genotoxicity (Sabnis 2008; Walsh *et al.*, 2005; Choudhury *et al.*, 2004; Sakagami *et al.*, 1988), mutagenicity (Sabnis 2008; Serafimova *et al.*, 2007; Malachova *et al.*, 2006; Klopman *et al.*, 1990; Ferguson & Baguley 1988), ototoxicity (Sabnis 2008; Tom 2000), percutaneous toxicity (Sabnis 2008; Burnett *et al.*, 1976), phototoxicity (Sabnis 2008; Kandela *et al.*, 2002) and has been classified as a recalcitrant molecule since it is poorly metabolized by microbes, is non-biodegradable, and can persist in a variety of environments. Its removal from wastewaters before their discharge is, essential to keep the environment safe which is of paramount importance.

There are many processes applied for the removal of synthetic dyes from wastewater include and these solar photo-fenton degradation (Duran *et al.*, 2008), photocatalytic degradation (Sun *et al.*, 2008) integrated chemical-biological degradation (Sudarjanto *et al.*, 2006), electrochemical degradation (Fan *et al.*, 2008) and adsorption (Hameed 2009). Although, activated carbon adsorption is one of the most widely used techniques for dye removal (Karaca 2008) but due to view of the high cost and problems in regeneration, a constant search for alternate low adsorbents.

Turmeric (*Curcuma longa L.*) is the most popular spices of India and is widely used for medicinal purposes (Joe *et al.*, 2004). India, the largest producer of turmeric producing of 4, 87,000 metric tons (Joe *et al.*, 2004). India is also the largest supplier of turmeric to the world market with 52,500 metric tons of export valued at INR 248.58 crores per year (Anon 2014). One of the major constituent of turmeric possessing pharmacological properties is curcumin. Curcumin properties have been widely published papers especially about its antioxidant, anti-inflammatory, cancer chemo-preventive and potentially chemotherapeutic properties (Sharma *et al.*, 2005). It is also popular as an antiseptic in Ayurveda medicine and as sunscreen lotion in cosmetic industry. After the extraction of curcumin (which constitute only about 1-5% of turmeric) over 95% is obtained as Nutraceutical Industrial Turmeric Root Spent (NITRS). It is observed from statistics that NITRS from nutraceutical and other allied industries including cosmetics is produced in abundance, which could be utilized as biosorbent for removing of crystal violet dye from water as the cost is low.

The major disadvantages in the use of NITRS are that it is not useful as feed or fertilizer since it has underwent mechanical, thermal and chemical processes. It cannot be used as a fuel also as the porous structure traps moisture producing either low calorific value or incomplete combustion and toxic gases generation like carbon monoxide and fused pyrenes. It is used presently in boilers which leave carbon foot print. This is neither economically feasible nor ecologically acceptable as it creates an unprecedented problem of pollution. Availability of

myriad tons of NITRS has triggered great interest in finding new applications. Our research school has already to use NITRS as filler material in thermoplastic and thermoset composites (Pashaei *et al.*, 2011; Syed & Syed 2016; Syed & Syed 2016a; Syed & Syed 2012; Syed *et al.*, 2011; Syed *et al.*, 2010; Syed *et al.*, 2010a; Syed *et al.*, 2009). In this study, the adsorption of CV onto nutraceutical industrial NITRS has been studied, in the present work as its, renewable, cheap, and abundantly available pore structure enhances adsorption capacity.

MATERIALS AND METHODS

Adsorbate preparation

Crystal Violet, methanaminium, N-[4-[bis(4-(dimethylamino)phenyl)methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-, chloride (1:1) a dark green powder, soluble in water, acetone, chloroform and highly soluble in ethanol and insoluble in ether and xylene. It is a monovalent basic toxic dye belonging to the class of triphenylmethane dyes with molecular Formula $C_{25}H_{30}ClN_3$ and molecular weight 407.98. Its solution is having pH of 0.0-2.0 and changes color to yellow in high acidic range and appears blue-violet at pH 2.0. Its λ_{max} is 590 nm. The dye was supplied by Sigma Aldrich Private Ltd, Mumbai, India.

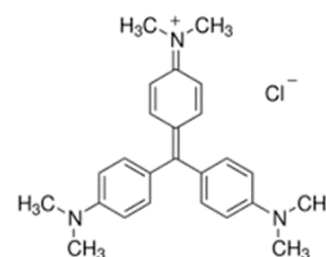


Figure 1 Structure of Crystal violet

Adsorbent preparation

The NITRS used in this study was procured from a local industry. The material after oven dried at 60°C for 24 h was sieved to get $\leq 177\mu$ (80 mesh) particle size which was stored in plastic bottles and used as and when needed.



Figure 2 Turmeric root, turmeric powder and NITRS

Surface characterization

The surface morphology of NITRS was visualized by a Scanning Electronic Microscope (Zeiss Scanning electron Microscope Evo/LS15). The functional groups present in the adsorbent were identified by FTIR. Infrared spectra of the NITRS prior to and post adsorption of CV were obtained using FTIR spectrometer (Inter-spec 2020, Spectro Lab, UK).

