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Preparation and characterization of Groundnut shell activated carbon as an efficient adsorbent for the removal of Methylene blue dye from aqueous solution with microbiostatic activity

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Abstract

This study describes about the preparation of low-cost and eco-friendly groundnut shell activated carbon (GSAC) by combined physical- and chemical-activation in a laboratory-scale facility. The fluorescent emission scanning electron microscope analysis exhibited well-defined pore formation and the energy dispersive X-ray analysis showed elemental composition of GSAC which is essential for the strong adsorption of the dye molecule. This study significantly emphasizes that GSAC would be the effective adsorbent to remove Methylene blue dye from aqueous solution that accompanied with significant microbiostatic activity. Utilization of groundnut shells serves dual purpose of simultaneous waste eradication, as well as cost-effective pollution treatment process.

1. Introduction

Wastewater from textile and dye-stuff industries causing water pollution, the one is a major issue in global concern. The colouring agents in these waste waters are toxic and carcinogenic, which are not only affect plants and organisms living in the water bodies, but also cause malfunctioning of human health [1]. Methylene blue is a commonly used cationic dye for colouring, this can also cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting and diarrhea [2].
Activated carbon (AC) mediated adsorption is the best amongst various dye removal processes; it just because of its simplicity, cost-cut and reusability of non-toxic adsorbent. Although, it has several drawbacks with regeneration hamper in large scale application [3]. Therefore, there is a growing need for finding a low-cost, renewable and easily available material from the surrounding areas, also for large economic-scale production to dye removal processes. In this case, agricultural wastes are an excellent option in the purification of contaminant from liquid and gas streams that evolve from industrial and domestic sources [4].
Thus our objectives in this study are: (1) to produce groundnut shell activated carbon (GSAC); and (2) to evaluate their methylene blue dye removal efficiency via column method along with investigation of their microbiostatic activity.

2. Experimental details

2.1. Preparation and characterization of GSAC
Groundnut shells were cut into small pieces and dried in sunlight until complete evaporation of moisture. The dried shells were physically activated at 400°C for 2 h in Muffle furnace and then impregnated with $ZnCl_2$ in the ratio 1:1 at 400°C for 2 h. After cooling, the excess $ZnCl_2$ were leached out by immersing it in 1M HCl solution for about 24 h. It was then repeatedly washed with hot distilled water, oven-dried at 80°C for 6 h and stored in air-tight plastic containers. Basic characteristics of GSAC (e.g., pH, yield, pore size, porosity, moisture content

and Brunauer-Emmett-Teller (BET) theory of surface area) were analyzed [5]. The surface morphology and element composition of the sample were analyzed using fluorescent emission scanning electron microscope (FESEM) 6701F with the energy of 15.0 V couple with energy dispersive X-ray (EDX) analyzer. Fourier Transform Infrared Analysis (FTIR) spectra of the carbon were recorded between 400 cm^{-1} and 4000 cm^{-1} using a the Thermo Nicolet, Avatar 370 spectrometer (Thermo Nicolet Inc., USA) to analyze the functional groups of the activated carbon.

2.2. Preparation of synthetic solution

Methylene blue (Practical grade) was purchased from Hi Media Laboratories Limited; Mumbai. A stock solution of 1.0 g/L was prepared by dissolving the appropriate amount of Methylene blue dye in 100 mL and made up to 1000 mL with distilled water. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH was adjusted with 0.1 M HCl or 0.1 M NaOH. All the adsorption experiments were carried out at room temperature (25±2°C).

2.3. Batch mode adsorption experiments for removal of dyes from aqueous solution

Batch mode experiments were carried out to investigate the factors influencing the rate and the extent of uptake of dye by the adsorbent such as Agitation time, Dosage and pH at a λmax of 670 nm (Methylene blue).
The adsorption percentage and capacity were calculated by:

$$\text{Percentage adsorption} = (C_i - C_t)/Ci \text{ x } 100\%$$
$$\text{Adsorption capacity, } q_m = (C_i - C_t)/W \text{ x } V$$

where: C_i = Initial dye concentration
C_t = Dye concentration at time t
W = Dry weight of adsorbent used
V = Volume of solution

2.3.1. Contact time and initial dye concentration study

Studies were carried out by shaking (model L-orbital) the adsorbent with 50 mL aqueous solution of dye at different concentrations, at their neutral pH and at room temperature in 250 mL conical flasks at 120 rpm. The preliminary kinetic studies have led to select the necessary data for fixing the concentration of dyes and dose of the adsorbent used for adsorption experiments.

