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Purification Of Water From Contaminated Dyes Through Adsorption By Agricultural Residues.

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ABSTRACT

The wastewater from industries especially those are associated with dyeing process (textile, leather, paper and biological stain etc.) is a serious threat to environment. The colored water contains residual dyes compounds which are highly toxic to human and aquatic environment. Brilliant Green (BG) is a triphenylmethane group of dye having carcinogenic and mutagenic properties that affect human beings and aquatic biota. There are number of technologies available for treatment of dye contaminated wastewater such as biological treatment, however these are not much efficient due to high cost and long duration requirement. In the present study, Batch orange modified plant peel (OPP) were used for removal of dye from synthetic wastewater .Studies of adsorption of payments were performed as a function at contact time, temperature, pH solution and BG concentration. The results showed the efficient removal of BG dye through adsorption on the Orange peel. The highest adsorption capacity (191 mg/g) was achieved temperature 20 ^{o}C and pH 3.0 with in duration of 4 hours. The adsorption capacity of Orange plant peel is efficient even at high BG dye concentration (500 mg/l) in water. Overall, these results demonstrated that the dye wastewater can be treated efficiently by using wasted Orange plant peel, making the process highly economical with subsequent management of agro based residues.

Keywords: Wastewater, agriculture waste, adsorption, dyes.

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INTRODUCTION

In the current scenario, the extensive increase in industrial activities consequences in generation of number of highly toxic pollutants [1]. Dye containing wastewater stream is one of the major source of toxic industrial waste. There are number of types of dyes which are used in the industrial processes such as printing of textile, paper, paints and carpet etc. The effluents containing dyes released after the printing are highly colored and may cause swear water contamination [2]. Among various groups of dyes, Brilliant green is a triphenylmethane class of dye which is extensively used in textile dyeing, biological stain, paper printing, veterinary medicine, dermatological agent, additive in poultry feed etc. [3,4]. BG have adverse effect to the humans and environment such as irritation to the gastrointestinal tract and respiratory tract, symptoms include nausea, vomiting and diarrhea while on degradation BG produces toxic gaseous like carbon oxides, nitrogen oxides, and sulfur oxides [2, 3].

In the above context there is need to develop of some advanced method of treatment for scavenging BG dye from wastewater in order to avoid its adverse impact on environment. Number of techniques have been developed such as biodegradation, coagulation, flocculation, chemical oxidation, adsorption, ozone treatment, photocatalysis, membrane filtration, and photocatalysis which have been applied for the treatment of dye contaminated wastewater [5, 6]. Among all of aforementioned methods of treatment, adsorption is an emerging and technology for decolarization of dye contaminated wastewater, as it provides high efficiency, economical, ease of operation and simplicity of design [7]. One of the major advantages of the adsorption technique is use of low cost materials such as agriculture based byproduct as adsorbent. In literature fruit shells and fruit peels adsorbent for example: jack fruit peel, pine-fruit-shell, banana peel, rambutan peel, and coconut shell have been studied for their potential to use as adsorbent for removal of dyes [4].

The orange fruit is an important agricultural product,which is cultivated in many countries and used in food and pharmacological sciences [8-10].

Orange is used in many ways either for its fruit and vegetative parts of plant. Mostly, it cultivated for its large sweet fruits which has been commercialized worldwide]. The fruit is used as a fresh vegetables, cooked, canned, added to casseroles, used in salads, alcohols, syrups, juices [11]. Moreover, it has high medicinal value as anti-viral effect, anticancer and anti-diabetic effect etc. The orange crop residues after harvesting is of no use and considered as solid waste which have no economic value. These crop residues such as peels of oranges plant can be used as an alternative low cost adsorbent which can further assist in reducing the cost of waste disposal and lowering wastewater contamination.

In the present study, Orange plant peel were uses as an adsorbent for its potential for removal of brilliant green dye from wastewater. The orange plant peel were collected and process through a series of process to convert in to final powdered product. The powdered material was analyze for its adsorption efficiency using brilliant green (BG) as model dye compound. Various factors such as pH, temperature, and time and pollutant concentration were optimized to achieve efficient decolarization of BG dye from wastewater.

MATERIALS AND METHOD

Materials

Brilliant Green dye [Chemical formula = $C_{27}H_{34}N_2O_4S$, FW = 482.62] was supplied by Koch Light laboratories Ltd. England. The structure of BG is described in figure 1. Other chemicals that were used are: Sodium hydroxide de (0.1 M NaOH) and sulphuric acid (0.1 M H_2SO_4), and sodium perchlorate ($NaClO_4$) All solutions were prepared in deionized water. For analysis of dye concentration UV-spectrophotometer was used. A list of materials and equipments used in the present study is given table 1.