Batch adsorption experiments

Adsorption of CV from aqueous solution by NITRS was investigated in batch method. The effects of initial dye concentration, pH, temperature, speed of agitation and adsorbent dosage, were studied. Batch adsorption experiments

were carried out by adding a known amount (50 mg) of NITRS into 250 ml Erlenmeyer flasks containing 50 ml of initial dye concentration (25-500 mg/L). The flasks were agitated (Kemi Orbital Shaker, India) at 175 rpm at 25±2°C for 180 min, until equilibrium was reached. The samples were centrifuged at 3000 rpm for 5 min. If the supernatant liquid is unclear, then the centrifugation was continued for 5 more min. The un-adsorbed dye solution from the supernatant liquid was removed carefully using micropipette and the absorbance of the colored solution was measured by a double beam UV/Vis spectrophotometer (Perkin Elmer- Lambda 25, USA) at 590 nm. The adsorbed amount of CV at equilibrium, q_e (mg/g) was calculated using equation (1).

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

Where, C_0 and C_e are concentrations (mg/L) of CV at initial and equilibrium, respectively, V is solution volume (L) and W is adsorbent weight (g). Same procedure was followed for kinetic studies, but the aqueous samples were agitated at pre-set time intervals. The concentrations of CV were measured as described above. The amount q_t (mg/g), of CV adsorbed at any time was calculated as per equation (2).

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

Where, C_t (mg/L) is the concentration of CV at time t . Initial dye concentrations of 50, 100 and 150 mg/L and 90 min adsorption time (15 min intervals) were selected for the study. For the optimum amount of adsorbent per unit mass of adsorbate, 50 ml of dye solution were used with different amounts of NITRS (0.025-0.300 g/L) till equilibrium was attained. To find the agitation speed on dye adsorption, 50 mg of NITRS and 50 ml of dye solution of concentration 50 mg/L were agitated at 75 - 200 rpm. To find the effect of pH on dye adsorption, 50 mg of NITRS and 50 ml of dye solution of concentration 50 mg/L were agitated in an orbital shaker with pH values of 2-12. The pH was adjusted with dilute HCl and/or NaOH, agitation was continued for 90 min. Contact time of about 90 min was sufficient to reach equilibrium at 175 rpm agitation and this was used for all further studies. At equilibrium the dye concentration was measured using double beam UV/Vis spectrophotometer at 590 nm. Solution pH was determined by pH meter (Systronics 802, India). Amount of dye removed was determined as per the equation (3).

$$\text{Dye removal efficiency \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \dots \dots (3)$$

Modeling studies

Adsorption isotherms

Adsorption isotherm, describes the retention of dye from the aqueous media to a solid-phase at a constant temperature and pH. The results of different parameters studied in different models provide information about interaction mechanisms, surface properties and affinities of the adsorbent. The most accepted equations for studying surface adsorption studies for single solute system are the Langmuir, Freundlich and Tempkin models. These models (Table 1) were used to test the equilibrium adsorption at ambient temperature.

Table 1 Non-linear two-parameter isotherm models

Two parameter isotherms	
Langmuir	$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e}$
Freundlich	$R_L = \frac{1}{1 + K_a C_0}$
Tempkin	$q_e = K_F C_e^{1/n_F}$
	$q_m = (RT/b) \ln A + (RT/b) \ln C_e$

Q_m = maximum adsorption capacity; K_a = Langmuir constant; R_L = separation factor; K_F, n_F = Freundlich constants; A, b = Tempkin constants; C_0 and C_e = concentration at initial and at equilibrium

Adsorption kinetics

Controlling of the adsorption process was determined by fitting experimental data with pseudo-first-order and pseudo-second-order model (Table 2). The controlling mechanism of the adsorption process was found by fitting the experimental data with the respective kinetic equations.

Table 2 Non-linear kinetic models

Pseudo-first order	$q_t = q_e [1 - \exp(-k_1 t)] \quad h_0 = k_1 q_e$
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad h_0 = k_2 q_e^2$

k_1 = rate constant for the pseudo-first order adsorption; k_2 = rate constant for the pseudo-second order adsorption; h_0 = initial adsorption rate

Thermodynamic parameters

Energy and entropy of a process help to understand feasibility and mechanism. Thermodynamic parameters, including standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were estimated by using rate law as also kinetic data to evaluate the feasibility and enthalpy of the adsorption process.

RESULTS AND DISCUSSION

Surface characterization of the Spent

Scanning Electron Microscopy (SEM)

NITRS morphology was studied by SEM displayed fibrous and porous structures (Figure 3a). This structures assist to enhance adsorption of dye. Figure 3b shows the pores and voids between the spaces, which are covered by CV.

