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Investigation on microwave and ultrasound-assisted cornhusk for the removal of emulsified engine oil from water

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ABSTRACT

This study focuses on the removal of synthetically prepared emulsified oil- in-water using raw and reformed/modified cornhusk as an adsorbent via rotary shaker (RS)-, microwave (MW)- and ultrasound (US)-assisted techniques and comparison of adsorption capacity with activated carbon. The chemical modifications were performed using cationic surfactant, cetyl pyridinium chloride solution (CPC, $C_{21}H_{38}NCl$), on pre-treated sodium hydroxide adsorbent. The binding of surfactant on adsorbent surface is characterized using Fourier transform infra-red spectroscopy analysis and further improvement of impinge surface morphology by scanning electron microscope. The batch studies were performed by varying the influencing process parameters such as contact time, pH, dosage, speed and temperature to confirm the enhanced condition for maximum adsorption capacity. The maximum adsorption capacity of 1,610, 1,566 and 1,698 mg/g has been achieved for MW and US reformed adsorbent and activated carbon. In addition, kinetics first-order, second-order, intra-particle diffusion model and isotherms Langmuir, Freundlich, Dubinin–Radushkevish and Flory–Huggins model data were compared with the experimental data to evaluate the fitness. The error analysis is performed to quantify the coefficient of determination and chi-square values.

Keywords: Emulsified oil removal; Reformed; Microwave; Ultrasound; Error analysis

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1. Introduction

Abrupt increase in the release of toxic pollutants into the environment alerted social and government bodies to frame stringent norms. One among the pollutant is oil-in-water which causes hazardous effects on human and aquatic species.

In general, oil exists in three different forms based on the size of the oil droplet as free (≥150 µm: 10%), dispersed (between 20 and 150 µm: 10–20%) and emulsified oil (<20 µm: 70–80%) in water [1,2]. The studies on palm oil mill effluent report that the concentration of oil and grease is about 4,000–6,000 mg/L of which 2,000 mg/L is in emulsified form [3]. The cheap and environment-friendly solution made researchers to focus on modified agricultural waste as adsorbent. The studies highlighted that modification by cationic surfactants offers additional advantages over anionic, zwitterionic and nonionic class of surfactant [4–7]. These substances, besides their surface activity, show antibacterial properties and are used as cationic softeners, lubricants, retarding agents, antistatic agents etc. The pre-treatment of adsorbent

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with NaOH degrades lignin and thereby increases the hydrophilicity of adsorbent.

The detailed investigation has been carried out for the removal of oil from different sources of oil using adsorbents is listed in Table 1. From the agricultural waste, Cornhusk was found to be an excellent adsorbent for the removal of Cd(II), Pb(II) and Zn(II) ions using unmodified and EDTA-modification [20]. The modification of adsorbent is very important to reduce the release of minerals. Subsequently, the exposure of modification process towards microwave (MW) and ultrasound (US) has higher susceptibility to be oriented in different fashions which in turn have more chance to improve batch adsorption efficiency. The MW treatment is an effective method for modification of surface chemistry of some of the coal-based activated carbon fibres, coconut shell, bamboo, cotton stalk rice and Jatropha hull [21–26]. US produces both mechanical and chemical effect through the formation of cavitational bubbles which cause many microcracks on the solid surface [27]. A wide investigation has been carried out for wastewater treatment on MW- and US-assisted coal-based activated carbon. But, very limited papers are available in terms of raw agricultural waste as adsorbents exposed to the respective for the preparation of absorbent using MW and US techniques.

Hence, this study is carried out for the removal of emulsified oil from water using raw, MW and US reformed cornhusk. The effect of the process parameter such as contact time, pH, dosage, speed and temperature were analysed for raw, reformed adsorbents such as RS-, MW-, US-assisted cornhusk are compared with commercially available activated carbon. In addition, kinetics and isothermal studies were accomplished.

2. Materials and methods

2.1. Preparation of oil-in-water emulsion

The emulsified oil-in-water is prepared by mixing 10% (v/v) of engine oil (Valvoline Turbo SAE 15w-40 API CH-4) in distilled water and stirring it using a magnetic stirrer at 1,000 rpm for 5 min. Then, the blend mixture is placed in 220 W ultra-sonicator bath for 12 min at 20 kHz. By means of quick cavitational phenomenon [28], stable synthetic emulsified oil-in-water is prepared and used for the entire study.

