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Journal of Advanced Scientific Research

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ISSN
0976-9595
Research Article

GREEN SYNTHESIS OF CHARCOLATED ADSORBENT DERIVED FROM *PUNICA GRANTANUM* STEMS AND ITS APPLICATION IN DYE REMOVAL OF METHYL ORANGE, CHROMOSEINT BLUE, ERIOCHROME BLACK -T AND MALACHITE GREEN

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Received: 07-11-2023; Accepted: 08-12-2023; Published: 31-12-2023

 https://doi.org/10.55218/JASR.2023141103

ABSTRACT

The existence of dye molecules prolonged in water effluents of special concern is removed through green synthesized *Punica Grantanum* stem adsorbent (PGSA) embedded in removal of dye as methyl orange, Chromoseint blue, Eriochrome black-T, malachite green. Charcolated adsorbent was subjected to characterization as, SEM, TEM and FTIR. PGSA was employed in parametric study of effect of pH, effect of adsorbent dose on dye removal, effect of adsorbent on concentration of dye and effect of temperature on dye removal. Maximum removal of dye was observed at basic pH 8, as adsorbent dose of 0.5g give maximum removal of dye molecules. Maximum dye concentration of 1×10^{-5}M show best result for dye removal and 30°C temperature was effective for various dyes giving removal efficiency. Experimental work was conducted on UV-Visible spectrophotometer with time gradient of 15 minutes time interval up to 180 minutes. So, this study revels use of charcolated adsorbent of Punica Grantanum stem is effective for dye removal purpose.

Keywords: Charcolated adsorbent, Dye removal, Adsorption, Characterization, Stem.

1. INTRODUCTION

Utilization of heavy metals, dyes and coloring pigmentation is increased due to heavy rise of industrialization and urbanization, which is one of the various serious issues in front of ecosystem [1]. Environmental pollution is of serious concern mainly affecting the water reservoirs of drinking and irrigated systems [2]. Toxic hazardous organic and inorganic matter facilized from dyes and heavy metals is distributed from effluents routes of chemical industries, refineries, dying industries, coloring industries, milling and ginning industries in water resources and definitely polluting the water resources, which is further used for irrigation purposes leading to accumulation of toxic matters in plants and animals, as causes hardly affects kidneys, bones, brain, central nervous system, liver etc [3, 4]. Major pollutant of water resources are dyes which are largely employed in sectors of cloth fabrication, so it is needfull to treat toxic waters before relieving it in fresh water streams [5].

Numerous techniques are available and prescribing treatment of wastewaters from several years as, membrane filtration, precipitation, physical and chemical methodology, neutralization, ion-exchange, electro-chemical filtration, adsorption, floating, ultrafiltration, reverse osmosis, coagulation, Nano filtration, electro dialysis etc; are of interest, but these all techniques require costly instrument and cost feeding process [6-9]. Numbers of green methods are available for adsorption of heavy metals and dyes, including husks of coconut, millet, olive, rice [10, 11]. Shell of almond, dende, hazelnut, peanut, walnut, along with barley straw, wheat straw, rice straw, rey straw, some stems and woods of birch, oak, softwood, albizza wood, pine wood, leaves of premna, syzygium, peterospermun are induced in adsorption of dye [12-18].

Methyl orange, chromoseint blue, eriochrome black-T and malachite green dyes are largely utilized in food industries, plastics, paper, cosmetics, rubber, and pharmaceutical industries, as discharge of effluents from

such sources contain dye residues [19-23]. Improper treated coloured wastewater discharged causes serious problems of (COD) chemical oxygen demand and increased toxicity [24-26]. It is noted that there are 10,000 various dyes and pigments exist, as production of these dyes is about 7×10^5tonnes [27]. During the dying process about 10-15% of dyes are effulated. Colored effulents is rated with problems as, low light penetration, low photosynthesis, damaging of aesthetic nature of water surfaces [28-32].