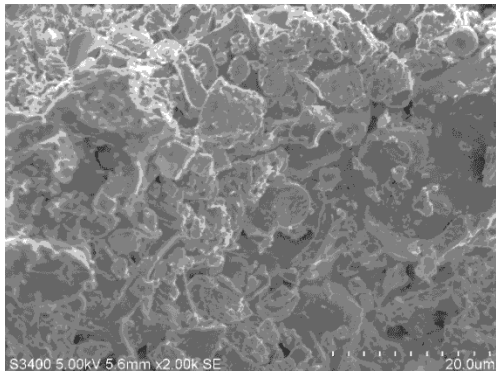


Figure 3a SEM image of NITRS

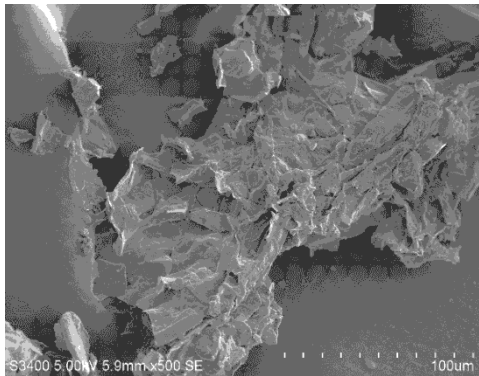


Figure 3b SEM image of CV- NITRS

FTIR characterization of CV adsorbed on NITRS

The FTIR spectroscopy was employed to analyze the possible interaction between NITRS and CV. The FTIR Spectra were recorded before and after adsorption of CV on to NITRS to determine any changes in the intensity and shift in position of peaks of the functional groups. Some changes were evident in the spectra after CV adsorption on to NITRS. The broad band around 3317 cm^{-1} is due to stretching of hydroxyl groups of cellulose, hemicellulose and lignin present in NITRS. The band at 1651 cm^{-1} are due to C=C stretching. The band at 1019 cm^{-1} is due to C-O single band. The band at 600 cm^{-1} was due to the presence of cellulose present in adsorbent. After the adsorption of CV peak is at 3288 cm^{-1} is due to O-H stretching. The band at 2020 cm^{-1} is due to C-H stretching and the bands at 1170 and 1018 which will be due to C-O stretching. The bands at 700 cm^{-1} - 600 cm^{-1} are due to C-Cl stretching and these observations confirm the interaction between the dye and adsorbent (Zhang *et al.*, 2011).

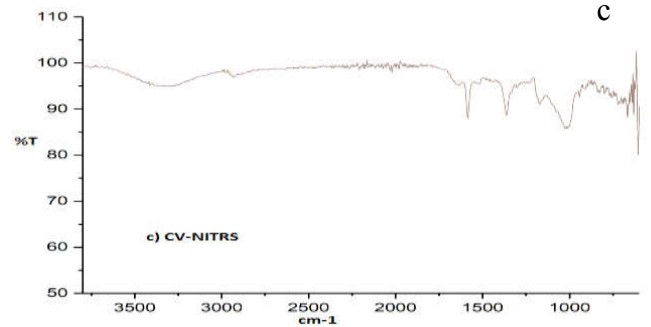
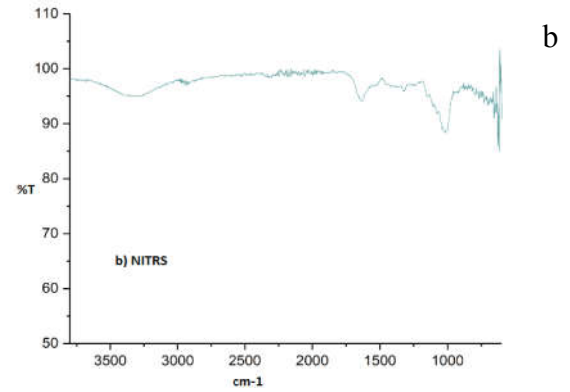
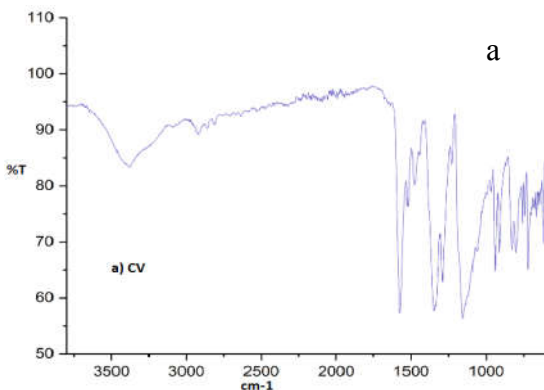


Figure 4 FTIR spectra of (a) CV, (b) NITRS and (c) CV adsorbed on NITRS

Influence of adsorption parameters

Initial dye concentration

The dye uptake increased from 20 to 170 mg/g of NITRS with increase in dye concentration from 25 to 500 mg/L (Fig. 5a). This may be attributed to the increase in the driving force of the concentration gradient with the increase in the initial dye concentration. The dye uptake increased with longer in contact time. For maximum removal of CV from aqueous solution needed 90 min contact time. Initial adsorption of dye was rapid due to the adsorption of dye on to exterior surface and later on the dye molecules enter into pores (interior surface), relatively at slower rate. The adsorption of CV increased with increase in concentration and remained almost constant after reaching equilibrium is reached. With the increase in CV concentration upto 100 mg/L adsorption increase thereafter decreases as shown in Figure 5b.