The presence of synthetically prepared emulsified oil-in-water was confirmed by colour appearance, electrical conductivity and turbidity test. Initially, the appearance of cloudiness shows the existence of minute oil droplets in emulsion form, and the conductivity is verified and found to be lesser than distilled water because of the presence of oil which is a poor conductor. The turbidity (Nephelo-Turbidity Meter 132) of oil-in-water is 128 NTU. In addition to the above tests, the stability of the emulsified oil is highly important to be monitored continuously for 3 d. The pH and concentration of prepared oil-in-water emulsion are 6.9 and 17,384 mg/L.

Table 1
Oil adsorption capacity of adsorbents in literature

Adsorbent	Oil source	Adsorption capacity (mg/g)
Chitosan-based polyacrylamide [8]	Crude oil	2,300
Chitosan and walnut shell [9]	Standard mineral oil, vegetable oil and cutting oil	77.2, 92.5 and 84
Chitosan[10]	Palm oil mill effluent	3,800
Chitosan powder and flake [11]	Palm oil mill effluent	1,940–1,980
Chitosan [12]	Palm oil mill effluent	7,920
Bentonite, powdered activated carbon and deposited carbon [13]	Oil field effluent	552, 468 and 570
Bentonite organo-clay/anthracite [14]	Synthetic and actual oil-in-water emulsions	21 and 0.07
Modified barley straw [15]	Canola oil	576
Modified barley Straw [16]	Mineral and canola oil	613.3 and 584.2
Natural wool fibres, recycled wool-based nonwoven material and sepiolite [17]	Real oily wastewater	5,560, 5,480 and 190
Hydrophobized vermiculite [18]	Standard mineral oil, canola oil, kutwell oil and refinery effluent	23, 6.12, 6.7 and 2.7
Expanded vermiculite [18]	Standard mineral oil, canola oil, kutwell oil and refinery effluent	15, 46.3, 11 and 80.9
Rubber powder [19]	Palm oil mill effluent	117.3

2.2. Preparation of reformed adsorbent

Blended adsorbent, cornhusk is washed with distilled water and dried in shady daylight for five hours followed by deep drying in hot air oven at 65˚C and labelled as raw cornhusk (raw). The average particle size of 0.2835 mm is chosen for this study. The chemical modifications were performed by sodium hydroxide, followed by cationic surfactant, cetyl pyridinium chloride solution (CPC, $C_{21}H_{38}NCl$). Pre-treatment with 0.05 M of NaOH is performed for 15 min in respective equipment (RS at 160 rpm, MW at 119 W and ultrasonicator at 20 kHz) for the better enhancement of surfactant over the surface of adsorbent. After treatment, excess of solution is decanted and the adsorbent is washed with distilled water and dried in hot air oven at the same temperature overnight. Surfactant treatments were carried out by soaking the washed and dried pre-treated adsorbent in 2.5 m mol/L of cationic solution in the respective equipment for 30 min. Then, the adsorbent is dried as NaOH-treated adsorbent, and samples were stored in airtight container as RS, MW and US-assisted adsorbents.

The reformation of cornhusk has been characterized by Fourier transform infra-red (FTIR) analysis (Make PerkinElmer Spectrum 10.03.09) for the confirmation of surfactant reformation on adsorbent surface which is shown in Fig. 1. The strong fall at 3,332 1/cm arises due to the vibration of OH stretch, and bands near 2,920 and 2,854 1/cm represent asymmetric and symmetric stretches of methyl C–H group [13] (derivatives of CPC).

The scanning electron microscope (SEM) image (from VEGA 3 Tescan) shown in Fig. 2 illustrates the surface morphology of the raw and reformed adsorbents at 500× (first row) and 1 k× magnification (second row). The raw surface is more or less smooth and has uniform circular spots on the surface. But MW and US reformed cornhusk do not possess such defined circular spots, since it has been modified into folding results in the reformation of irregular surface area. Hence, the FTIR and SEM analyses confirm the reformation on the surface of the adsorbent.