2.3.2. Adsorption dose Studies

Effect of the adsorbent dose was studied by agitating 50 mL of different concentration of dye with different doses of adsorbent (250, 500, 750 & 1000 mg) for a time greater than their equilibrium time at their natural pH. Experimental conditions were selected to assess the effect of adsorbent dose.

2.3.3. pH Study

The effect of pH on the removal of dye was studied by using 50 mL of dye solution of desired concentration adjusted to a desired initial pH value mixed with known concentration of carbon and agitated for a time interval greater than equilibrium time. The pH of the dye solution was adjusted using dilute HCl or dilute NaOH. After agitation, the adsorbent and adsorbate were separated by centrifugation and supernatant was estimated spectrophotometrically at 670 nm for Methylene blue.

2.4. Column experiment for Removal of dyes from aqueous solution

Methylene blue dye was prepared at various concentrations (10, 25, 50 and 100 ppm) and passed through the column (7.9 × 1.2 cm) filled with 1000 mg of GSAC at the flow rate of 6 drops/min. Adsorption efficiency was calculated by UV-Vis spectroscopy analysis and compared with commercial AC (Hi Media Laboratories Limited, Mumbai, India).

2.5. Microbiostatic efficiency of GSAC

Four different bacterial cultures (such as, *E. coli*, *Salmonella* sp., *Serritia* sp and *Pseudomonas* sp.) and five different fungal cultures (such as, *Aspergillus* sp., *Fusarium* sp., *Basidiomycetes* sp., *Mucor* sp and *Penicillium* sp.) were used in this study. The bacterial cultures were inoculated in nutrient broth and fungi cultures were inoculated in potato dextrose broth. The same set-up was prepared with 100 mg of GSAC and commercial AC,

separately. The inoculated broth tubes were incubated at 37°C in room temperature. After 24 h incubation, optical density (o.d) of the broth was measured at 670 nm and recorded. The microbiostatic activity percentage was measured by the given formula:

$$\text{Microbiostatic activity (\%)} = \frac{\text{(Control O.D - Test O.D)}}{\text{Control O.D}} \times 100$$

3. Results and Discussion

Literature pertains due to the increasing demand of AC, there is a strong need for the sort of cost-cut, easy availability, highly efficient and eco-friendly precursors for the preparation of AC that should be cost-effective with commercially available AC [6]. On the contrary, ground nut shell has received much less attention as a precursor for the preparation of AC. So, this study was another attempt to explore groundnut shell as an inexpensive precursor for the preparation of AC.

3.1. Characterization of activated carbon

The yield and basic characterization of GSAC are as presented in Table 1. From the result it can be observed that the obtained yield (56.60%) of GSAC may be due to tar formation and liberation of volatile particles, and weight of the sample increased after chemical activation because of impregnated $ZnCl_2$ that used during chemical activation [7].

Table 1: Characterization of Groundnut shell AC

S. No.	Parameters	
	Characteristics	Results
1	Yield	56.60%
2	pH	5.7
3	Pore size	17.140Å
4	Porosity	73%
5	Moisture content	0.1 g/mL
6	BET Surface area	364.023 m^2/g
7	Langmuir Surface area	395.5394 m^2/g

The surface areas of BET and Langmuir were 364.0239 and 395.5394 m^2/g, respectively. It clearly shows that the obtained surface area and pore size are depending on the amount of introduced $ZnCl_2$ and activation temperature [8]. Similar results have been explained in various studies with different types of precursors along with $ZnCl_2$ activation [9,10]. It is an evident that movement of the volatile substances through pore passages was not hindered and were released from the carbon surface with the activation of $ZnCl_2$. The mechanism of pore formation in GSAC by $ZnCl_2$ activation is not widely known. However, Smisek and Cerney (1970) [11] have explained that $ZnCl_2$ mainly degrades cellulose by dehydration during pyrolysis which causes aromatization of the carbonaceous skeleton.

Well-developed porous surface of GSAC was observed via FESEM micrograph (2500×) which is considered as channels to the micro porous network (Figure. 1a). It showed that the adsorbent have rough texture with heterogeneous surface and a variety of randomly distributed pore size. EDX analysis of GSAC (Figure. 1b) showed the presence of four elements–carbons (88.62%), oxygen (15.30%), Zinc (0.72%) and Chloride (0.36%). Presence of oxygen may be attributed to the little amount of moisture in the carbon. Very low level of Zinc and Chloride were observed, because of the usage of $ZnCl_2$ as an impregnating chemical to activation of carbon.