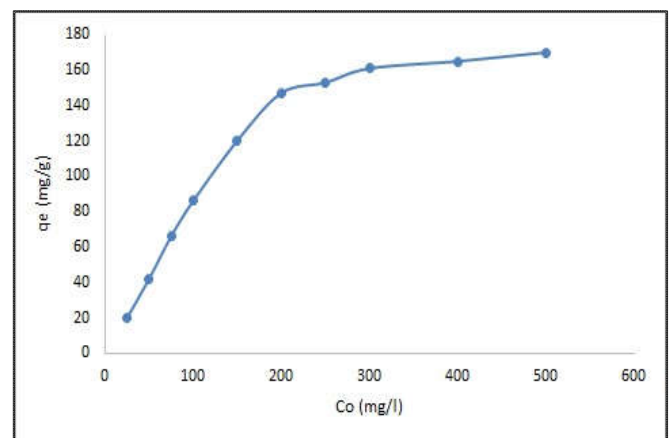


Figure 5a Effect of initial dye concentration

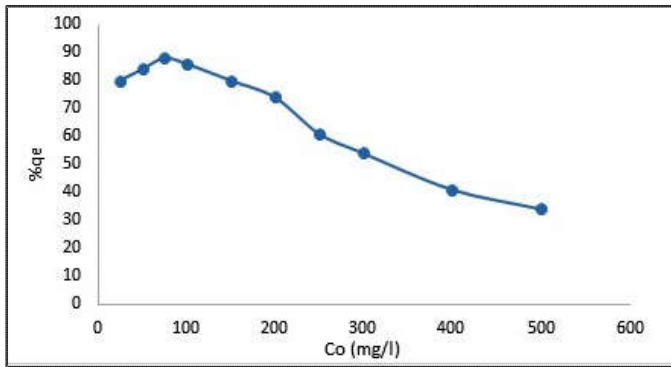


Figure 5b Initial dye concentration with % qe

Adsorbent dosage

Adsorbent dose has a marked influence on the adsorption process, since it determines the adsorption capacity of the adsorbent for a given initial concentration of the adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of adsorbent dosage on CV adsorption was investigated in the range of 0.025–0.300 g. It was observed that the percent of CV removal increases with increase in adsorbent dose. The yield for CV on to NITRS increased with increase in adsorbent dose. Further increase in the adsorbent dose did not significantly change the adsorption yield. This is due to the binding of almost all dye molecules on the adsorbent surface and the equilibrium between dye molecule onto the adsorbent and in the solution (Chowdhury & Das 2012). The results are depicted in Figure 5c.

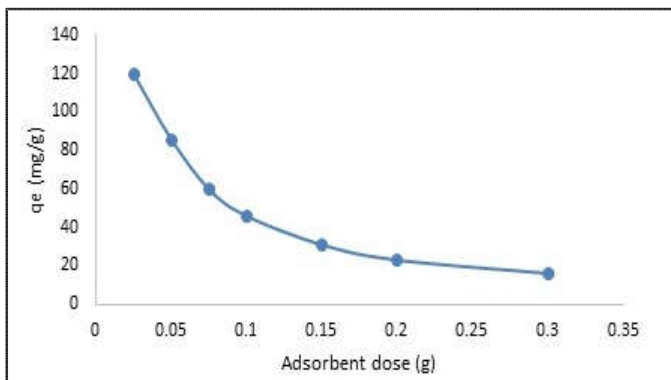


Figure 5c Effect of adsorbent dosage

Effect of contact time

The effect of contact time for the removal of CV onto NITRS was performed in the range of 15, 30, 45, 60, 90, 120, 150 and 180 min. In the initial 15 min it showed rapid adsorption to the extent of 70% of adsorption takes place, as the contact time increase there was an increase in adsorption until 90 min then gradually it reached equilibrium. As there was increase in contact time up to 180 min it showed only 4% CV removal onto NITRS showed in the figure 5d. Aggregation of dye molecule with increase in contact time, it makes dye molecule to diffuse deeper into adsorbent structure with higher energy site. This aggregation negates the influence of contact time as the mesopores get filled up and start offering resistance to diffusion of aggregated dye molecules in adsorbents. This was

the reason for an insignificant enhancement in adsorption after 90 min.

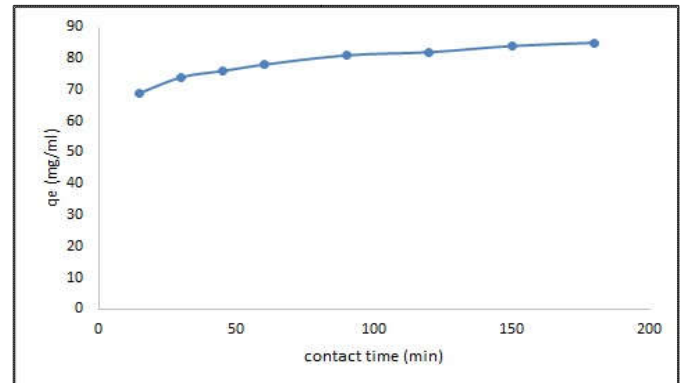


Figure 5d Effect of contact time

Effect of speed of agitation

In adsorption process, speed of agitation is an important parameter for the removal of CV by NITRS, due to the influence of dispensation of the solute in the bulk solution of external boundary formed. The varying speed of agitation on adsorption of CV onto NITRS studied, the speed of agitation was studied from 75, 100, 125, 150, 175 and 200 rpm. As the increase in speed of agitation adsorption increases, at 175 rpm maximum CV removal was found (fig 5e) then there was slight decrease in adsorption when it reaches 200 rpm. The reason for this was the film boundary layer being surrounded by sorbent particle.