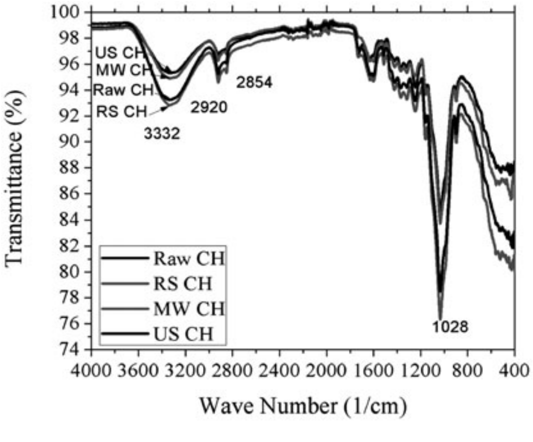

Fig. 1. FTIR analysis for raw, rotary shaker (RS CH)-, microwave (MW CH)- and ultrasound (US CH)-assisted cornhusk.

The surface area, total pore volume and pore size were determined by N_2 adsorption at −196˚C using micromeritics ASAP 2020 V3.00 H model for raw, RS, MW and US-assisted cornhusk are given in Table 2, and the cross-sectional area of the four adsorbents were found to be 0.1620 nm^2. The maximum surface area was observed for RS and MW-assisted adsorbent, whereas that of US-assisted adsorbent is lesser than the raw adsorbent, but pore size is higher, which is an unexpected result and may be due to ultrasound waves, which disrupt the surface and increased the pore volume by release of volatile matters from adsorbent. The average densities of the raw, RS, MW and US adsorbents were 0.7069, 0.7506, 0.7491 and 0.7145 g/cm^3, respectively.

2.3. Batch Study

The batch study was performed at 160 RPM in rotatory shaker at various conditions for the measured amount of raw and RS, MW and US assisted adsorbents (raw, RS, MW and US CH). The batch adsorption was carried out for a contact time of 180 min at pH 6.9, dosage 10 g/L at 160 RPM and room temperature to find the dynamic equilibrium time for each adsorbent. After the batch process, solution was separated to measure emulsified oil concentration in spectrophotometer (spectroquant pharo 300). The impact of acidic and basic condition of oil-in-water on the removal of emulsified oil was experimented at pH range of 2–10 at 120 min, 10 g/L, 160 RPM and 37˚C. The dosage was varied from range 2.5 to 20 g/L at the condition of 120 min, pH 6.9, 160 RPM, room temperature. The speed of 140–220 RPM was varied at 120 min, pH 6.9, 10 g/L and room temperature. The temperature varied at the range of 298–318 K at 120 min, pH 6.9, 10 g/L and 1,450 RPM. The entire batch experiments were duplicated, and the average values were used for the emulsified oil removal calculation.

2.4. Determination of emulsified oil

The concentration of emulsified oil-in-water is analysed using spectroquant pharo 300 photometer at wavelengths between 200 and 350 nm. The solvent petroleum ether is used to extract oil, and the

