Synthesis, Characterization and Statistical Optimization of Hydrophobic/Oleophilic Polystyrene Coated ZnO-Cotton Composite as Vegetable Oil Adsorbent

[1]Amtul Qayoom*, [1]Saeeda Nadir Ali, [2]Rafiq Ahmed, [1]Neha Kanwal and [3]Shazia Nisar
[1]*Department of Chemistry, NED University of Engineering and Technology, Karachi, Pakistan.*
[2]*Department of Polymer and Petrochemical Engineering, NED University of Engineering and Technology, Karachi, Pakistan.*
[3]*Department of Chemistry, University of Karachi, Pakistan*
amtulq@neduet.edu.pk*

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Summary: Cotton being easily available, low cost and highly porous natural material is excellent candidate as adsorbent base. However, its super hydrophilicity hinders its applications as oleophilic adsorbent. In the present study, pristine cotton was impregnated with ZnO and stearic acid to provide it with rough surface and hydrophobic properties followed by dip coating of polystyrene for further enhancement of its oil adsorption capacity. The surface morphology of polystyrene coated ZnO impregnated non-woven cotton (PS@ZnO-NWCotton) and polystyrene coated ZnO impregnated woven cotton (PS@ZnO-WCotton) showed increased surface area, roughness and pores as compared to pristine cotton. FTIR spectra confirmed conjugation of polystyrene and ZnO with cotton. Different thermal degradation behavior of pristine cotton and PS@ZnO-NWCotton further confirmed the presence of ZnO and polystyrene onto cotton. PS@ZnO-WCotton exhibited lotus-effect high hydrophobicity with a water contact angle of 145±2° and super oleophilicity with an oil contact angle of 0°. Oil adsorption capacities of synthesized composites were found to have an inverse relationship with viscosity of adsorbate oil which could be due to easy mobility of lighter oils. Oil adsorption capacity of PS@ZnO-NWCotton for coconut oil was maximized by optimizing temperature, duration and oil/water ratio using central composite design (CCD). Good agreement was found between predicted values obtained by the model and the experimental values (R^2 = 0.8904) for adsorption of coconut oil by PS@ZnO-NWCotton. Under the optimum conditions, the PS@ZnO-NWCotton adsorbed more than 12 times of its weight with acceptable reusability till third cycle.

Keyword: Hydrophobic, Oleophilic, Polystyrene, Cotton, Adsorption, Lotus effect, Central composite design.

Introduction

Cooking oil are plant, animal or synthetic fats used for frying, cooking and other culinary practices. Besides their use in cooking and frying, various processed food products such as salad dressing, mayonnaise, margarines and butter also contain vegetables oils. After few frying cycles, used cooking oil (UCO) from household and restaurants is discarded into the drainage without any prior disposal treatment [1]. Inappropriate discharge of UCO poses serious environmental concerns by clogging of channels and sewers. Oil layer on water acts as a barrier and detrimentally affects aquatic biota and increases biochemical and chemical oxygen demands by preventing oxygen from entering into water bodies [2]. In addition, seepage of discarded oil into soil through drainage interferes with the biological systems of the terrestrial flora and soil microbes [3]. Toxic oil degradation by-products in water and soil ultimately enter into human bodies through food chains and cause detrimental effects [4]. Therefore, it is important to appropriately treat kitchen and restaurant wastewater and separate waste oil before discharging it into the sewer system to protect the local environment.

Generally, physical, chemical and biological methods such as grease trap system [5], membrane separation [6], fractional freezing [7], gravity separation [8], biodegradation [9] etc. are used to separate used cooking oils, grease and fats from domestic effluents. Higher maintenance cost and space limitations in domestic kitchens and small restaurants hinder in adopting these techniques. Therefore a more compact and effective removal system of waste cooking oil needs to be developed. Adsorption of oil pollutants has several advantages over other oil separation techniques such as being low cost, fast, and simple and energy efficient. Another important aspect of adsorption methods is absence of any secondary pollutant. Several sorbent materials have been utilized for the removal of oily contaminants from the water such as activated carbon [10], sawdust [11], peat [12], hydrophobic aquatic plants [13], hydrophobic/oleophilic sponges [14], butyl rubber [15] and other carbon-based products; inorganic sorbents, such as organoclay [16], bentonite

*To whom all correspondence should be addressed.

[17]. Synthetic polymers such as polyurethane, polypyrrole, polysiloxane and polydimethylsiloxane have also been used for the oil absorption but poor environmental compatibility and low adsorption capacity of these polymers restricts their use [18].

Cotton is mainly comprised of cellulose, a most common, nontoxic, biodegradable and easily available biopolymer. Its low density, high surface area and loose internal structure make it a good candidate as adsorbent [19]. In addition, Van der Waals, intermolecular as well as intermolecular hydrogen bonds between -OH groups and oxygen on cellulose provide it aqueous insolubility and mechanical strength. However, the same hydroxyl and oxygen groups make cotton highly hydrophilic which is a disadvantage. One way of suppressing hydrophilic nature of cotton is altering its surface properties and its roughness by using different approaches e.g. spray coating [20], in situ crosslinking [21], triggered click reaction [22] etc. Polystyrene is a petroleum based polymer having super oleophilic and hydrophobic properties. As most of the polystyrene products are disposable, continuous rise in waste polystyrene is causing environmental pollution. Usually waste polystyrene is disposed of by incineration which generates harmful gases such as CO and CO_2. Other solution is landfilling. Therefore, it is desirable to find uses of waste polystyrene to overcome these issues.

In this study, we aimed to coat cotton surface with waste polystyrene for suppressing its hydrophobic nature. We assume that weaving of cotton fibers might affect its adsorption characteristics therefore two types of cotton surface were used i.e. 100% pure non-sterilized cotton balls to represent non-woven cotton fiber and woven cotton fabric. Cotton was also impregnated with *in Situ* ZnO for increasing surface roughness followed by polystyrene coating to suppress hydrophilic properties of cotton. Hence, polystyrene coated ZnO impregnated cotton composite adsorbent was developed for separation of oil from water before releasing it into the kitchen's plumbing system.

Experimental

Materials

Commercially available 100% pure cotton balls were used as pristine non-woven cotton (NWC) fibers and 100% pure cotton fabric (gsm: 204) was used as woven cotton (WC) fiber. Zinc acetate ($Zn(CH_3COO)_2.6H_2O$), stearic acid ($CH_3(CH_2)_{16}COOH$), methanol (CH_3OH), ethanol (C_2H_5OH) and tehtrahydrofuran (THF) ($(CH_2)_4O$) were of laboratory grade and supplied by Sigma-Aldrich, Germany. All the chemicals were used without any prior treatment and double distilled water was used throughout the studies. Olive oil ($Viscosity_{20°C}$=85 cP) and coconut oil (0 $Viscosity_{20°C}$ = 80 cP) were purchased from local market for the proposed study. Used disposable polystyrene cutlery was collected from student canteen in the vicinity of NED University of Engineering and Technology, Pakistan. Prior to use for the proposed study, the cutlery was cleaned with detergent and washed thoroughly with water. 1% polystyrene solution was prepared by dissolving cleaned polystyrene cutlery in THF.