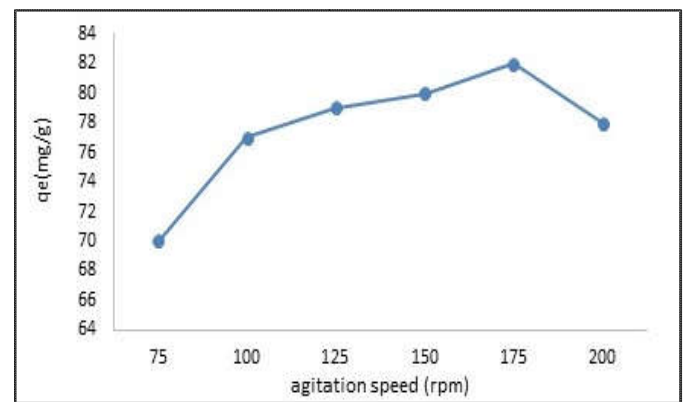


Figure 5e Effect of agitation speed

Effect of pH

In adsorption pH is considered as one of the important parameter. The effect of pH was studied by varying the pH in the range of 2 - 12 for CV adsorption, thus CV decolorizes at low pH due to structural changes, so the effect of pH was studied from 2 to 12. It shows that as pH increase there was an increase in adsorption till pH 6 then there was slight decrease in adsorption of CV onto NITRS (fig 5f). This shows that electrostatic mechanism was not the only mechanism for CV adsorption onto NITRS. Hence all further parameters were carried out in neutral condition. Decrease in adsorption at lower pH may be due to competition of H⁺ ions with dye molecules.

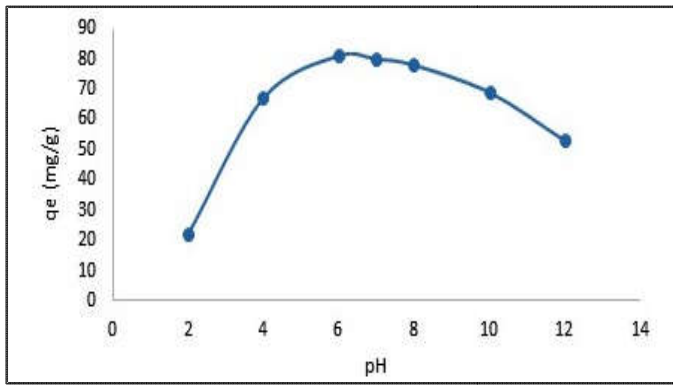


Figure 5f Effect of pH

Effect of Temperature

Temperature is an additional factor which influences the adsorption process. The adsorption studies were carried out at 30°C to 50°C with different dye concentration and the results are shown in Figure 5g. It can be observed that with increase in temperature, the adsorption capacity increased marginally, which indicates that the process is exothermic in nature. The enhancement in adsorption with temperature may be due to the increase in the mobility of the dye molecule with increase in their kinetic energy and the enhanced rate of intra-particle diffusion phenomenon (Ahmad & Kumar 2010; Zameer *et al.* 2010).

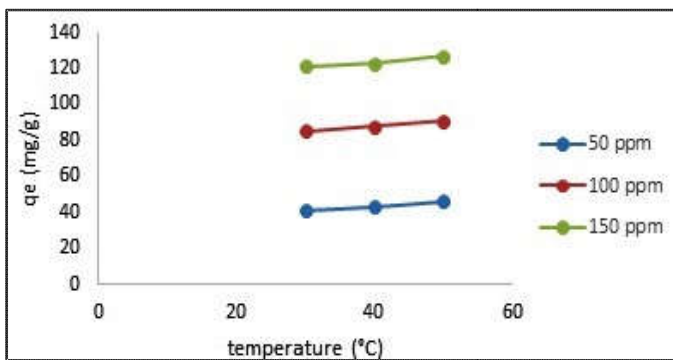


Figure 5g Effect of temperature with initial dye concentration

Adsorption isotherm

Adsorption isotherm parameters are important for the description of how molecules of adsorbate interact with adsorbent surface. In the present case, an attempt has been made to understand the adsorption of CV on to NITRS using different adsorption isotherm models. Langmuir and Freundlich isotherms are the well-established models for predicting the adsorption capacities and to fit the experimental data. The Langmuir isotherm model assumes that the monolayer adsorption takes place on to the surface of adsorbent containing finite number of identical adsorption sites of uniform energies (Langmuir 1916). The Langmuir equation is shown below:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad R_L = \frac{1}{1 + K_a C_0} \quad \dots\dots(4)$$

Where, q_e is the amount of dye adsorbed on to adsorbent (mg/g) at equilibrium; C_e is the equilibrium concentration (mg/L) of the dye in solution. The values of Q_m and K_a are determined from the intercept and the slope of q_e vs C_e , where,

Q_m is the monolayer adsorption capacity (mg /g) and K_a is the Langmuir constant (L/mg) related to the free energy of adsorption. The equilibrium experiments were conducted for different initial concentrations of CV in the range of 25-500 mg/L. The Q_m value of 181 mg/g obtained for this isotherm is too high from the experimental value of Q_m (86 mg/g). However, the value of R^2 of 0.990 shows good fitting of this isotherm to the experimental data. The separation factor R_L is an important parameter of Langmuir isotherm (Webber & Chakkravorti 1974). The values of R_L describe whether the adsorption in a system studied is unfavourable ($R_L > 1$), Linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values calculated were between 0.120 and 0.027 indicate favourable adsorption of CV on to NITRS. The decrease in R_L with an increase in the initial concentration indicates that the adsorption is more favourable at high concentration. However, the large difference between Q_m (181 mg/g) and q_e (86 mg/g) has made the authors to explore other adsorption isotherm models.