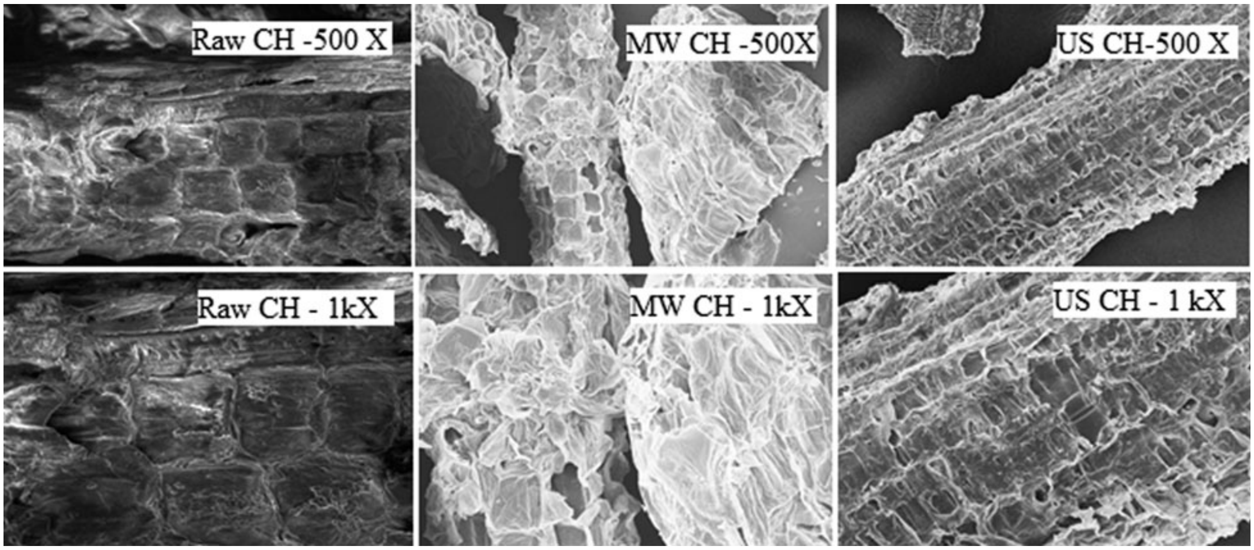

Fig. 2. SEM analysis of raw, MW (MW CH)- and US-assisted (US CH) at 500× (first row) and 1 k× (second row).

Table 2
Adsorbents characterization

Adsorbent	Raw CH	RS CH	MW CH	US CH
Surface area (m^2/g)	0.7877 ± 0.0069	1.0425 ± 0.0106	1.0390 ± 0.0092	0.6064 ± 0.0209
Pore volume (mL/g)	0.1809	0.2395	0.2387	0.1393
Pores size (Å)	989.641	1,013.356	1,027.034	1,008.209

concentration is analysed in spectrophotometer from the corresponding absorbance obtained in standard curve. The concentration is determined using Eqs. (1) and (2).

$$\text{Adsorption capacity } (\text{mg/g}) = (C_0 - C_t) \times \frac{v}{m} \qquad (1)$$

$$\text{Removal of emulsified oil } (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

where C_0 and C_t are initial and final concentration of emulsified oil at time t in mg/L, v is volume of oil-in-water in one litres, and m is the mass of the adsorbent in gm.

3. Results and discussion

3.1. Effect of contact time

The effect of contact time on removal of emulsified oil by raw, RS, MW, US and AC adsorbents conducted for 0–180 min is shown in Fig. 3.

It is distinct that the adsorption capacity increases with increase in contact time till saturation phase. The adsorbents chosen for the study show active rapid

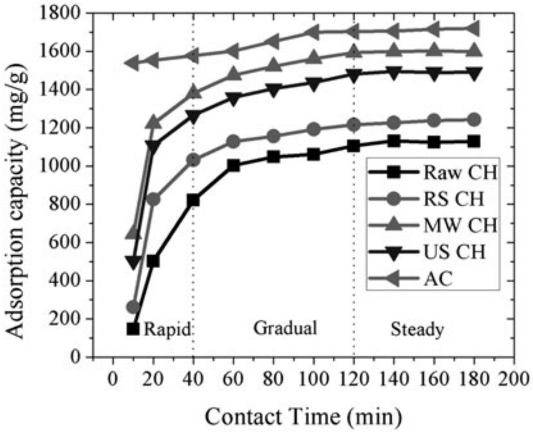

Fig. 3. Effect of contact time on adsorption capacity for raw, RS (RS CH)-, MW (MW CH)-, US (US CH)-assisted cornhusk and activated carbon at 6.9 pH, 10 g/L, 160 RPM and room temperature.

phase near 40 min and gradual phase near 100 min, and further increase in time leads to steady phase. The reason for active rapid phase is due to the availability of unoccupied bare sites on surface of the adsorbent. As the time increases, the availability of bare site decreases resulting in a moderate gradual phase and later reaches saturated steady phase. But from the obtained data, contact time is fixed as 120 min for remaining studies. There is noticeable difference in adsorption capacity of raw and rotatory shaker assisted adsorbent with other assisted techniques, MW, US and activated carbon. When compared to AC (1,698 mg/g) adsorption capacity, MW assisted adsorbent shows 1,561 mg/g, and US adsorbent gives 1,436 mg/g at 100 min. But between raw and RS adsorbents showed 1,060 and 1,192 mg/g are observed at transition from gradual to steady phase. The oil-holding capacity of MW assisted cornhusk is more than the US assisted cornhusk. The reason may be due to the difference in impact of microwaves and ultrasound waves on the adsorbent surface. Microwaves are reported to generate hot spots within the adsorbent, whereas ultrasounds creates hot bubbles which collapse on the surface, resulting in hot spots formation on the surface and making it porous [29]. So the chemical modification on the adsorbents with NaOH and cationic surfactant also varies because of exact inverse cause on and within the surface results in different effects on adsorption of oil molecules for MW and US assisted cornhusk. In RS, a kind of normal mixing takes place so the enhancement of NaOH and cationic surfactant on the surface of the adsorbent could be moderate. The results are found to be reliable for RS assisted adsorbent reported on removal of emulsified oil from SMO (standard mineral oil), CO (Canola oil) at 15 and 20 min by CPC modified barley straw [12]. The effect of microwave and ultrasound has been studied during adsorption process [21–27]; however, these results cannot be used for comparison, since MW and US has been used for the adsorbent modification process in this study.