Synthesis of polystyrene coated ZnO impregnated cotton composite adsorbent

Pristine non-woven cotton ball and woven cotton fabric were washed thoroughly with distilled water and dipped in methanol for 5 minutes to remove water resistant contaminants followed by drying for at 80°C. Pre-treated non-woven cotton ball and woven fabric were soaked in ethanolic solution of 0.1 M Zinc acetate (100 ml) for 1 hr, then 100 mL ethanolic solution of 0.1 M sodium hydroxide was added gradually with vigorous stirring. Drop by drop 0.05 M stearic acid 100 (100 mL) was introduced in the mixture and the system was kept on with continuous stirring for further half an hour. The cotton was treated with stearic acid because of its well-known role as nontoxic surface hydrophobic modification agent [10, 21]. Modified cotton balls and fabric were then dried under ambient conditions for 4 hrs followed by oven drying at 100° C for one hr. Finally, polystyrene coated ZnO impregnated cotton composite was synthesized by soaking the dried cotton balls and fabric for 5 min in 1% polystyrene solution. Synthesized polystyrene coated zinc oxide impregnated non-woven cotton (PS@ZnO-NWCotton) and polystyrene coated zinc oxide impregnated woven cotton (PS@ZnO-WCotton) composites were dried at 70° C till constant weight was obtained.

Oil adsorption capacity (OAC) for experimental materials was considered as the ratio between the weights of absorbed oil (m_{oil}) in comparison with the weight of dry adsorbent (m_o). It was calculated by the formula;

$$OAC = \frac{m_{oil}}{m_o}\ gg^{-1} = \frac{m_{total} - m_o}{m_o}\ gg^{-1}$$

where, m_{oil}, m_o and m_{total} are the masses of absorbed oil, dry sorbent and mass of adsorbent after adsorption respectively.

Characterization of PS@ZnO-Cotton composites

Surface morphology of pristine NWC, WC, PS@ZnO-NWCotton and PS@ZnO-WCotton was observed using a SEM (Scanning Electron Microscope, Jeol JSM-6380A, Japan) at x50, x100, x500, x1000, x1700 and x4000 magnification. Attenuated Fourier transform infrared (FTIR) spectra were recorded using Thermo Scientific Nicolet iS10 FTIR spectrometer at room temperature onto Attenuated Total Reflectance (ATR) ZnSe crystal at the wavelength range of 4000–650 cm^{-1} with a resolution of 4 cm^{-1} by averaging 16 scans and using the Smart iTR™ ATR accessory. Thermal gravimetric analysis (TGA) was conducted on TGA/DSC 3 + STAR e System, Mettler Toledo at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

10 µL of each liquid was dropped on pristine WC and PS@ZnO-WCotton. The pictures of droplets were taken using high resolution digital camera. Water contact angles were measured at room temperature using image processing software ImageJ (v. 1.53c, National Institutes of Health, Bethesda, MD, USA. https://imagej.net/software/fiji/)

Statistical optimization of factors for enhanced oil adsorption capacity of PS@ZnO-NWCotton composite

Response Surface Methodology uses statistical and mathematical techniques for the optimization of process variables and their responses. Among response surface designs, central composite design is considered as most effective for optimization of experimental variables. OAC of PS@ZnO-NWCotton composite was optimized with respect of three significant variables temperature, duration of adsorbate-adsorbent interaction and oil-water ratio. Face cantered composite central composite design (FCCCD) was developed using MINITAB® version 17 software. The central composite design (CCD) is specified by three operations namely: 2n factorial runs, 2n axial runs and six center runs, where n is the number of factors (Fig. 1). Table-1 presents lower, nominal and higher values of independent variables. Central composite design used in this study is divided into 8, 6, and 6 factorial points, axial points, and 6 replicates at the central point, respectively, which gives a total of 20 experiments (Table-2). Experiments were conducted according to the design. Goodness of data were evaluated by normal and residual plots. Regression and ANOVA analysis were used to test the effect of each variable from the obtained results.

Table-1: Independent variables and their levels.

Factors	Levels		
	-1	0	+1
Oil Water Ratio	1.1	-	2.1
Temperature	25	30	35
Duration	1	5.5	10

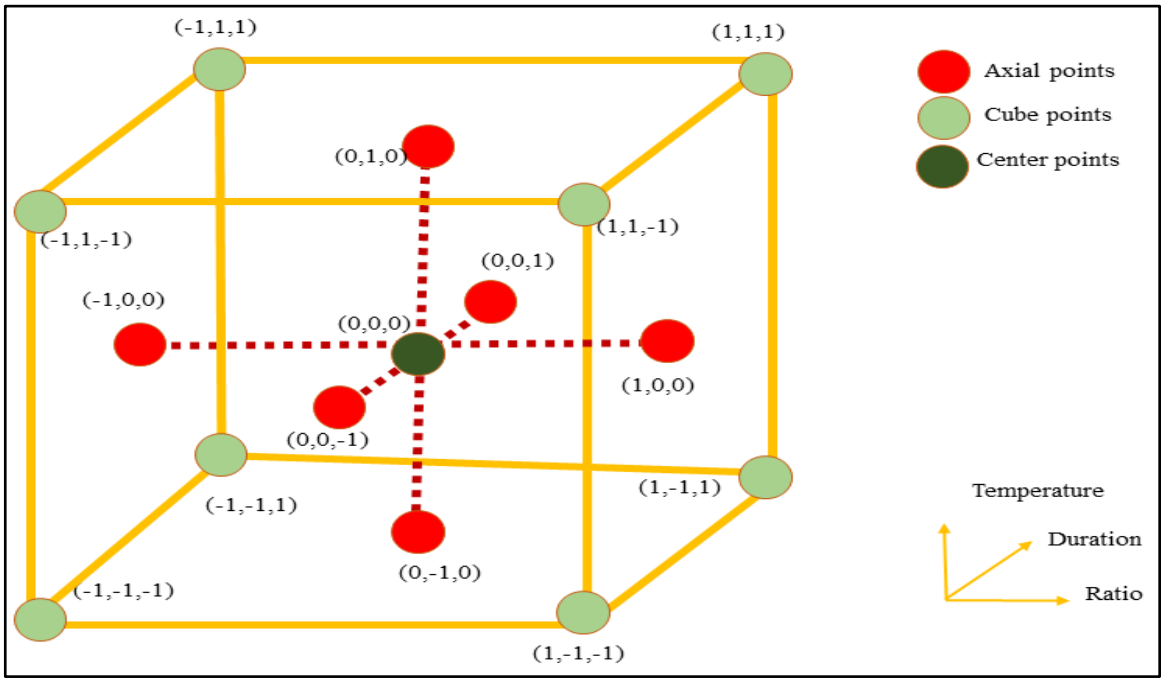

Fig. 1: Central Composite Design (CCD) of PS@ZnO-NWCotton composite, the dark green circles represent the center point, light green circles represent the cube points and red color represents axial points.

Table-2: Design matrix and responses of central composite design (CCD) used in the study.