Freundlich isotherm model is an empirical equation which assumes that the adsorption process takes place on heterogeneous surface (Freundlich 1906). The capacity of adsorption by NITRS is related to the CV concentration at equilibrium which follows the equation:

$$q_e = K_F C_e^{1/n_F} \quad \dots\dots(5)$$

Where, K_F and n_F are the Freundlich constants related to adsorption capacity [mg/g and (mg/L)^{-1/n_F}] and adsorption intensity respectively. The latter is also known as the heterogeneity factor (n_F) which indicates whether the nature of adsorption is linear ($n_F=1$), chemisorption ($n_F < 1$), or a physisorption ($n_F > 1$). In the present study, the values of $n_F = 0.42$ indicate that the adsorption is physisorption and favours normal Langmuir Isotherm. The values of K_F and n_F are calculated from the intercept and slope of the plot $\ln q_e$ versus $\ln C_e$. The fitting of Freundlich isotherm to the experimental data has R^2 value of 0.775, where R is the correlation coefficient shows that the process is linear. It could be inferred that the adsorption of CV on to NITRS is favourable at experimental conditions and the process is physisorption. To enhance the validity of the two models studied, authors have attempted to explore Tempkin model to fit in the data.

Tempkin model describes the process by considering some indirect adsorbate-adsorbate interactions on adsorption (Amela *et al.*, 2012). This isotherm explains that, the linear decrease in heat of adsorption of all the molecules in the layer is the impact of these interactions. The linear form of Tempkin isotherm is:

$$q_m = (RT/b) \ln A + (RT/b) \ln C_e \quad \dots\dots\dots(6)$$

with $B = RT/b$

Where, q_m is adsorption capacity (mg/g), C_e is equilibrium dye concentration (mg/L). A and B are Tempkin constants, related to equilibrium binding constant (L/g) and heat of adsorption (J/mol), respectively. The values of A and B can be calculated from intercept and slope of the linear plot q_m versus $\ln C_e$. Tempkin isotherm fit well to the experimental data with R^2 value 0.925, where R is the correlation coefficient shows that the process is linear.

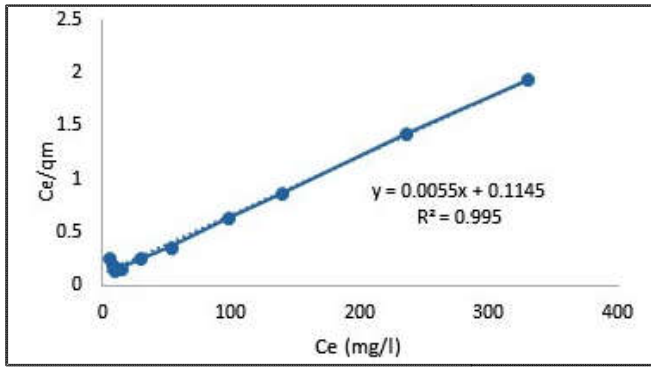


Figure 6a Langmuir isotherm model

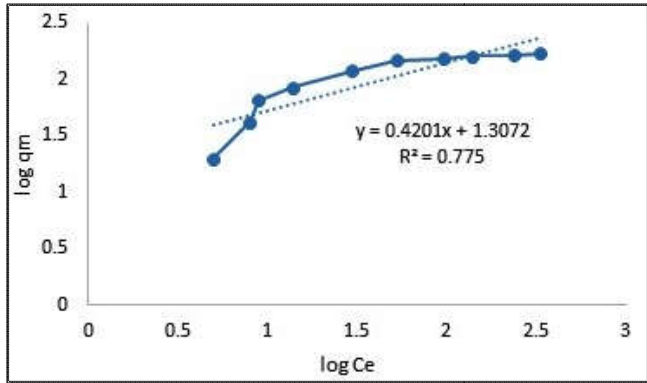


Figure 6b Freundlich isotherm

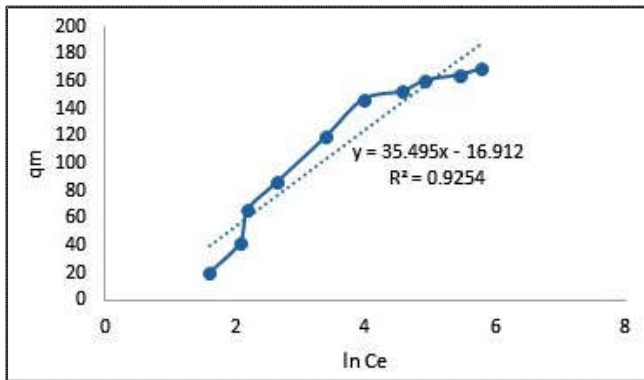


Figure 6c Tempkin isotherm

Table 2 Isotherm constants of CV-NITRS system

Langmuir isotherm			Freundlich isotherm			Tempkin isotherm			
q_m	b	R_L	R^2	K_F	n	R^2	A	B	R^2
181	0.048	0.12	0.994	20.286	0.42	0.775	1.606	35.495	0.925

Adsorption kinetics

Kinetic models were studied to find the potential rate-controlling steps involved in the process of adsorption. The concentrations of CV were 50, 100 and 150 ppm at the time of kinetic studies. Kinetics studies at different temperatures (303 K, 313 K and 323 K) reveals the change in rate of adsorption at different temperature. The adsorption kinetic data were analysed by non-linear analyses (MS Excel 2010) using pseudo-first order (Lagergren 1898) and pseudo-second order (Ho & McKay 1998) models. The estimated parameters are shown in Table 3.