3.2. Effect of pH

The effect of pH on adsorption capacity is examined at pH 2, 4, 6, 8 and 10 and presented in Fig. 4. The acidic and basic environment of the oil-in-water is adjusted using HCl and NaOH solutions. As the pH increases, adsorption capacity of raw, RS, MW, US-assisted cornhusk and AC decrease. The evaluated maximum capacity at pH 2 for AC, US and MW are 1,680, 1,618 and 1,658 mg/g, respectively. The acidic condition increases the capacity of reformed adsorbent to perform closer to untreated AC. The performance of MW assisted adsorbent is higher than the US assisted adsorbent. For raw and RS, adsorption capacity increase to 1,431 and 1,570 mg/g at 120 min. In this study, for the effect of pH, the performance of RS assisted is higher than raw. The acidic media triggers the interaction of oil molecules and cationic surfactant ions on the surface of the adsorbent. But the interaction varies with different modification of cornhusk. As discussed before, the interaction of surfactant on the adsorbent varies with effect of normal mixing without external force and with microwaves and ultrasound waves. So the adsorption capacity of adsorbent is in the order of AC < MW < US < RS < raw in both acidic and basic environment. Since adsorption capacity of AC is expected to be the best, the adsorption results of this study is compared with the unmodified AC, and as expected, AC is found to give the maximum adsorption. The reason for very less absorbability at the basic condition is that emulsified oil-in-water has undergone hydrolysis with addition of NaOH to produce fatty acids and glycerol which is having more solubility in water than in solvent [17]. In other way, the positively charged reformed adsorbent surface significantly attracts oil molecules due to electrostatic forces in acidic environment. As the pH of the solution increases, the number of negative sites increases, and these negative sites do not favour the adsorption of oil molecules due to electrostatic repulsion. The similar pattern is reported in the removal of dyes onto bagasse fly [30]. Hence, it is clear that the possibility of maximum adsorption occurs at acidic pH. The safest condition for the discharge is 6 to 9 as per central pollution control board norms in India, so neutral condition is maintained for further examination.

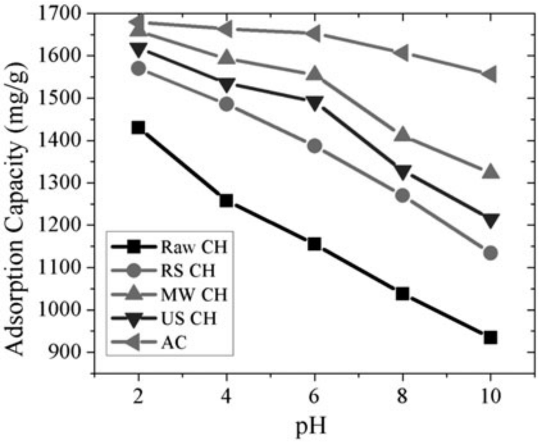

Fig. 4. Effect of pH on adsorption capacity for raw, RS (RS CH)-, MW (MW CH)-, US (US CH)-assisted cornhusk and activated carbon 120 min, 10 g/L, 160 RPM and room temperature.

3.3. Effect of dosage

Fig. 5 shows the effect of dosage on emulsified oil adsorption by raw and assisted adsorbents at 2, 5, 10, 15 and 20 g/L. The adsorption dosage pattern increases with increase in dosage up to certain limit, after which increase in dosage does not play role on adsorption. For this study, the initial concentration of emulsified oil-in-water is 17,384 mg/L for which 10 g/L is sufficient for maximum adsorption. At the dosage of 10 g/L, AC, US and MW showed 1,703, 1,467 and 1,573 mg/g adsorption capacity. Similarly, raw and RS also reflect the adsorption capacity of 1,148 and 1,204 mg/g. The increase in dosages increases the adsorption capacity due to the availability of more surface area for adsorption of emulsified oil. The details of the surface area, pore volume and pore sizes of raw, RS, MW and US are given in Table 2. It is observed from the table that surface area for MW and RS are closer, but the adsorption capacity of MW is higher than the RS assisted adsorbent because the pore size of MW is higher. This shows that pore size and pore volume play major role on adsorption along with the surface area. Unexpectedly, the surface area of US is lesser than raw, but pore size of US is higher. The reason may be due to that bubble collapses on the surface increase the pore size. The emulsified oil-holding capacity of US is extreme and equal to the MW assisted adsorbent which has higher surface area and pore size.