Run Order	Independent Variable			OAC (g g^{-1})	OAC (g g^{-1})
	Oil/Water ratio	Temperature (°C)	Duration (min)	Actual	Expected
1	1.5	30	5.5	8.09	8.31
2	1.5	35	5.5	11.66	10.52
3	1.0	25	1.0	6.1	5.75
4	2.0	35	1.0	9.69	9.83
5	1.0	30	5.5	4.25	4.07
6	1.5	30	5.5	7.7	8.31
7	1.5	30	5.5	7.65	8.31
8	1.5	30	5.5	6.65	8.31
9	2.0	25	1.0	5.62	5.83
10	1.5	30	5.5	8.59	8.31
11	1.5	30	1.0	8.7	8.46
12	1.5	25	5.5	9.1	8.94
13	1.0	35	1.0	6.315	6.54
14	2.0	30	5.5	7.89	6.78
15	1.5	30	10.0	11.56	10.52
16	1.0	25	10.0	7.43	7.61
17	1.5	30	5.5	8.66	8.32
18	2.0	35	10.0	11.435	12.09
19	2.0	25	10.0	9.62	9.71
20	1.0	35	10.0	6.67	6.77

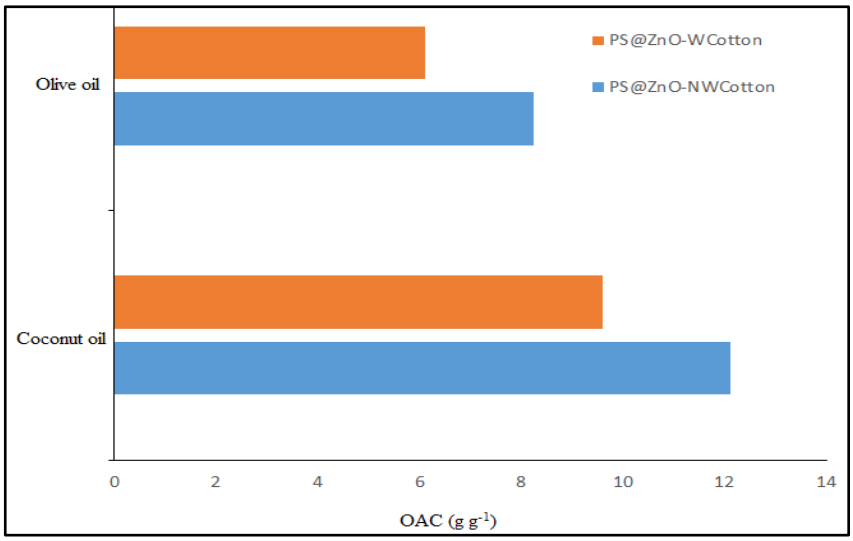

Fig. 2: Oil adsorption capacities of PS@ZnO-NWCotton and PS@ZnO-WCotton for coconut and olive oil.

Result and Discussion

Hydrophobic and oleophilic behavior of PS@ZnO-Cotton composites

Olive oil and coconut oil were used to evaluate the effect of oil viscosity on OAC of PS@ZnO-NWCotton and PS@ZnO-WCotton (Fig. 2). It was found that OAC was higher for coconut oil with lower viscosity while more viscous olive oil adsorbed to lesser extent on both cotton composites. This observation may be attributed to higher mobility of low viscous coconut oil through pores of the adsorbent while more viscous olive oil slowly filled and blocked adsorbent spaces[26]. OAC capacity of PS@ZnO-NWCotton was also compared with PS@ZnO-WCotton. Several steps such as spinning the fiber into yarn, warping, sizing and weaving are involved in converting staple fiber into woven cotton fabric. Due to these additional manufacturing steps, resulting cotton fabric becomes denser and rigid as compared to porous and fluffy staple cotton fibers. Difference in physical properties of cotton fiber and fabric led to synthesis of respective adsorbents with different adsorption capacities. As a result, PS@ZnO-NWCotton exhibited higher adsorption capacities as compared to PS@ZnO-WC. Other factors affecting oil adsorption capacities of cotton such as duration, oil water

ratio and temperature were optimized using statistical studies mentioned in section 3.5.

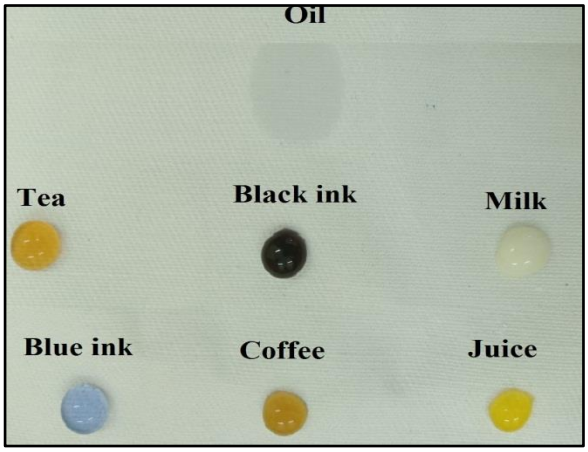

Fig 3: Common household liquids droplets on PS@ZnO-WCotton demonstrating its hydrophobic/ oleophilic properties.

Fig. 3 illustrates hydrophobicity of PS@ZnO-WCotton composite for water and different water based household solvents i.e. water, orange juice, ink, coffee, milk. 10 µL of each of these liquids were dispensed onto PS@ZnO-WCotton. It can be observed that all water based household liquids formed spherical drops which were not adhered on adsorbent surface. 10 µL of kitchen oil was also dispensed onto PS@ZnO-WCotton surface which penetrated into the composite quickly exhibiting its oleophilic property. When ink drops was placed on the PS@ZnO-WCotton, it rolled off easily from fabric and washed off easily with flowing water without leaving any stain i.e. lotus effect like water repellency (Fig. 4 a, b, c). Lotus effect water repellency can be attributed to increased surface roughness due to incorporation of ZnO and coating of low energy polystyrene[27]. When PS@ZnO-NWCotton composite was immersed in a beaker containing oil/water mixture, it floated on the mixture surface and absorbed oil layer from the mixture without interacting with aqueous phase without interacting with aqueous while pristine cotton sank in the bottom of the oil/water mixture and adsorbed dye colour and found to adsorb colored dye from water phase (Fig. 4 c, d, e). It could be due to the reason that hydrophobicity caused by polystyrene layer on the cotton did not let water enter into the internal area of cotton and therefore cotton remained light weighted and floating on the water surface. Contact angle of water droplet were measured using ImageJ software. Different water droplets were dispensed on the surface of the PS@ZnO-WCotton and their contact angles were measured using ImageJ software. The average contact angle of water droplet was found to be 145±2 indicating high hydrophobicity of PS@ZnO-WCotton while oil drop was instantly adsorbed and spread onto PS@ZnO-WCotton resulting 0^o contact angle (Fig. 5).

FTIR Analysis

The FTIR spectra of pristne NWCotton and PS@ZnO-NWCotton were recorded to observe deposition of PS and ZnO on the NWCotton surface. Fig. 6 compares the spectra of NWCotton and PS@ZnO-NWCotton. The characteristics peaks of NWcotton include a broad diffused peak at 3345 cm^{-1} (O–H stretching), a diffused peak at 2917 cm^{-1} (C–H stretching), sharp peaks at 1714 cm^{-1} (C=O stretching) and 1300 cm^{-1} (C–H bending) and a small peak at 1023 cm^{-1} (C–O stretch) [28]. It is interesting to see that both the FTIR spectra in Fig. 6 are almost similar except for the peak at 1057 cm^{-1} (Zn–O–Zn asymmetric vibrations) [29], the broadness of the peaks, changes in peaks intensity and small shift in peak positions in case of PS@ZnO-NWCotton. The broadness of peaks shows strong intermolecular interactions and increase in intensity of the peaks affirming that the cotton surface is covered by PS and ZnO [17]. On the other hand, shifting of peak positions such as 1714 to 1645 cm^{-1} and 1300 to 1318 cm^{-1} might be due to the interactions between NWCotton and other constituents of the composites further support the preparation of PS@ZnO-NWCotton composites.