The FTIR spectra in the range 400 to 4000 cm^{-1} of GSAC was presented in (Figure 2). This type of analysis used for identification of organic functional groups presented on the surface [12]. In the FTIR spectrum a significant peak at 1453 cm^{-1} is assigned to the characteristic CH_2 bending vibrations and is probably ascribable to carbonyl groups which are highly conjugated in the graphene layer. This is consistent with the basic nature of the carbon. Peak located at 1602 cm^{-1} are due to Conjugated C=C Sretching Vibrations. The peak located at 2923 cm^{-1} is due to CH_2 Stretching vibrations.
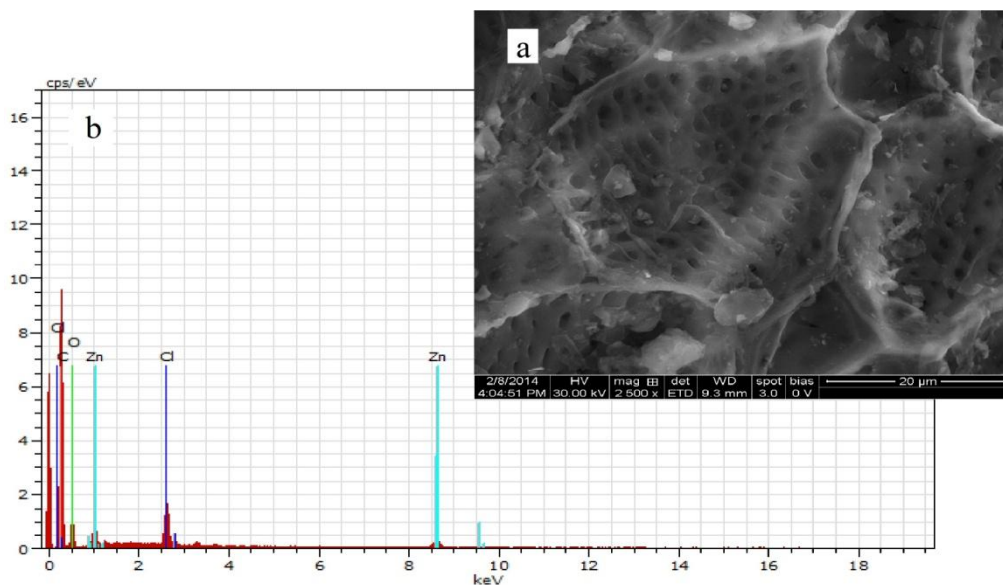
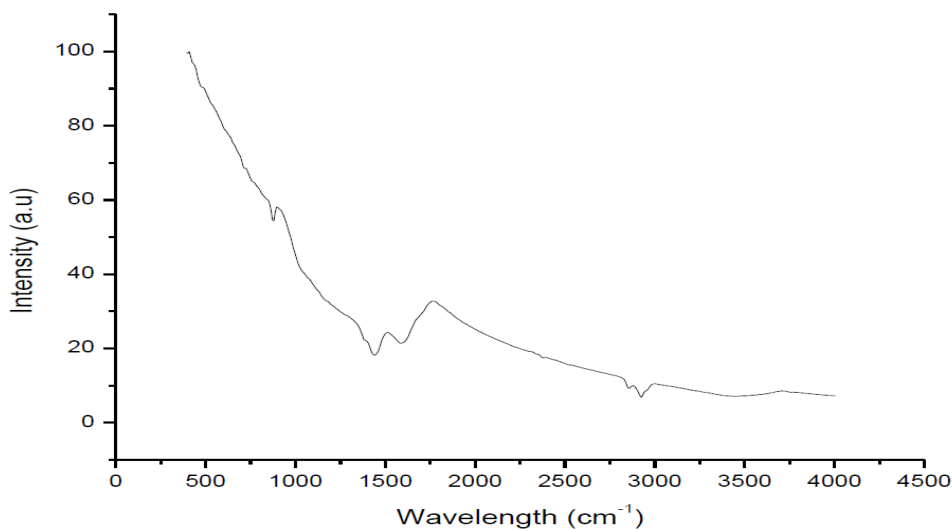**Figure 1**: Analysis of GSAC (a) FESEM and (b) EDX.