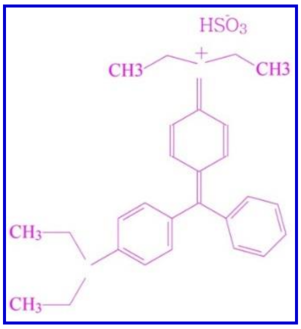

Figure 1: Structure of brilliant green dye

Table 1: List of materials and equipment's

Chemicals	Equipment's
Brilliant Green Dye	Magnetic Shaker
NaOH	UV-Vis Spectrophotometer
H_2SO_4	Scanning Electron microscope
$NaClO_4$	
Deionized water	

Preparation of adsorbent

Orange plant peel (OpP) was washed with de-ionized water and dried for five days in oven at 60 °C. This biomass was grind and sieved until we get the particle in range from 75-150µm.Then we were mixed 15 g of powdered peel with 100 mL of 1.0M H_2SO_4 . Thereafter stirred for 2h at 80 °C , then filtered and again washed with de-ionized water. In presence of H_2SO_4, soluble components of OpP dissolved in acidic solution and OpP surface get oxidized. Filtered material was further oxidized by adding 100 mL of 1.0M $NaClO_4$ for 18h at temperature of 80 °C. After 18h, treated powdered peel was filtered through filter paper and washed several times with de-ionized water. After washing, the material was again dried at 60 °C and stored for further adsorption studies.

Adsorption studies

Batch equilibrium adsorption studies were performed by placing 0.025 g of the adsorbent (OpP) in 10 mL of dye solutions. The effect of contact time on dye adsorption was performed in a series of conical flask containing 0.025 g of the OpP and 10 mL of BG and samples were collected at different time interval between 0 to 240 minutes. The sample taken after each interval of time was analyzed for measurement of concentration BG in the supernatant solution. For analysis of remaining dye concentration in the solution UV-Visible spectroscope was used.

Optimization of Factors (Temperature, pH, Dye concentration)

Using the aforementioned experimental conditions and adsorbent dose, various factors were optimized for efficient adsorption of brilliant green dye. The adsorption process was analyzed at three temperatures i.e. 20, 30 and 40 ^oC. The temperature was maintained by placing the conical flask containing dye solution and adsorbent in shaking water bath. Later on under the most suitable temperature (20 ^oC) the adsorption process was subjected to different pH ranges between 3.0 to 10. The pH of the solutions were maintained by using 0.1M NaOH and 0.1M HCl solutions. All the experiments were performed at dye concentrations of 200 mg/L and 500 mg/L.

Analysis

The concentration of brilliant green at various intervals was measured by using HACH LANGES DR-6000 UV-Visible spectrophotometer at maximum wavelength (624 nm). The samples were withdrawn and filter using syringe filters to separate the dye solution from adsorbent material. The filtered samples then analyzed for remaining dye concentration by measuring absorbance using spectrophotometer as mentioned above. The adsorption of dye was calculated by following equation:

$$\text{Adsorption (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

Where C_0 is the initial dye concentration and C_e is the dye concentration (mg/L) at equilibrium. The surface morphology was analyses by scanning electron microscope to see the change in surface characteristics before and after adsorption. The graphical representation of data is performed by using Microsft Excel 2013 version.

The flow chat diagrams and images were developed by using Microsoft Visio 2013 software.

RESULTS AND DISCUSSIONS

Effect of contact time of BG adsorption

The effect of time on adsorption of BG on OpP adsorbent is illustrated in figure 2. It was found that the adsorption of dye increase with the increase in the contact time and after 120 min, the adsorption of the dye becomes constant. This may be due to the saturation of vacant adsorbent sites which are responsible for adsorption of dyes. At high dye concentration of 500 mg/L, the maximum adsorption up to 151 mg/g was achieved after 240 minutes. On the other hand the lower dye concentration 200 mg/L showed a lower adsorption capacity (76.2 mg/g) after 240 minutes. The lower dye concentration showed low adsorption potential because of low availability of dyes ions and these ions only attached on the surface of the adsorbent where the internal sites remained vacant due to efficiency dyes ion in solution. When high dye concentration was used it provides more dye ions concentration in the solution which can be combined with all available sites on the adsorbent, thus showing high rate of adsorption at higher rates [12].