This study is related with preparation of adsorbent in green manner from *Punica Grantanum* stems and revealed it in dye removal application with various parameters of pH, adsorbent dose, dye concentration and temperature study [33-36]. It is estimated that *Punica Grantanum* stem adsorbent fits best for removal efficiency of dyes [37-40].

2. MATERIAL AND METHOD

2.1. Preparation of *Punica Grantanum* stem adsorbent

Stems of *Punica Grantanum* plant was obtained from fields of pomegranate, as the stems were cleaned with water and dried in bright sunlight for four days [41]. After dying of stem material, stems were powdered with help of grinder into fine particles and subjected to oven at temperature of 120°C for three days [42-44]. After completion of drying, color of powdered stem material changes from pale brown to dark brown color [45]. Fine stem material further was meshed with cotton cloth to obtain more fine particles and subjected to muffle furnace at 200°C for 24 hours to obtain charcoaled adsorbent stem material and subjected to analytical characterization as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR).

2.1.1. Physiochemical parameters

Physiochemical properties were determined as, iodine number, moisture content, total ash content, decolorizing power, bulk density, acid soluble matter, pH value and water soluble matter [46, 47].

Table 1: PGSA parameters

Physicochemical parameters	PGSA
Iodine number	1009.0 mg/g
Decolorizing power	26.7 mg/g
Bulk density	0.748 g/cc
Moisture content	11.2 %
Total ash content	2.98 %
Acid soluble matter	9.88 %
Water soluble matter	5.18 %
pH value	6.80

3. CHARACTERIZATION

Punica Grantanum stem adsorbent was subjected to scanning electron microscopy (SEM) resulted for granular shape of adsorbent particles, as agglomerated nature is observed. Morphology of particles shows minimum size of 15 to 38 nm with porous form shown in fig. 1. Transmission electron microscopy result for ball shape morphology of adsorbent particles with minimum size of 18 to 30 nm shown in fig.2. Adsorbent of nanosize with pores on surface has ability of adsorption of heavy metals and removal of dyes [48-52]. FTIR data show presence of various phytoconstituents on surface of adsorbent, as interfering in adsorption process shown in fig. 3.