Figure 2: FTIR spectra of GSAC

3.2. Effect of contact time and initial dye concentration

Effect of contact time on adsorption of methylene blue on GSAC is presented in (Figure 3). Results indicated that rate of dye removal progressively increased as the agitation time increased. To increase the rate of colour removal with agitation time may be attributed to decrease in diffusion layer thickness surrounding the adsorbent particles. The equilibrium time increased with dye concentration and it was dependent on initial dye concentration for the range of concentration used for the study. The maximum equilibrium time of methylene blue by GSAC (500 mg) was recorded as 20 h. The removal curves (Figure 3) are single, smooth and continuous. Further, it revealed that with increase in dye concentration, percentage removal of dye decreased whereas the amount of the dye adsorbed / unit weight of the adsorbent (mg/g) increased in the range of concentration tested suggesting that, dye removal using adsorption technique is concentration dependent. Similar results have been reported by several authors for adsorption of dyes using low cost materials [13].

3.3. Removal Adsorption (Dose study)

Effect of adsorbent dose on adsorption of Methylene blue using GSAC was illustrated in Figure 4. Different doses of adsorbents ranging from 250 mg, 500 mg, 750 mg and 1000 mg for 50 mL dye were considered and other process parameters were maintained constant.
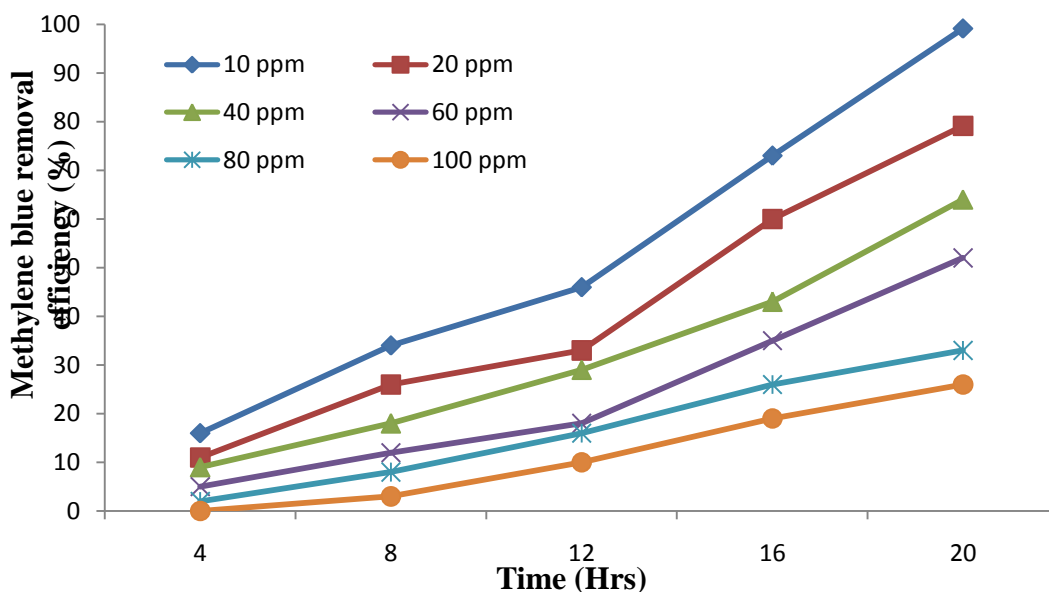
Figure 3: Effect of contact time and initial dye concentration in methylene blue adsorption by GSAC
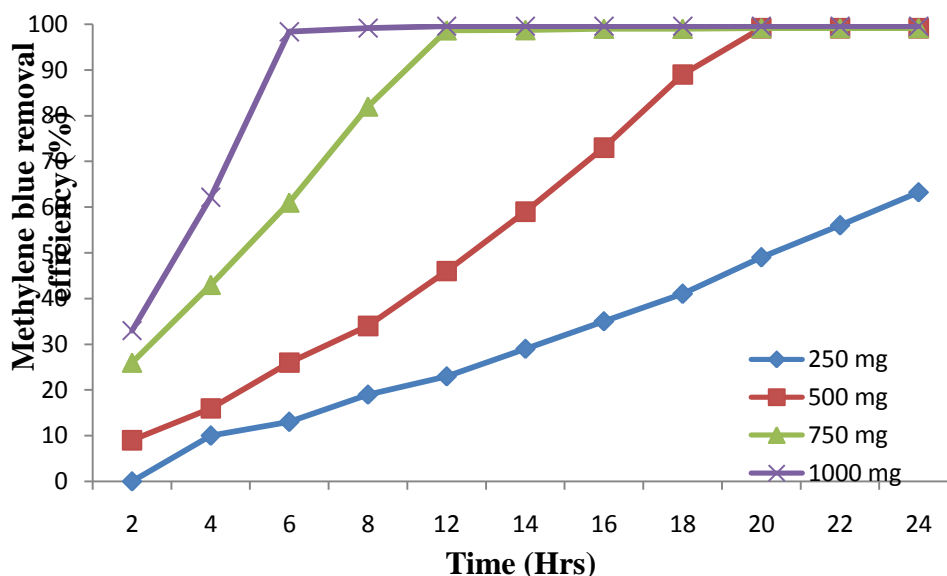