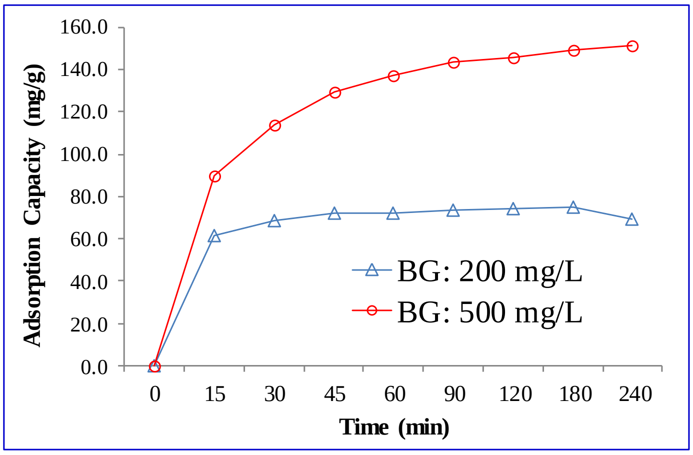

Figure 2: Effect of time on adsorption of Brilliant Green at dye concentrations of 200mg/L and 500 mg/L.

Effect of the temperature of dye adsorption

The adsorption capacity of BG was analyzed at temperature ranges between 20 to 40 °C and described in figure 3. The adsorption capacity of the BG decreases with the increase in the solution temperature, where higher concentration of BG showed high adsorption at all solution temperatures. This is because of more utilization of adsorption capacity of adsorbent material due to high driving forces by high concentration gradient pressure [13]. The maximum adsorption was observed at 20 °C for both solution concentrations. It was found that adsorption of 69.3 mg/g achieved at dye concentration of 200 mg/L. whereas the high dye concentration (500 mg/L) showed increased in dye removal efficacy that is up to 179.2 mg/g. This increase was due the more contact of dye molecules with adsorbent material at high concentration. On the other hand the high temperature decrease the dye removal efficiency even at high dye concentration, where 500 mg/L dye solution showed adsorption capacity of 120 mg/g. This kind of trend has also been reported in other studies where increase in temperature decrease the adsorption capacity of the various adsorbents such as neem leaf powder [14] and saw dust [3].

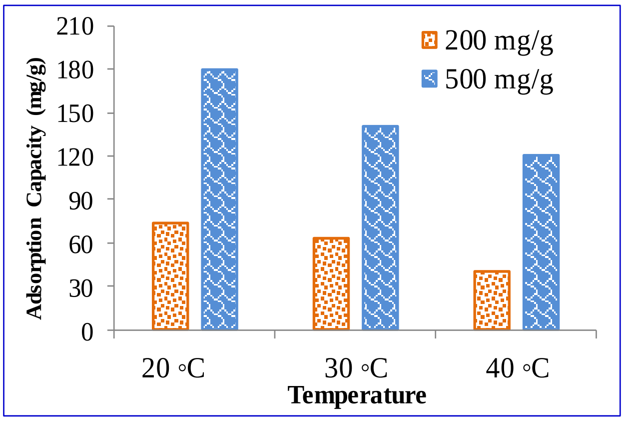

Figure 3: Effect of temperature on adsorption of Brilliant Green at dye concentrations of 200mg/L and 500 mg/L.

Effect of solution pH

The pH is very important factor that may affect the adsorption capacity of adsorbent. Because, variations in pH of the wastewater can cause changes in surface charge of adsorbent material and ionization rate of dye molecules [3].Figure 4 shows the adsorption pattern of BG onto OpP decreased with the increase in the solution pH. The maximum adsorption capacity was achieved at pH level 3.0 with 500 mg/L dye solution concentration, where 190 mg/g of dye removal was observed. On the other hand the low concentration dye solution (200 mg/L) also showed its maximum decolarization rate at pH 3.0. As pH increases in both solution the dye removal efficiency decreases. At pH 10.0 lowest dye removal efficiency was observed where adsorption capacity of 51.2 and 150.8 was achieved at dye solution concentrations of 200 mg/L and 500 mg/L respectively. Overall, in both BG solution concentrations, the decolorization rate was decreased from pH 3.0 to 6.0 and later on the decolarization rates remained constant up till pH 10. This phenomenon is due the structural changes in BG which affected its adsorption onto surface of adsorbent. Mane et al., [3] reported that the BG dye is remained stable up till pH 3.0, where further any change in pH either increase or decrease makes BG unstable and causing structural changes.

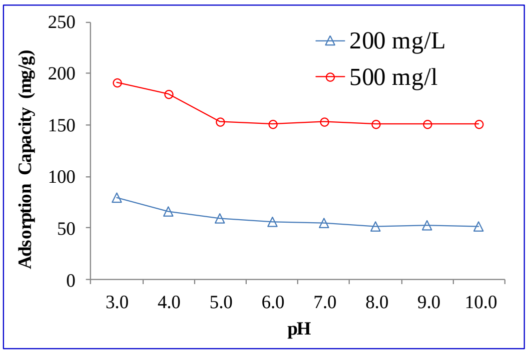

Figure 4: Effect of pH on adsorption of Brilliant Green at dye concentrations of 200mg/L and 500 mg/L.