With the MW and US assisted techniques, adsorption capacity of emulsified oil hold-up by MW is higher than US, RS and raw adsorbent. The reason for higher adsorption hold-up for MW is due to higher surface area, pore volume and pore size. But, irrespective of the lesser surface area, pore size and volume, US could hold oil molecules more than RS and raw. Even though the RS assisted adsorbent shows good surface area, still the oil uptake by the adsorbent is lesser than the other assisted techniques and the reason may be due to week bonding of oil molecules on the modified surface of adsorbent. Altogether, the results match well with MW assisted cornhusk. The adsorption capacity also increases with increase in concentration due to decrease in resistance to the uptake of emulsified oil, and also, it is evident that higher percentage of removal is achieved with lower initial concentration of emulsified oil. The similar pattern of adsorption has been observation for palm oil mill effluent treatment by rubber powder [17].

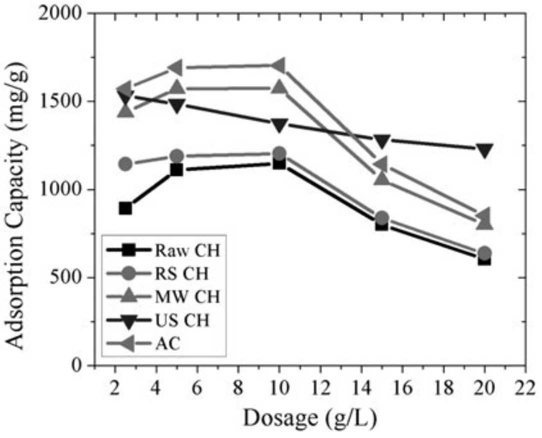

Fig. 5. Effect of dosage on adsorption capacity for raw, RS (RS CH)-, MW (MW CH)-, US (US CH)-assisted cornhusk and activated carbon 120 min, 6.9 pH, 160 RPM and room temperature.

3.4. Effect of speed

The effect of rotatory shaker mixing speed (140, 160, 180, 200 and 220 rpm) on emulsified oil adsorption capacity is examined and given in Fig. 6. As the batch process mixing speed increases, the adsorption capacity decreases except in MW up to 200 rpm and then started to rise from 220 rpm. But when compared to 140 rpm, the adsorption capacity is less for 220 rpm except US. The raw and RS assisted adsorbents show equal adsorption capacity at 140 and 180 rpm. But MW shows higher adsorption capacity at 140, 160 and 220 rpm than US assisted adsorbent. At 220 rpm, RS and US show similar adsorption capacity. The maximum adsorption obtained for raw, RS, MW, US and AC are 1,294, 1,302, 1,584, 1,435 and 1,685 mg/g, respectively, at 140 rpm. With reference to the earlier discussion made on effect of dosage, the oil-holding capacity of adsorbent is in the order of AC < MW < US < RS < raw. As described under the effect of contact time, hot spot generated interiorly in MW cornhusk, and hence, as the speed decreases, there is even distribution of oil molecules deep into the MW assisted adsorbent resulting in more oil uptake capacity than US, RS and raw adsorbent. At high speed till 200 rpm, there is possibility of dispersion of oil droplet back into the solution results in reduction in adsorption capacity due to weak bond of adsorbent and adsorbate. Surprisingly after 200 rpm, there is a slow rise in adsorption capacity of raw, RS and MW; this may be due to that maximum exposure of sites to oil molecules results in deep penetration into the adsorbent microspores. But still maximum adsorption capacity is observed at 140 rpm, so the lowest speed is preferred for maximum adsorption. Because at highest speed, there is a high possibilities of oil molecules to