SEM Analysis

Pristine NWCotton, pristine WCotton, PS@ZnO-NWCotton and PS@ZnO-WCotton samples were spur coated with a very thin conducting layer of gold before taking SEM micrographs at x100, x500, x1000 and x1700 magnification. It can be observed in Fig. 7 that pristine NWCotton consists of discrete yet tangled cotton fibers with smooth surfaces. In PS@ZnO-NWCotton, the cotton fibers are fully coated with dense polystyrene interconnections. Woven cotton fibers can be seen in SEM micrograph of WCotton. In SEM micrograph, PS@ZnO-WCotton appears to be coated with polystyrene layer. However, in PS@ZnO-WCotton, polystyrene appears to be merely coated on the fabric resulting in imperfect polystyrene coating. However, polystyrene coating is more uniform in PS@ZnO-NWCotton because of its loose and porous structure. Moreover, surface of PS@ZnO-Cotton is rough and more porous as compared to pristine cotton. There are many studies in which ZnO is used to increase surface roughness of cotton to enhance its surface area [30][31]. Therefore, it is assumed that roughness of PS@ZnO-Cotton is also due to the impregnation of ZnO. Low energy polystyrene coating onto cotton found to be more porous as compared to pristine cotton. These pores may facilitate entrance of oil into the adsorbent.

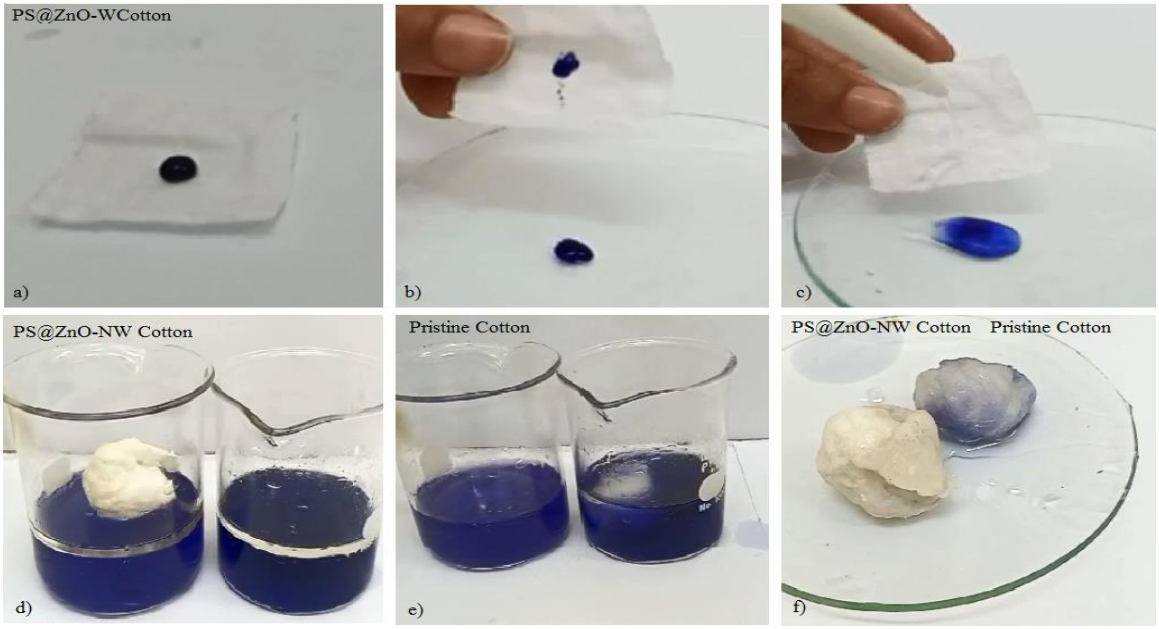

Fig. 4: (a) Spherical droplet of blue dyed water onto PS@ZnO-WCotton; (b) water droplet rolled off from PS@ZnO-WCotton surface by tilting it (c) adhered water was easily rinsed off without leaving any stain (d-e) illustrates adsorption of oil from dyed oil water mixture (water was dyed with blue ink). (d) PS@ZnO-NWCotton (e) pristine cotton (f) and PS@ZnO-NW Cotton and pristine cotton after 24 second immersion in dyed oil water mixture).

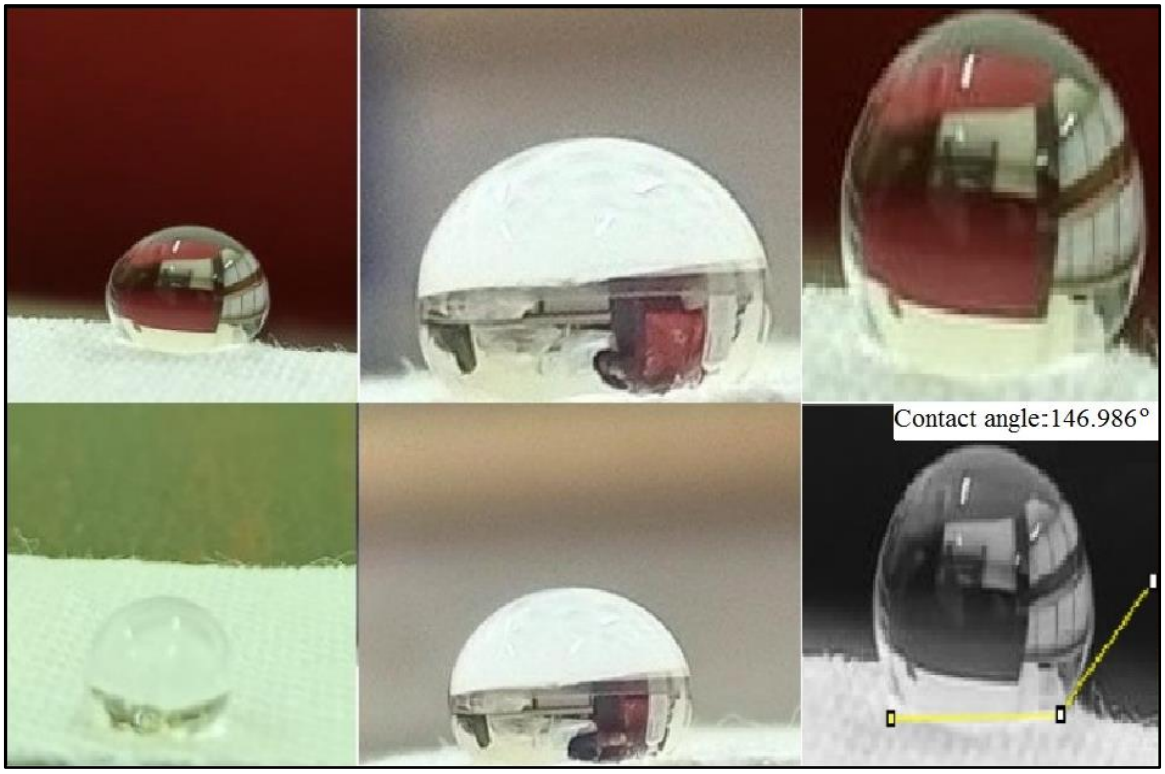

Fig. 5: Droplets of water on PS@ZnO-WCotton Composite used to determine contact angle.