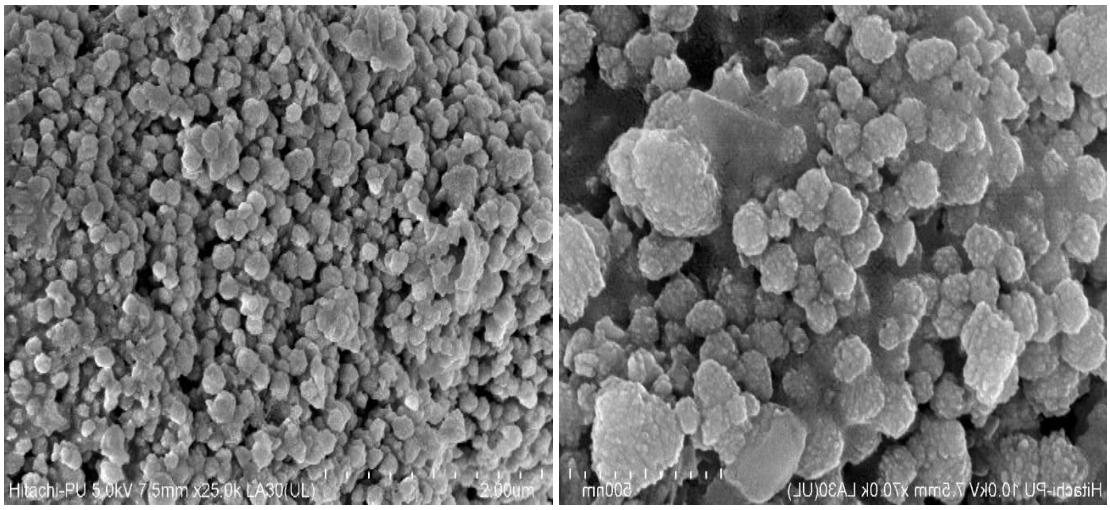

Fig. 1: SEM image of PGSA

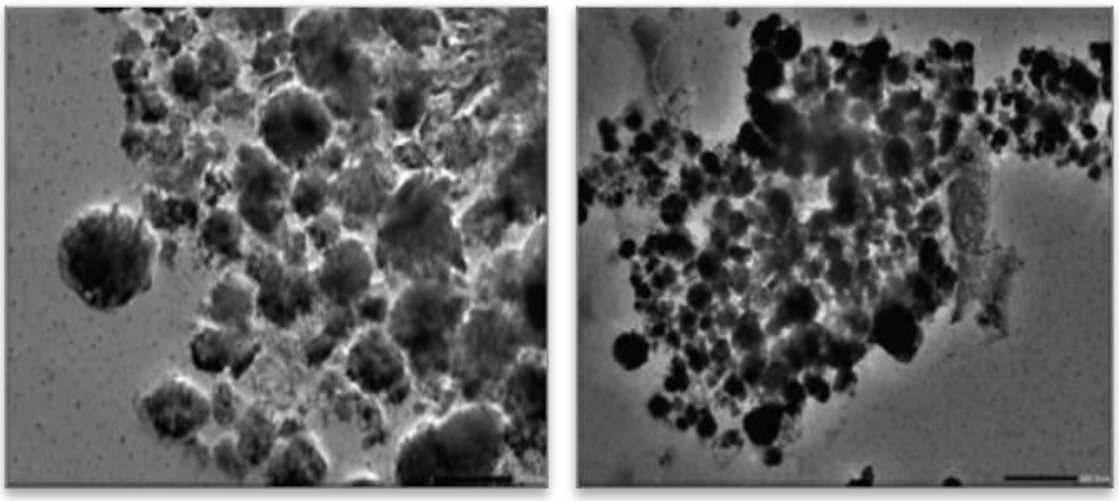

Fig. 2: TEM image of PGSA

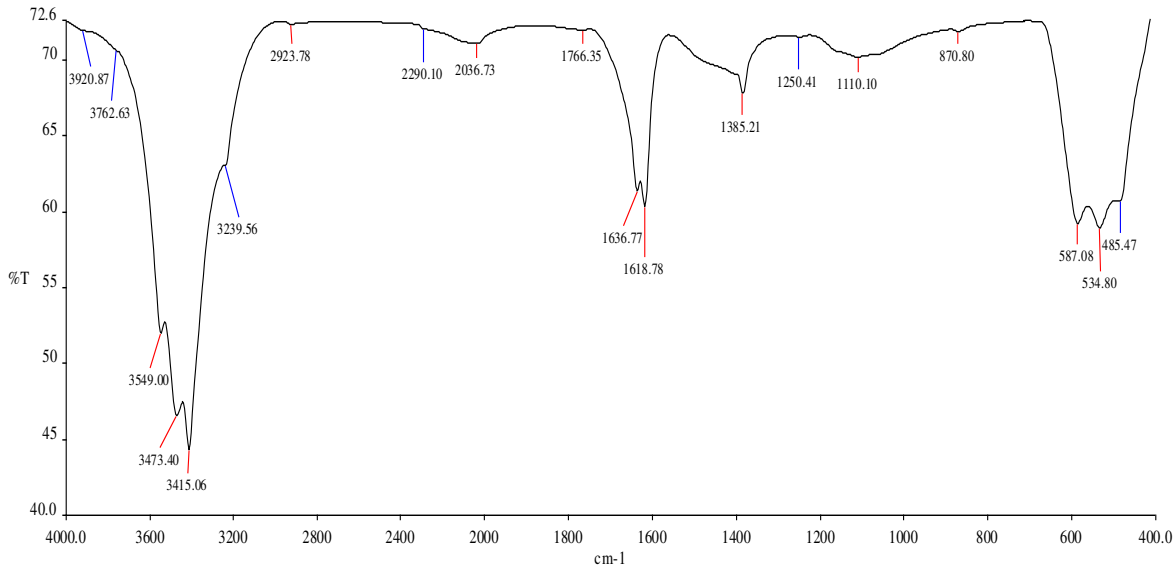

Fig. 3: FTIR image of PGSA

3.1. Batch experiment

Removal of dyes study was carried by PGSA on methyl orange, Chromoseint blue, Eriochrome black-T and malachite green dye under parameters as, effect of pH on dye removal, effect of PGSA dose on dye removal, effect of PGSA on concentration of dyes and effect of temperature on removal of dye [53]. All solutions are prepared in aqueous medium [54]. Experiment was carried out in sunlight for maximum removal of dye by PGSA, as experiment was carried out for 180 minutes and aliquots of sample was verified at every 15 minutes of time interval with 300 rpm agitation towards spectrophotometer.

3.2. Effect of pH

pH experiment was carried out with constant PGSA dose of 0.5g and dye solution of 0.1mg/l. Experimental solutions was prepared in distilled water, as pH was maintained by addition of HCl and NaOH. Flasks of various pH ranging from pH 2, 4, 6, 8, 10 and 12 were prepared with addition of PGSA, properly stirred on magnetic stirrer for homogeneity of solution [55, 56]. At every 15 min of time interval 2ml aliquots is extracted from flask, agitated at 300 rpm and subjected to spectrophotometer, as this experiment is carried out up to 180 minutes and same procedure repeated for every 15 minutes. Methyl orange dye is removed with

maximum efficacy of 84.32% at pH 8 by PGSA. Chromoseint blue dye is reduced with 76.16% at pH 8, Eriochrome black -T dye is removed with 85.36% at pH 10 and malachite green dye removed with 82.92% at pH 10. Dye removal is tabulated in table 2.