Figure 4: Effect of adsorbent ion in methylene blue adsorption by GSAC

The percent removal of dye increased with increase in adsorbent concentration and attained a plateau after a particular adsorbent concentration for the dye studied (Figure 4). Maximum quantitative removal of 99.62% was obtained at an adsorbent dose 1000 mg/50 mL at 6 h. In other GSAC dose also efficient removal more than 90 % was obtained at longer duration. Further it revealed that with increase in dose of absorbent, the percentage of dye removal has been increased. Similar result has been reported by several authors [14]. The low adsorption percentage can be ascribed to the fact that all the adsorbents have a limited number of active sites that would have achieved saturation above a certain adsorbate concentration.

3.4. Effect of pH on dye adsorption

The effect of pH on adsorption of methylene blue onto GSAC was investigated in different pH range of 3.0, 5.0, 7.0, 9.0 and 11.0 with fixed dye concentration (10 ppm) and fixed GSAC dose (500 mg/ 50 mL) at 6 h (Figure 5). The removal capacity of GSAC showed no discernible pattern over entire pH range. Maximum methylene blue uptake (99.45%) occurred at pH of 9.0 with a adsorption loading of 500 mg/50mL and lowest adsorption (71.12 %) occurred at an initial pH of 3.0. Similarly removal percentage was measured as 90.23%, 98.35% and 93.87% for pH level of 5.0, 7.0 and 11.0 respectively. The results obtained are in close agreement with previously reported studies [15,16].
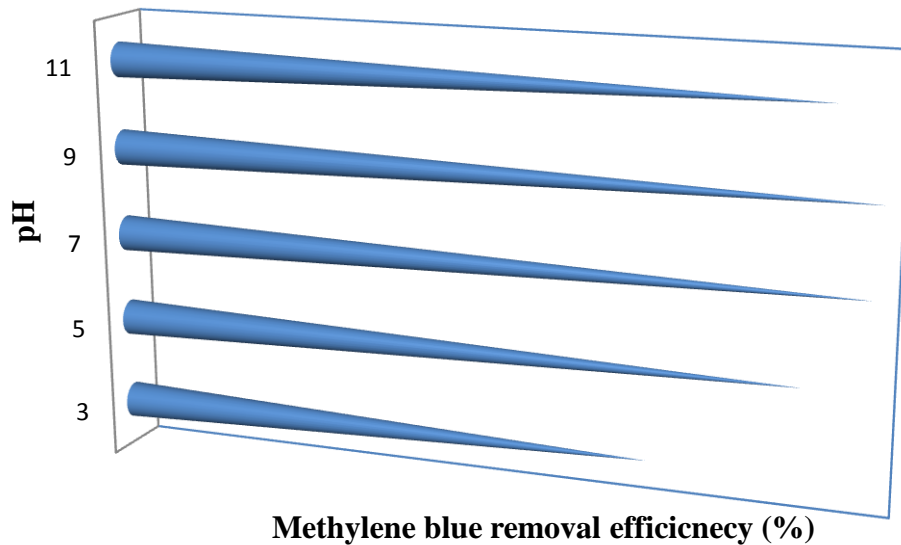
Figure 5: Effect of pH in methylene blue adsorption by GSAC