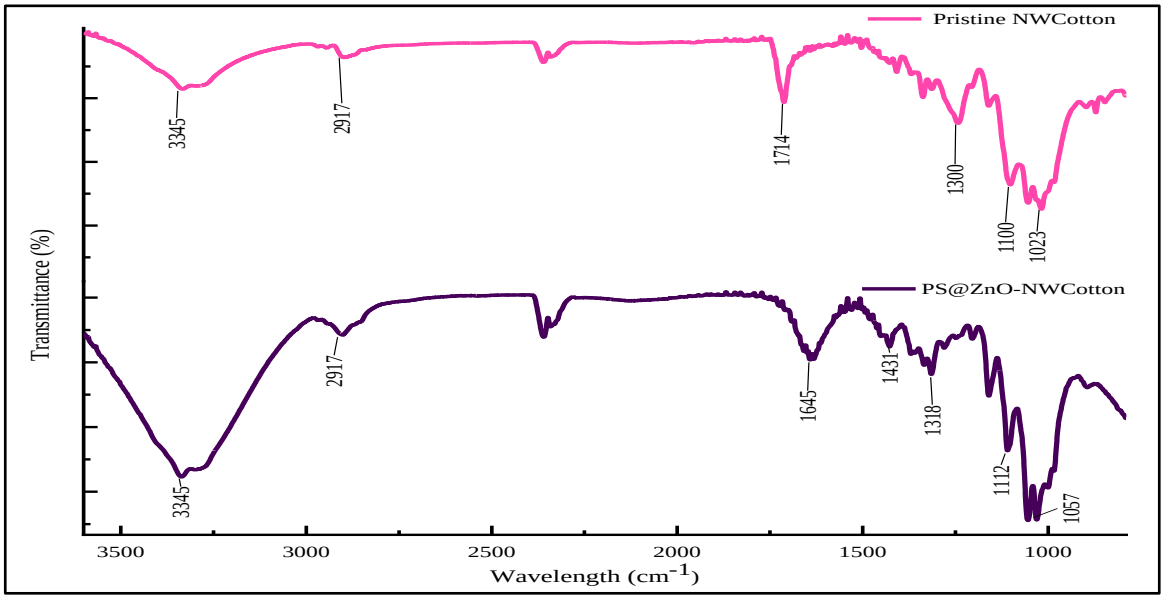

Fig. 6: FTIR spectra of Pristine NWCotton and PS@ZnO-NWCotton Composite.

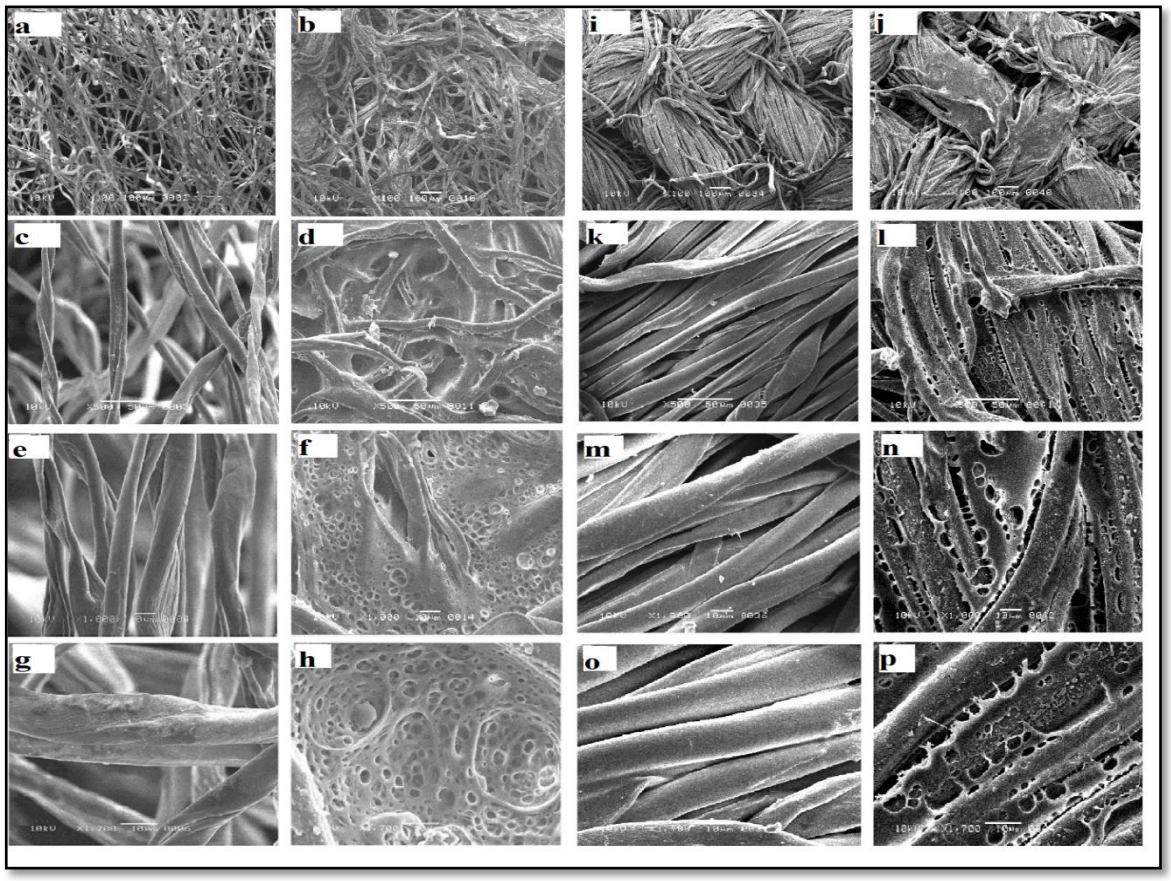

Fig. 7: Scanning Electron Microscopic images of pristine NWCotton (a, c, e, g), PS@ZnO-NWCotton composite (b, d, f, h)), Pristine WCotton (i,k,m,o) and PS@ZnO-WCotton (i,l,n,p) at x100, x500, x1000 and x1700 magnification.

Thermo gravimetric Analysis

Thermal degradation of pristine NWCotton and PS@ZnO-NWCotton were observed by thermo gravimetric analysis (Fig. 8). Decomposition of pristine NWCotton and PS@ZnO-NWCotton was divided into three zones. In the first zone (0-290^{o}C), elimination of moisture content instigated thermal degradation of cotton due to dehydration of glucose groups present in the cellulose macromolecules yielding volatile product and aliphatic char. The PS@ZnO-NWCotton decomposed at 254 ^{o}C, whereas, decomposion of pristine NWCotton occurred at 290 ^{o}C with slight weight loss of 1%. Earlier decomposition of PS@ZnO-Cotton as compared to pristine cotton could be due to depolymerization of polystyrene [32][33]. There is a significant change in second zone (291-377 ^{o}C) where the curves display major downfall starting from 291^{o}C till 377^{o}C due to further thermal cracking of cellulose macromolecules with 16% weight loss difference. In third (377-534 ^{o}C) thermal decomposition zone, the rate of weight loss of PS@ZnO-NWCotton turned out to be slower than pristine cotton which might be due to the residue of zinc oxide. Moreover, presence of ZnO residues raised weight of PS@ZnO-NWCotton char by 18% of PS@ZnO-NWCotton.