3.3. Effect of PGSA adsorbent on dye removal

Various PGSA doses of 0.5g, 1g, 1.5g and 2g was practiced for dye removal of methyl orange, Chromoseint blue, Eriochrome black-T and malachite green dye. Dye solution of 0.1mg/l of pH 8 is prepared of every dye, as adsorbent dose varies from 0.5g to 2g. Maximum dye removal was observed at 0.5g adsorbent dose and as the adsorbent dose increases up to 2g dye removal efficiency decreases because surface area of adsorbent decreases for removal of dye molecules [57]. Methyl orange shows maximum removal of 83.11% with 0.5g adsorbent dose, same result as, 83.02% removal of Eriochrome black-T and 82.96% removal for malachite green dye with 0.5g PGSA was observed. Chromoseint blue dye result for maximum removal of 82.22% with 1g adsorbent dose. Result are tabulated in table 3.

3.4. Effect of PGSA on concentration of dye

Dye removal experiment was carried out at different dye concentration of 1×10^{-5}M, 2×10^{-5}M, 3×10^{-5}M, 4×10^{-5}M, 5×10^{-5}M, 6×10^{-5}M, 7×10^{-5}M and 8×10^{-5}M with constant PGSA of 0.5g. Solution of each dye was prepared per liter and experimented with PGSA of 0.5g and pH 8 [58]. Aliquots from dye solution was extracted for every 15 minutes of time interval till 180 minutes, as results were detected on spectrophotometer. Maximum removal of dye is obtained at dye concentration of 1×10^{-5}M, as dye concentration increases dye removal decreases because dye molecules increases and lower adsorption sites are available for adsorbent. Methyl orange dye shows maximum dye removal of 84.46%, Eriochrome black-T dye shows 74.62%, Chromoseint blue dye show 83.02% and malachite green dye result for 82.96% dye removal.Result of dye removal are tabulated in table 4.