3.5. Column adsorption experiment

The colour adsorption property is an important quality of AC and is measured in terms of dye adsorption. Higher volume of dye adsorption indicates the better quality of the AC [17]. Highly appreciable adsorption efficiency (>99%) against all the concentrations of methylene blue used in this indicated the high affinity and better quality of GSAC which is similar to commercial AC (Figure 6).
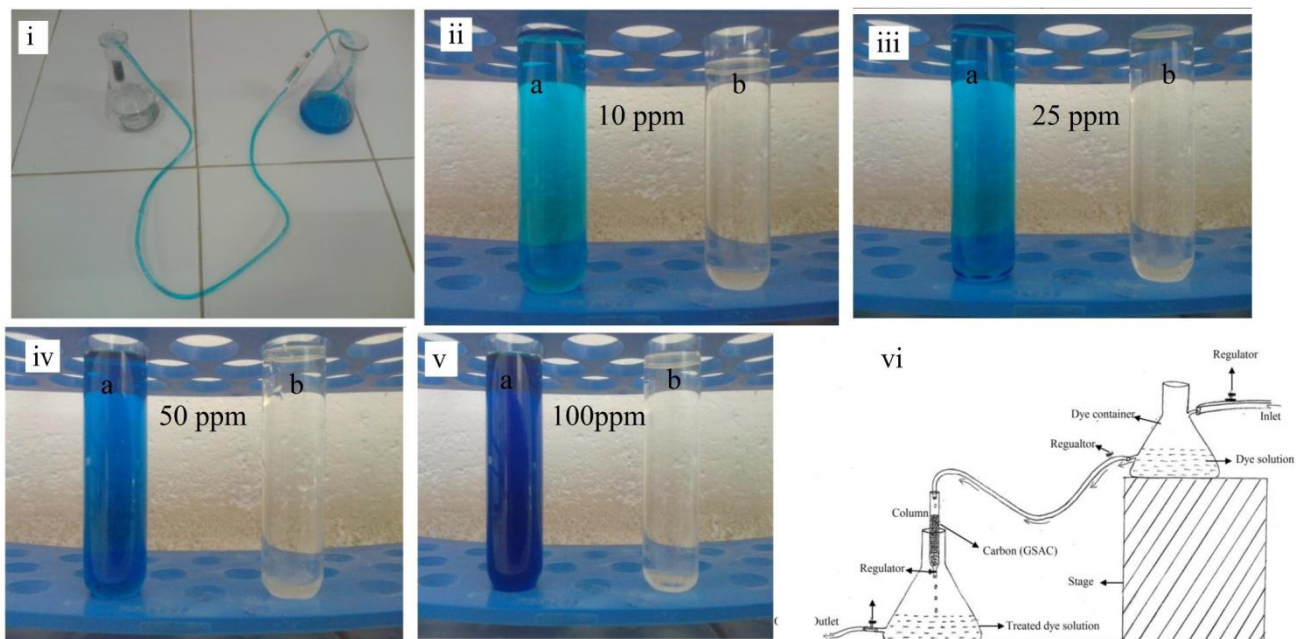

Figure 6: Column experiment for Methylene blue adsorption by GSAC.(i) Experiment setup, (ii–v) un treated (a), and trated dye soution (b), (vi) proposed column experiment model setup for dye removal.