Statistical optimization of factors for enhanced oil adsorption capacity of PS@ZnO-NWCotton composite

The probability value or p-value is a measure of alterations in results that is observed and has occurred under null hypothesis by random chances. If it is less than 0.05 it indicates that the term is significant. Conversely, a larger (insignificant) value suggests that changes in the predictor are not related with changes in the response. In Table-3 the p-values for the model are 0.001 indicating high significance of the model. Lack of fit exhibited p-value much greater than 0.05 i.e. 0.231, therefore error in predication can be ignored. All the linear and square except square of duration carry p-value less than 0.05 hence these terms need to be included in the regression equations. The predictor factors duration, temperature and oil/water ratio are significant because their p-values are 0.005, 0.021 and 0.001 respectively. However, 2-way interaction terms have p-values greater than the common alpha level of 0.05, which indicates that it is not statistically significant. Coefficient of determination (R^2) was used to as a measure of the efficiency of correlated model. The value of determination coefficient (R^2 = 0.8904) suggests that only 10.96% of the total deviations are not explained by the model. The adjusted determination coefficient value (Adj. R^2 = 0.7917) also indicated significance of the model. Standard deviation (s) of the data points around the fitted values is 0.9103 which indicates a better fit. Regression equation is given at low viscosity is given below.

$$Y = \beta_o + \beta_1 X_1 - \beta_2 X_2 - \beta_3 X_3 - \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{21} X_2 X_1 + \beta_{31} X_3 X_1 - \beta_{32} X_3 X_2$$

$$OAC = 38.5 + 26.48 X_1 - 3.64 X_2 - 0.207 X_3 - 11.56 X_1^2 + 0.0568 X_2^2 + 0.0578 X_3^2 + 0.322 X_2 X_1 + 0.226 X_3 X_1 - 0.0179 X_3 X_2$$

Whereas X_1 is oil/water ratio (v/v), X_2 is temperature (^{o}C) and X_3 is duration (min).X_1, X_2 and X_3 are the variables. β_O is the regression constant at low viscosity. β_1, β_2 and β_3 are the linear regression. β_{11}, β_{22} and β_{33} are the quadratic term and are the cross-product regression term.

Table-3: Analysis of variance (ANOVA) for oil adsorption capacities (OACs) on PS@ZnO-NWCotton Composite

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	67.299	7.4777	9.02	0.001
Linear	3	35.027	11.6758	14.09	0.001
Duration (min)	1	10.588	10.5884	12.78	0.005
Temperature (^{o}C)	1	6.241	6.2410	7.53	0.021
Oil/Water ratio	1	18.198	18.1980	21.96	0.001
Square	3	23.739	7.9129	9.55	0.003
Duration (min)*Duration (min)	1	3.770	3.7703	4.55	0.059
Temperature(^{o}C) *Temperature (^{o}C)	1	5.552	5.5522	6.70	0.027
Oil/water ratio*Oil/Water ratio	1	22.954	22.9538	27.70	0.000
2-Way Interaction	3	8.533	2.8442	3.43	0.060
Duration (min)*Temperature (^{o}C)	1	1.304	1.3041	1.57	0.238
Duration (min)*Oil/Water ratio	1	2.060	2.0605	2.49	0.146
Temperature (^{o}C) *Oil/Water ratio	1	5.168	5.1681	6.24	0.032
Error	10	8.288	0.8288		
Lack-of-Fit	5	5.533	1.1067	2.01	0.231
Pure error	5	2.754	0.5508		
Total	19	75.587			

S	R-sq	R-sq (adj)	R-sq (pred)
0.910363	89.04%	79.17%	52.16%

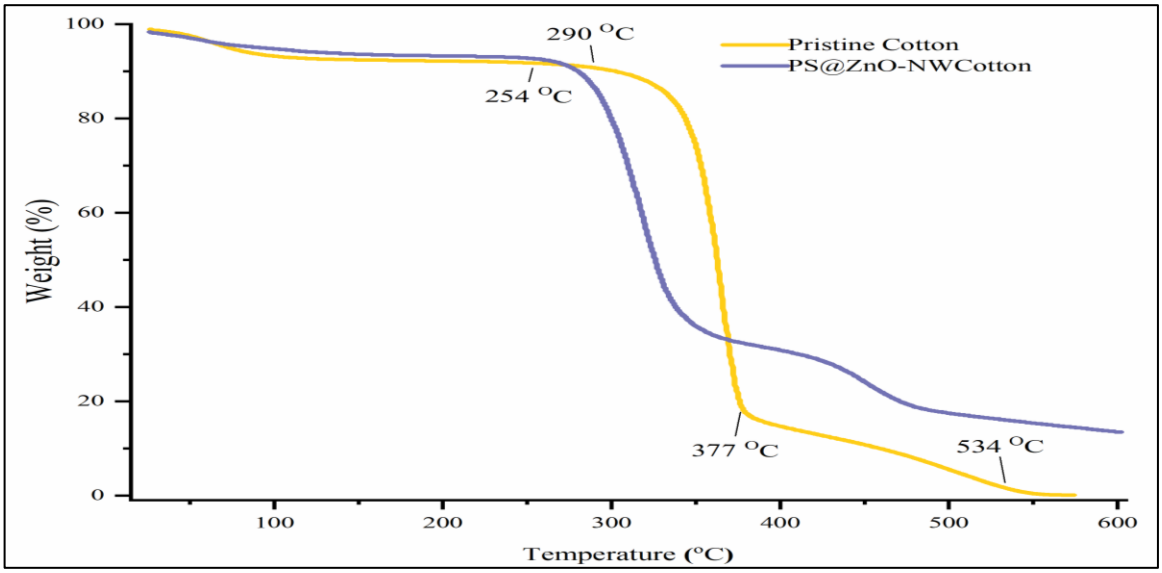

Fig. 8:Thermogravimetric analysis of pristine NWCotton and PS@ZnO-NWCotton.

The residual analysis is an important tool for the diagnosis of proposed model and prediction of the response. Fig. 9 presents residual plots for the confirmation of model adequacy. It can be seen that response model for adsorption of coconut oil onto PS@ZnO-NWCotton composite exhibit normal distribution and there is no systematic pattern. Plots show normal distribution of residuals for all observations. Therefore, it can be assumed that the proposed model was sufficiently satisfactory for describing adsorption of coconut oil onto PS@ZnO-NWCotton composite.