3.5. Effect of temperature on dye removal

Temperature effect experiment was studied at temperature of 10°C, 20°C, 30°C and 40°C as temperature was maintained accordingly. Dye solutions of 0.100mg/l with constant adsorbent dose of 0.5g at pH 8 was maintained. Aliquots were removed at every 10 minute time interval up to 100 minutes [59]. Maximum dye removal was observed at 30℃ which is very close to room temperature. Methyl orange dye result for 70.53%, Chromoseint blue dye for 67.12%, Eriochrome black -T dye for 65.73% and malachite green dye for 61.60%. As rise in temperature is observed above 30°C, dye removal efficiency decreases and it is observed that rise in temperature from 40°C to 70°C dye removal rate decreases, so highest dye removal was observed at 30°C.Result are tabulated in table 5.

Table 2: Effect of pH on removal of dyes

pH	% removal of dyes			
	Methyl orange	Chromoseint blue	Eriochrome Black-T	Malachite green
2	79.43±0.18	69.85±0.23	77.60±0.74	82.12±0.56
4	81.07±0.12	71.68±0.2	79.44±0.3	83.15±0.14
6	81.39±0.02	73.18±0.52	80.81±0.23	84.11±0.15
8	84.32±0.41	76.16±0.20	82.71±0.02	82.90±0.07
10	83.47±0.25	75.60±0.31	85.36±0.29	82.92±0.25
12	81.46±0.21	71.58±0.20	83.74±0.41	82.28±0.07

Table 3: Effect of PGSA adsorbent on dye removal

Adsorbent dose	% removal of dyes			
	Methyl orange	Chromoseint blue	Eriochrome Black-T	Malachite green
0.5g	83.11±0.32	73.43±0.08	83.02±0.23	82.96±0.12
1g	81.70±0.25	82.22±0.04	81.25±0.21	82.46±0.03
1.5g	77.14±0.02	67.40±0.08	78.55±0.02	82.23±0.54
2g	73.31±0.09	64.45±0.07	69.54±0.05	81.13±0.45

Table 4: Effect of adsorbent on concentration of dye

Conc. of dye	% removal of dyes			
	Methyl orange	Chromoseint blue	Eriochrome Black-T	Malachite green
1×10^{-5}	84.46±0.12	83.02±0.12	74.62±0.07	82.96±0.04
2×10^{-5}	83.75±0.04	73.82±0.07	73.52±0.02	82.46±0.02
3×10^{-5}	82.59±0.23	70.80±0.50	77.57±0.02	82.23±0.03
4×10^{-5}	81.81±0.18	70.54±0.69	76.85±0.08	81.13±0.07
5×10^{-5}	80.73±0.04	71.12±0.86	68.10±0.16	80.14±0.02
6×10^{-5}	79.66±0.17	69.35±0.25	60.92±0.19	75.07±0.18
7×10^{-5}	78.93±0.29	68.58±0.01	56.72±0.24	74.84±0.23
8×10^{-5}	78.07±0.24	69.33±0.12	54.29±0.13	73.70±0.02

Table 5: Effect of temperature

Temperature(°C)	% removal of dyes			
	Methyl orange	Chromoseint blue	Eriochrome Black-T	Malachite green
10	67.68±0.06	65.88±0.12	61.06±0.03	58.80±0.18
20	68.24±0.09	65.31±0.19	62.30±0.07	60.09±0.60
30	70.53±0.13	67.12±0.16	65.73±0.46	61.60±0.08
40	69.72±0.08	66.80±0.02	65.36±0.23	61.40±0.17

Expressed as mean ± standard deviations

4. CONCLUSION

Activated charcoal adsorbent produced from *Punica Grantanum* stem adsorbent (PGSA), as a very low cost synthesis and embedded in dye removal study of methyl orange, Chromoseint blue, Eriochrome black -T and malachite green dye with various parameters as, pH study, Adsorbent dose, Concentration of dye and Effect of temperature were studied. Characterization study of charcolated adsorbent included SEM, TEM for morphology and survey of porous nature of particles and FTIR reveled presence of phytoconstuients stretching.

Conflict of interest

Authors readily declare that this research does not contain any conflict of interest and is not associated with any one, as there is no financial assistance for the research there is low data availability for characterization and research is self-funded.

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