Table 3 Experimentally determined and theoretically predicted parameters for absorption kinetics models.

Initial Concentration [ppm]	Temp [K]	$Q_{E_{exp}}$ [$mg \cdot g^{-1}$]	Pseudo First order			Pseudo Second order				
			$Q_{E_{pred}}$ [$mg \cdot g^{-1}$]	k_1	R^2	χ^2	$Q_{E_{pred}}$ [$mg \cdot g^{-1}$]	k_2	R^2	χ^2
50	303	41	30.88	9.11E-02	0.47	1.31	34.63	3.88E-03	0.69	0.74
	313	43	33.07	9.96E-02	0.62	0.66	36.42	4.47E-03	0.84	0.28
	323	46	35.38	8.93E-02	0.70	0.71	39.35	3.56E-03	0.88	0.26
100	303	85	76.88	1.42E-01	0.51	0.72	81.41	3.88E-03	0.81	0.28
	313	88	79.88	1.57E-01	0.59	0.36	83.46	5.02E-03	0.86	0.13
	323	91	82.06	1.45E-01	0.54	0.62	86.57	3.91E-03	0.83	0.23
150	303	121	101.21	1.19E-01	0.59	1.37	109.15	2.05E-03	0.85	0.51
	313	123	105.42	1.29E-01	0.68	0.71	112.18	2.46E-03	0.91	0.20
	323	127	110.13	1.38E-01	0.61	0.79	116.59	2.66E-03	0.88	0.25

Based on coefficients of determination (R^2) and chi-square values (χ^2) the pseudo-second order model fitted better than pseudo-first order with the experimental data at all initial CV concentrations (50, 100 and 150 ppm) at different temperature (Figures 7a, 7b and 7c). The rate of adsorption was very high initially and slowed down gradually to become stagnant when it reached the maximum adsorption. The adsorption capacity (q_e) increased with increase in temperature. These results show that the adsorption processes were not rate-limiting. The data also show that adsorption process occurred in multiple steps where the solute molecules move from the bulk solution to solid surface followed by diffusion of the solute molecules to the pores of the NITRS.

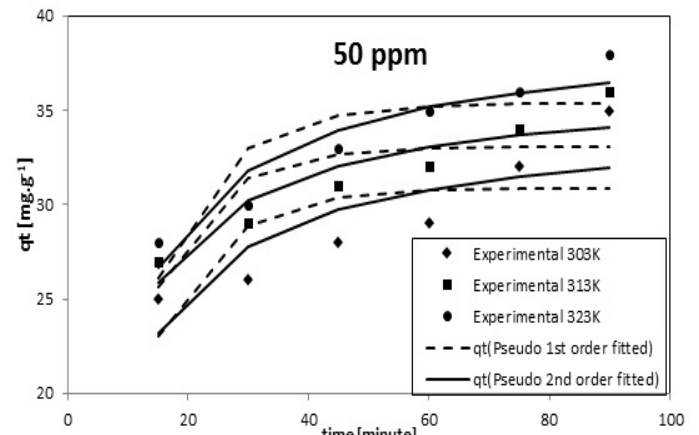


Figure 7a Kinetic model fits for 50 ppm initial concentration of CV on NITRS system at different temperatures

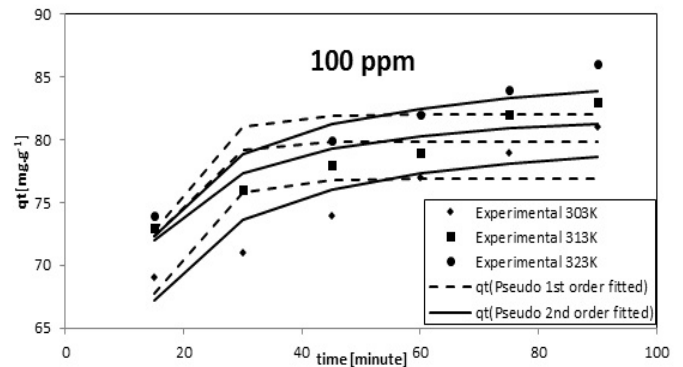
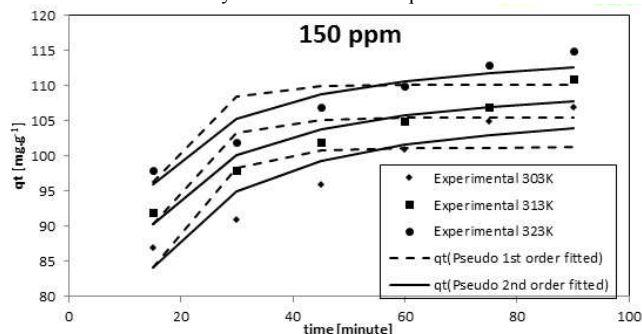