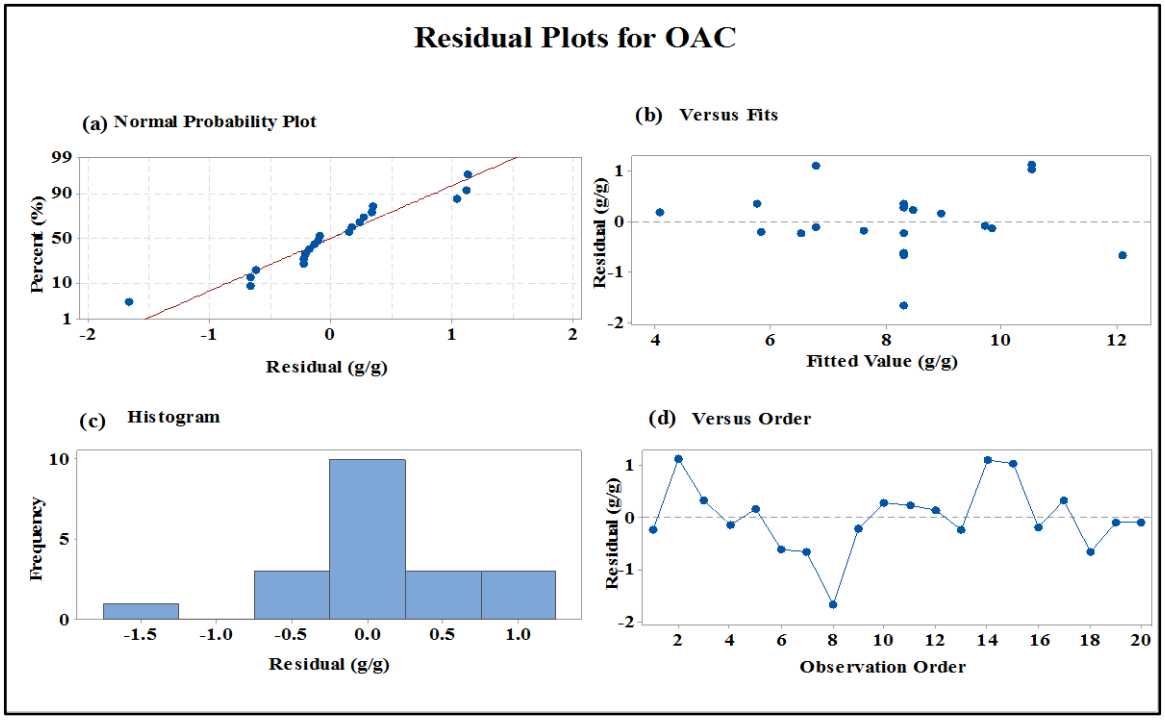

Fig. 9: Different residual plots for OAC testing the suitability of the anticipated model (a) normal probability plot (b) plot of residuals vs. the fitted values (c) histogram (d) residuals vs. the order observation of data.

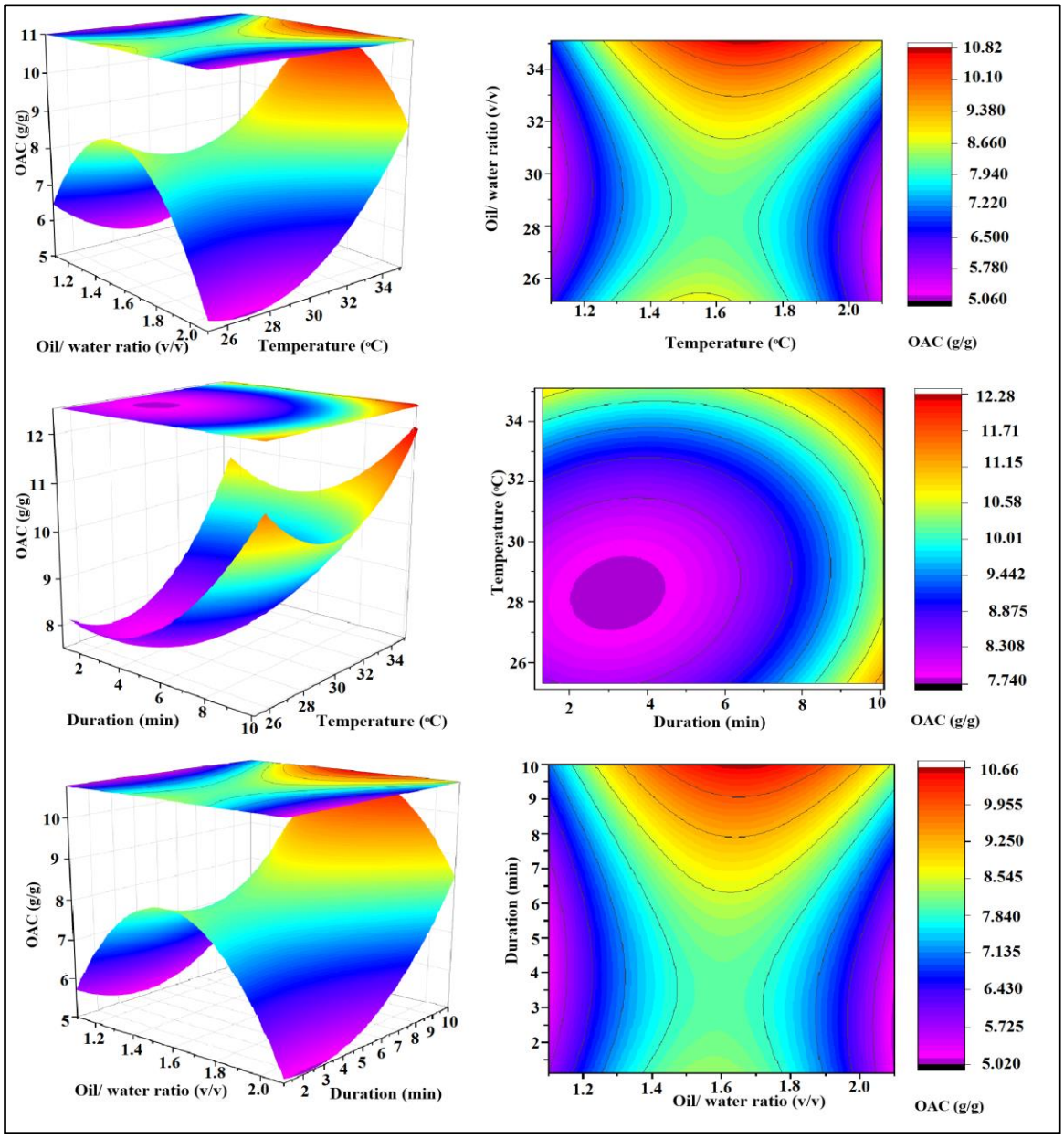

Fig. 10: 3D Surface response and contour plots for the adsorption of coconut oil onto PS@ZnO-NWCotton (a) OAC (g/g) versus temperature (°C) and oil/water ratio (b) OAC (g/g) versus duration (min) and temperature (°C) (c) OAC (g /g) versus oil/water ratio and duration (min).