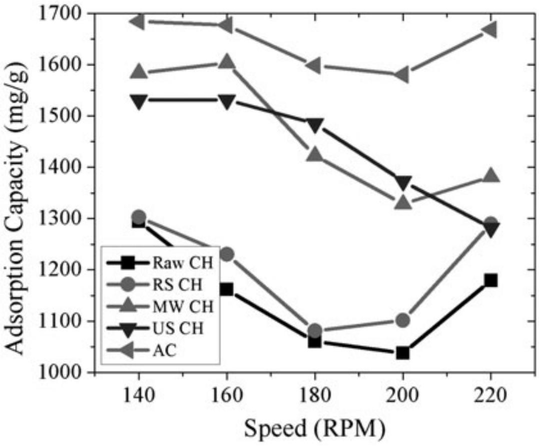

Fig. 6. Effect of speed on adsorption capacity for raw, RS (RS CH)-, MW (MW CH)-, US (US CH)-assisted cornhusk and activated carbon 120 min, 6.9 pH, 10 g/L and room temperature.

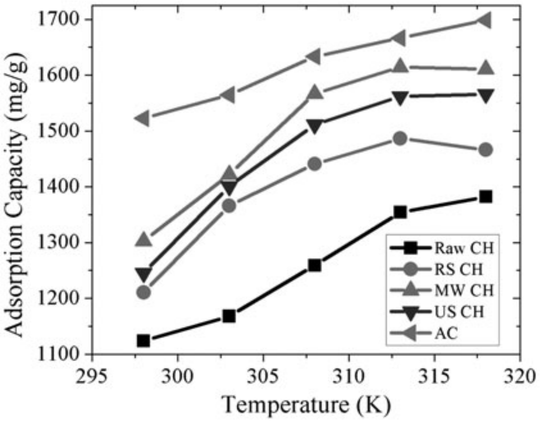

Fig. 7. Effect of temperature on adsorption capacity for raw, RS (RS CH)-, MW (MW CH)-, US (US CH)-assisted cornhusk and activated carbon 120 min, 6.9 pH, 10 g/L and 140 RPM.

get attached and diffuse at highest speed, and similar investigation has been reported in the removal of oil using rubber powder [19].

3.5. Effect of temperature

The impact of temperature on adsorption capacity is evaluated at 298, 303, 308, 313 and 318 K, and results are shown in Fig. 7. As the temperature increases, the capacity of adsorption also increases, but limited improvement in adsorption is observed after 313 K. The adsorption capacity of RS, MW and US is closer at 298 and 303 K, and the variation within the assisted adsorbent is of negligible amount. Then, after 303 K, each assisted adsorbent started to follow its own track after 308 and reaches almost saturation after 313 K. So optimized temperature is set as 313 K, and the adsorption capacity is found to be 1,667, 1,562 and 1,615 mg/g for AC, US and MW adsorbent, respectively. For raw and RS, the adsorption capacity is increased to 1,355 and 1,487 mg/g. The temperature of the solution plays a major role in molecular moments, which in turn increases the interaction between adsorbent and adsorbate [31]. Hence, increase in temperature increases the diffusion rate of oil molecules across the adsorbent surface. Among the assisted adsorbents, MW shows higher emulsified oil uptake than US. Similarly, between raw and RS assisted cornhusk, the performance of RS is higher than raw. The reason for MW assisted to be in lead may be due to the porosity created during chemical modification of adsorbent. The oil molecules were in motion as the temperature increased, resulting in good interaction and thus penetrate deep into the surface than on the surface. But the moment of molecules with in US assisted adsorbent must be lesser even though there is oil movement because the porosity started to generate from the surface of the adsorbent in chemical modification which has higher holding capacity on the surface and movement of the molecule is lesser than MW. The interaction between oil molecule and adsorbent is weaker for RS assisted adsorbent even though it has high pore volume and its adsorption capacity is lesser than MW, US and AC, but higher than raw.

Throughout the study on effect of contact time, pH, dosage and speed, the MW assisted cornhusk had shown performance closer to activated carbon than the US assisted, RS assisted and raw adsorbent. But the improvement in the performance of US assisted adsorbent increases drastically from 1,436 to 1,562 mg/g at condition optimized based on the parameters considered in this study, whereas MW assisted adsorbent showed adsorption uptake from 1,561 to 1,615 mg/g. For raw and RS adsorbent, the variations are from 1,060 to 1,355 and 1,192 to 1,487 mg/g, respectively. When compared between MW and US, MW assisted adsorbent oil uptake is maximum at the beginning, but US showed overall promising improvement with the effect of time, pH, dosage, speed and temperature. The emulsified oil adsorption capacity of raw and RS was also found to be improved at optimized condition.