Variation in surface Morphology of Adsorbent (OpP)

The image of the OpP from scanning electron microscope showing surface morphology before and after adsorption of BG dyes is illustrated in figure 5. The image (figure 5a) shows that the surface of OpP adsorbent is highly rough and having pores. These pores are highly suitable for adsorption of dyes and remove from wastewater. In figure 5b the image of adsorbent after adsorption of BG dye clearly shows that dyes particles are diffused into the pores of the OpP adsorbent and adherence of the adsorbent surface.

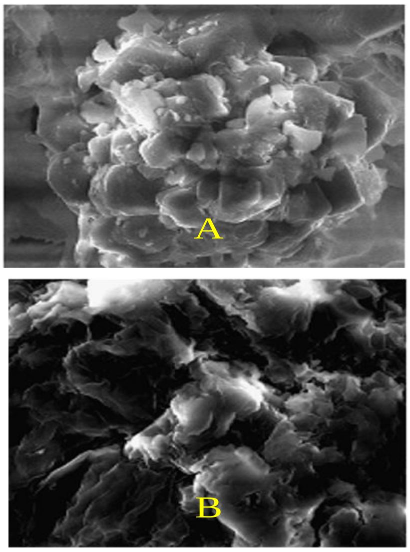

Figure 5: Surface morphology of OpP adsorbent (A) Adsorbent surface before dye adsorption (B) Adsorption surface after dye adsorption

Overall performance of the adsorption process

The performance of the adsorption of BG on OpPadsrobent at 200mg/L BG concentration is summarized in table 2. It shows that the optimum time for decolonization of dye was 240 minutes where 38% of adsorption efficiency was achieved. Furthermore, it was further optimized for temperature and pH. At lower operating temperature (20 ^{o}C) and acidic pH the adsorption efficiency was maximum that is up to 39.7%.

Table 2: Overall performance of dye removal through Orange plant peel at dye (BG) concentration of 200 mg/L: Maximum and minimum adsorption capacity.

	Effect of Operating factors					
	Time (min)		Temperature		pH	
	15 min	240 min	20 ^{o}C	40 ^{o}C	3.0	10
Adsorption Capacity (mg/g)	61.3	69.2	73.3	40.2	79.4	51.2
Adsorption efficiency (%)	30.6	34.6	36.6	20.1	39.7	25.6

On the other hand the adsorption efficiency was also very effective even at high BG solution concentration (500 mg/L) (Table 3). After 240 minutes of adsorption process adsorption efficiency was 30.2 %. Similar to that in BG concentration 200 mg/L, the higher concentration (500 mg/L) also showed the maximum adsorption performance at 20 ^{o}C temperature and pH 3.0, where 38.2% of dye removal was achieved. The major limitation of the current study is requirement of low pH for efficient adsorption process, thus an additional process of water stabilization may be required. Similarly, the high temperature conditions also decrease the process, thus for efficient removal of dyes from wastewater mild climatic conditions are highly favorable.

Table 3: Overall performance of dye removal through Orange plant peel at dye (BG) concentration of 500 mg/L: Maximum and minimum adsorption capacity.

	Effect of Operating factors					
	Time (min)		Temperature		pH	
	15 min	240 min	20 ^{o}C	40 ^{o}C	3.0	10
Adsorption Capacity (mg/g)	90.1	151.3	179.2	120	191	150.8
Adsorption efficiency (%)	18.0	30.26	35.8	24.1	38.2	30.2

Optimum condition such as temperature and pH play a crucial role in adsorption process [15]. The pH affects the surface charge and degree of ionization of the contaminant molecule (adsorbate) [16] while temperature effects the penetration of dyes in the adsorbent pores and creation of new active sites [17]. Overall these results showed that BG can efficiently be removed by using OpP even at high BG concentration (500 mg/L) at operating conditions as: time = 240 min, Temperature = 20 ^oC and pH = 3.0.

CONCLUSION

The present studies showed that the wasted agriculture waste Orange such as plant peels as adsorbent material has high potential for removal of toxic dyes from wastewater. The adsorbent material achieved efficient removal of dye even at high concentration of dyes. The operating conditions such as duration, temperature and pH played very important role in adsorption process. The dye removal was increased with the increase in initial concentration of dye and decreased as solution temperature increases; where maximum adsorption was found at 20 ^oC and pH 3.0.

In general, it can be concluded that the agriculture residues are highly suitable for application in wastewater treatment process due its dual benefits i.e. treatment of dye contaminated wastewater and management of agriculture wastes.

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