3D surface plots and contour plots were plots to understand impact of process variables on adsorption capacity of PS@ZnO-NWCotton composite. In response surface and contour plots, the OAC of PS@ZnO-NWCotton composite was plotted along with two continuous variables, while the third variable was kept constant at its central value. Fig 10 (a) presents 3D and contour plots for OAC against oil/water ratio and temperature while keeping the duration of adsorbent and adsorbate contact fixed at 10 minutes. OAC found to initially increase with increasing oil/water ratio and maximum adsorption was observed at 1.5:1 oil/water ratio but higher amount of oil content in oil/water mixture resulted in lower OAC. It may be due to inability to adsorb oil after saturation of the oil adsorbing sites on PS@ZnO-NWCotton composite at higher oil/water ratio. Another expected observation is increase in OAC on increasing temperature which could be due to higher mobility and decreased viscosity of oil at higher temperature [34]. Fig. 10 (b) presents OAC versus duration and temperature. Both of these variable positively affected OAC i.e. higher adsorption occurred

when adsorbent remained in contact with adsorbate for longer period of time at higher temperature. 3D surface response and contour plots in Fig. 10 (c) further confirmed previously observed effect of oil/water ratio and duration of adsorption onto oil adsorption capacities i.e. higher adsorption of oil onto PS@ZnO-NWCotton composite at 1.5: 1 oil/water ratio and longer contact duration

Reusability

Reusability of adsorbent is an important factor to determine its potential for practical applications and cost of the process. In this study, PS@ZnO-NWCotton composite was immersed in 1.5: 1 oil water mixture at 30°C for 5 minutes and mechanically squeezed to remove adsorbed oil followed to by drying PS@ZnO-NWCotton composite in an oven at 60°C for half hour and reused again under similar conditions. The same process was repeated ten times. The result of reusability studies are given in Fig. 11. It was found that adsorbent retained its oil adsorption capacity till three cycles and then exhibited gradual decrease in its adsorption capacity which can be attributed to incomplete removal of adsorbed oil from active sites and pores of PS@ZnO-NWCotton because of less efficient manual squeezing [35]. Reusability of adsorbent was also evaluated by replacing manual squeezing with washing of used adsorbent with n-haxane followed by drying in oven at 60°C for half hour. The regenerated PS@ZnO-NWCotton composite was reused under similar conditions.

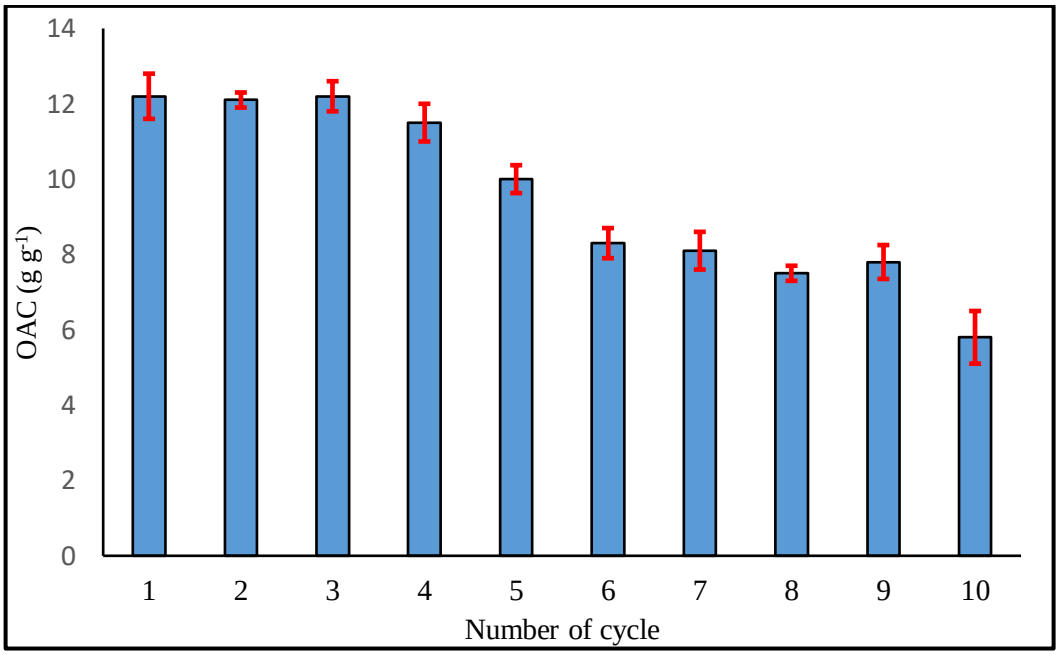

Fig. 11: Reusability of PS@ZnO-NWCotton for the adsorption of coconut oil up to ten cycles.

Table-4: Comparison of oil adsorption capacities of other adsorbent with proposed adsorbent.

S.No	Adsorbate Oil	Adsorbent	OAC	Ref
1.	Vegetable oil	Nano Cellulose Aerogel	13.73 ± 0.62 g g^{-1}	[36]
2.	Vegetable oil	Human Hair	4606 mg g^{-1}	[37]
3.	Vegetable oil	Silica Aerogel	14.6 g g^{-1}	[38]
4.	Palm-based cooking oil	Surfactant-Modified Sago Hampas	15.147 g g^{-1}, 18.880 g g^{-1}	[39]
5.	Vegetable oil	Highly fluorinated graphene oxide and ZIF-8 Composites	150-600 wt %	[40]
6.	Sunflower oil	ABS and ABS/ZnO Electrospun membrane	Up to 6.3 g g^{-1}	[41]
7.	Coconut oil	ABS and ABS/ZnO Electrospun Membrane	Up to 7.3 g g^{-1}	[41]
8.	Sunflower oil	Chitin/halloysite Nanotubes (C/HNTs) Composites	6.4 g g^{-1}	[42]
9.	Vegetable oil	Luffa sponge functionalized with stearic acid	15 ± 2 g g^{-1}	[43]
10.	Waste cooking oil	Magnetic Palm Oil Empty Fruit Bunch Biochar	54.36, 51.52, 47.42 mg g^{-1}	[44]
11.	Vegetal oil	Sugarcane bagasse fibers reinforced in Polyurethane for Sorption	10.3 ± 1.1g g^{-1}	[45]
12.	Peanut oil	PDMS-CNF-Fe/Fe3C foam	900%	[46]
13.	Olive oil	Lignin/PU composite foams	9.6 g g^{-1}	[47]
14.	Vegetable oil	Juncus effusus/polyurethane composite	1.3 g g^{-1}	[48]
15.	Soya bean oil	Poly (sulfur/oil) impregnated cotton (PSOIC) composite	9.52 g g^{-1}	[49]
16.	Food oil	Polystyrene waste/surfactant modified bagasse blend	6.8 - 11.8 g g^{-1}	[50]
17.	Palm oil	Chitosan beads	1667.93±39.61 mg g^{-1}	[51]

Comparison with other hydrophobic/oleophilic Adsorbents

The OAC of PS@ZnO-NWCotton was compared with the maximum oil adsorption capacity of previously reported oleophilic adsorbents for uptake of vegetable oils (Table-4). The maximum OAC of proposed adsorbent is better than many other reported adsorbents. It suggests that PS@ZnO-NWCotton has potential for its commercial applications as efficient kitchen oil adsorbent.

Conclusion

In this study, polystyrene coated ZnO impregnated Cotton adsorbents using non-woven and woven cotton were prepared for the adsorption of vegetable oils. The experimental studies showed that even though non-woven and woven cotton is made up of same cellulose fibers; their adsorption capacities were significantly different. We may conclude that steps involved in conversion of non-woven cotton into woven form via spinning, warping, sizing and weaving lowers adsorption capacities of later. ZnO impregnation onto cotton fiber resulted in increasing its roughness and polystyrene coating suppressed its hydrophilic properties and turned it into hydrophobic and oleophilic adsorbent with water droplet contact angle to be about 145±2. Statistical optimization of adsorption of oil onto PS@ZnO-NWCotton composite resulted in higher OAC values at 1.5: 1 oil/water ratio and longer contact duration. The present study resulted in an oleophilic adsorbent which have been prepared using low cost abundantly available cotton fibers and waste polystyrene and may provide environmental benefits.

Declaration of Conflict of Interest

The authors declare that they have no direct or indirect conflict of financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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