Figure 7b Kinetic model fits for 100 ppm initial concentration of CV on NITRS system at different temperatures

Figure 7c Kinetic model fits for 150 ppm initial concentration of CV on NITRS system at different temperatures

Adsorption thermodynamics parameters

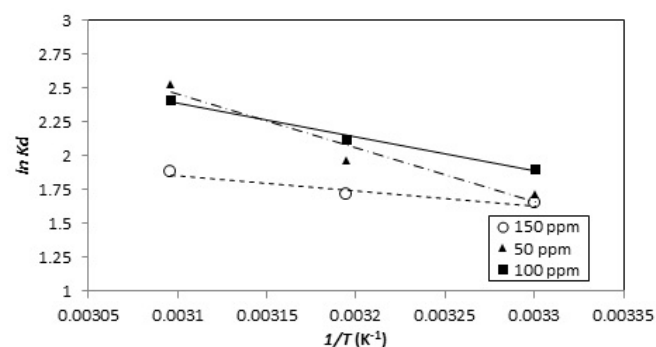
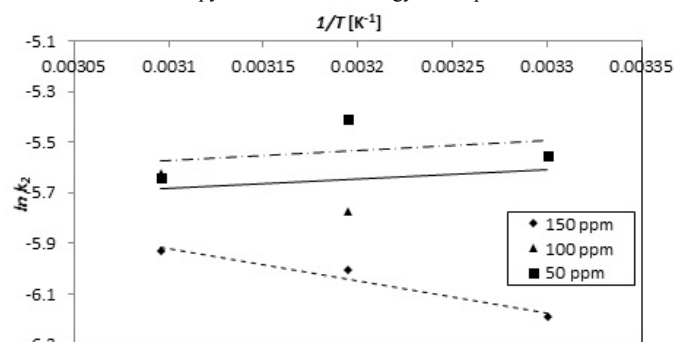
Energy and entropy are the key factors in the interaction process design. The standard Gibbs free energy change (ΔG°) indicates the degree of spontaneity of the adsorption process. For significant adsorption to occur, the free energy change (ΔG°) of adsorption must be negative. The Gibbs free energy, entropy and enthalpy changes of adsorption were calculated by Vant Hoff and Gibbs-Helmholtz equations

Where, K_L is the thermodynamic equilibrium constant ($l\ mol^{-1}$) and T is the temperature (K). C_{ac} and C_e are the initial and equilibrium concentration ($mg\ l^{-1}$) of dye in solution respectively. ΔH° and ΔS° can be determined from the slope and the intercept of the Van't Hoff plots of $\ln(K_L)$ vs $1/T$. The thermodynamic parameter estimates are provided in Table 4. The positive ΔH° value suggests the endothermic nature of adsorption and the negative ΔG° values indicate the feasibility and spontaneity of the adsorption process. The ΔG° is negative for all studied temperatures indicating that the adsorption of CV onto NITRS would follow a spontaneous and favorable trend. The ΔG° value decreases with increase in temperature indicating an increase in adsorption at higher temperatures. The positive value of ΔS° suggests good affinity of CV towards the adsorbent and increased randomness at the solid solution surface.

Table 4 Thermodynamic parameters of CV-NITRS system

Initial Concentration [ppm]	Temperature [K]	ΔG° [kJ mol ⁻¹]	ΔS° [J mol ⁻¹ K ⁻¹]	ΔH° [kJ mol ⁻¹]	ln A	E_a [kJ mol ⁻¹]
150	303	-4.14	44.52	9.39	1.95	10.65
	313	-4.46				
	323	-5.04				
100	303	-4.78	84.14	20.75	6.83	-3.07
	313	-5.52				
	323	-6.47				
50	303	-4.32	122.22	32.85	6.84	-3.41
	313	-5.12				
	323	-6.78				

The relatively low value of ΔH° suggests that the adsorption process is physical as the standard enthalpy change for chemical reaction is normally $>200\ kJ\ mol^{-1}$. This has been further confirmed by activation energy values of the adsorption process at different initial concentrations (50, 100 and 150 ppm) which ranged from ~ -3.41 - $10.65\ kJ\ mol^{-1}$ (Table 4) using the Arrhenius equation and the kinetic constant from the Pseudo second order model.


Figure 8a Plot of thermodynamic equilibrium constant vs $1/T$ to determine the enthalpy and Gibbs free energy of the process

Figure 8b Plot of pseudo - second order kinetic constant vs $1/T$ to determine the activation energy of the process

CONCLUSION

The results of the investigation proved that Nutraceutical Industrial Turmeric Root Spent is an effective adsorbent for the removal of Crystal violet (CV) dye from aqueous solution. The process of CV adsorption is endothermic and almost spontaneous. The results fitted well with pseudo-second order kinetic model. The low ΔH° value indicated the process is predominantly physical. The SEM photos and FTIR spectra confirmed the absorption of CV onto NITRS. The use of spent material from nutraceutical industries opens a new route to cleaner, cheaper and efficient technology based on a new class of adsorbents.

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