3.6. Microbiostatic efficiency

Microbiostatic activity of GSAC was observed as 91, 80, 57, 48, 46, 45, 42, 37 and 35% against *Fusarium* sp., *Aspergillus* sp., *Serritia* sp., *Mucor* sp., *Penicillium* sp., *E.coli*, *Salmonella* sp., *Pseudomonas* sp and *Basidiomycetes* sp., respectively, which is significantly more active than commercial AC (Figure 7). GSAC may work as a resultant immobilized biomass and it could work as BAC. This may be similar to the mechanism of the biological regeneration proposed in the BAC process [18,19]. However, the precise mechanism involved in microbial inhibition is still unclear. Therefore, further studies are required to elucidate the mechanisms of inhibition.
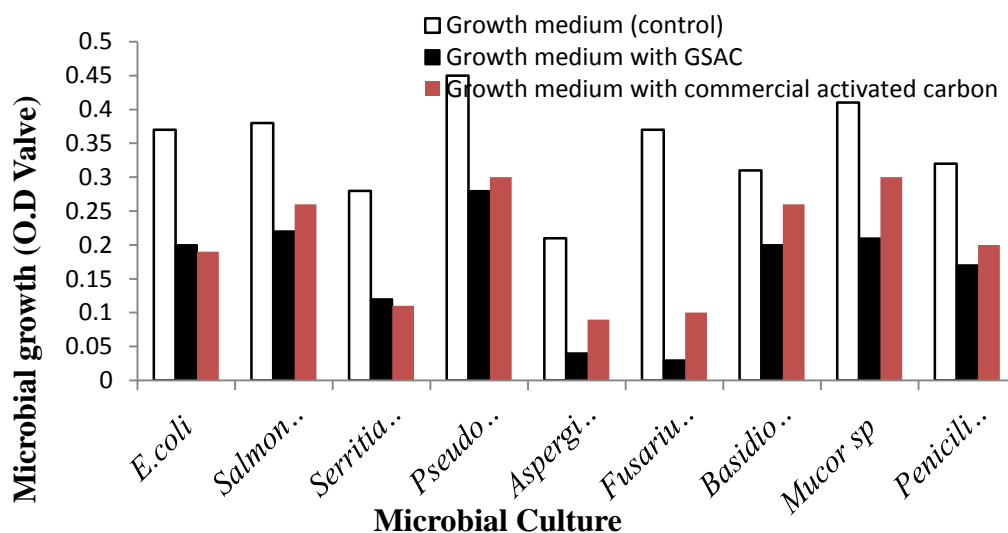
Figure 7: Microbiostatic actiivty of GSAC

Conclusions

This study reports a simple and efficient method for AC preparation using an easily available material, such as groundnut shell. GSAC was synthesized and characterized by different techniques including FESEM and EDX. GSAC showed high methylene blue adsorption efficiency on Batch and column mode; moderate microbiostatic activity against different microbial strains which is used in this study. Further studies are required to elucidate the precise mechanisms involved in dye adsorption and microbial inhibition before the GSAC are applied as an adsorbent for various water treatment processes.

References

1. Amin N.K., *J. Hazard. Mater.*, 165 (2009) 52–62.
2. Senthilkumaar S., Varadarajan P.R., Porkodi K., Subbhuraam C.V., *J. Colloid Interface Sci.* 284 (2005) 78–82.
3. Vijayakumar G., Tamilarasan R., Dharmendra Kumar M., *J. Mater. Environ. Sci.*, 3 (2012) 157–170.
4. Mutare E., Chigondo F., Nyamunda B.C., *Int. J. Res. Rev. Appl Sci.* 13 (2012) 486–494.
5. Rajeshwari S, Venckatesh R, Sangeetha G., *E-J Chem.* 7 (2010) 1314–1319.
6. Olusegun S,, Ugba E., *Int. J. Comput. Eng. Manage.*, 16 (2013) 21–26.
7. Asadullah M, Anisur Rahman M, Abdul Motin M, Borhanus Sultan M. *J Surf Sci Technol.* 23(2007) 73–80.
8. Molina-Sabio M, Rodriguez-Reinoso F. *Coll Surf A: Physicochem Eng Aspects*. 241 (2004) 15–25.
9. Khalili N.R., Campbell M., Sandi G., Golas J. *Carbon*, 38 (2000) 1905–1915.
10. Qian Q., Machida M., Tatsumoto H., *Biores. Technol*. 98 (2007) 353–360.
11. Cerney S., *Activated Carbon*. Elsevier, New York (1970) 10–48.
12. Namasivayam C., Kavitha I.R., *Microchem. J*. 82 (2006) 43–48.
13. Rajasekhar K.K., Shankarananth V., Srijany C., MarySonyPhilo L., Lavanya reddy V., Haribabu R., *J. Pharm. Res.* 2 (2009)1528-1529.
14. Rajasekhar K.K., Haribabu R., *Asian J. Chem.* 21(2009) 1531-1533.
15. Agarwal GS, Bhuptawat HK,Chaudhari S., *Biores. Technol.* 97 (2006) 949-956.
16. Barkat M., Nibou D., Chegrouche S, Mellah A., *Chem Eng Process: Process Intens*. 48 (2009) 38-47.
17. Kailappan R., Gothandapani L., Viswanathan R., *Biores Technol.* 75 (2000) 241–243.
18. Sirotkin A.S., Koshkina L.Yu, Ippolitov, K., *Water Res.* 35 (2001) 3265–3271.
19. Yamanaka H, Moriyoshi K., Ohmoto T., Ohe T., Sakai K., *J Biosci BioEng*. 105 (2008) 157–160.

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