3.6. Comparison of AC with reformed and raw adsorbent

The comparison of effect of contact time, pH, dosage, speed and temperature with activated carbon on removal of emulsified oil from synthetically prepared oil-in-water by reformed adsorbent and raw cornhusk is investigated. The reformed cornhusk by MW assisted adsorbent competes well with the activated carbon. The performance confirm that MW shows more adsorption capacity than US, RS and raw. Because microwaves interact directly with the adsorbent in NaOH, cationic surfactant solution exposed for modification provides quick volumetric heating, where huge thermal gradient from interior to the surface of the adsorbent allows microwave-induced reaction. This temperature gradient releases lighter components (volatile matters) in the particle and make it highly porous, thereby increasing the interaction of adsorbent with NaOH and cationic surfactant. The hot spot is generated inside the particle due to high temperature at the centre of the adsorbent in MW assisted treatment. But the difference of adsorption capacity between MW and US at 313 K is negligible after varying pH, dosage, speed and temperature. The combined effect of other parameters improved the performance of US assisted adsorbent equal to that of MW assisted adsorbent. Generally, ultrasound waves in solid and liquid medium attributes cavitation bubble collapses which generate extreme temperature and pressure around the solid–liquid interface [32]. These enhance the interaction of NaOH and surfactant on the adsorbent and clean up solid particles on the surface. The ultrasound waves is reported to disrupt the surface of the adsorbent and increase the adsorption capacity [33]. In FTIR analysis, the transmittance is in the order of US < MW < raw < RS, and these results show that the interaction of CPC, cationic surfactant with adsorbent due to US shows higher transmittance than MW assisted adsorbent. The reason may be due to that surface modification is highlighted than interior modification with MW. Similarly, the results of FTIR analysis for US, MW and RS and raw are closer, and it reflects in adsorption capacity of emulsified oil in entire study. The SEM images of US assisted adsorbents show ruptured and corroded surface at 500× and 1 k× magnification but at similar magnification, MW assisted cornhusk shows lesser disturbance on the surface and partially similar to raw adsorbent. This also proves that modification takes place on the surface and within the particles in US and MW and supports the results obtained in this study for adsorption capacity. The maximum adsorption for MW, US, RS and raw cornhusk could be obtained by maintaining the contact time at 120 min, pH near 7, dosage at 10 g/L, speed at 140 rpm and temperature at 313 K.

3.7. Kinetics study

It is well known that adsorption process is controlled by mechanisms such as mass transfer, diffusion control, chemical reaction and particle diffusion. In bulk diffusion, adsorption steps are assumed to be rapid and not rate-determining. But in batch reactor, bulk diffusion and adsorption steps are rate-limiting. The adsorption rate parameter is intra-particle diffusion in most of the contact time. In order to clarify the adsorption process, the experimental data are compared with first-order, second-order and intra-particle diffusion model in this study. The linearized forms of Lagergren first-order [34] and second-order model [35] are given as Eq. (3) and (4)

$$\log(q_e - q_t) = \log q_e - K_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t are the amount of emulsified oil adsorbed at equilibrium and time t in (mg/g) and $K_1$and K_2 are rate constant for pseudo-first-order and pseudo-second-order, respectively, in 1/min and g/mg min. The plot of log (q_e–q_t) vs. t and t/q_t vs. t gives K_1 and K_2 value.

Intra-particle diffusion [36,37] model proposed by Weber and Morris is given in Eq. (5):

$$q_t = k_{id} t^{1/2} + I \tag{5}$$

where k_{id} is the intra-particle diffusion rate constant (mg/g min^2), the plot of q_t vs. $t^{1/2}$ gives intercept I which indicates the thickness of the boundary layer effect, which is said to be prominent at MW and US assisted adsorbents, and the slope gives k_{id} value. The kinetics parameters for pseudo-first-order, pseudo-second-order and intra-particle diffusion models are presented in Table 3. The experimental q_e values for raw, RS, MW and US adsorbents match with pseudo-second-order calculated q_e values, which clearly supports that the kinetics favours pseudo-second-order model. The R^2 values remain close to unity for the same model. In case of intra-particle diffusion, I values is higher for MW and US, that is 1.271 and 1.272, hence the emulsified oil adsorption shows also higher values compared to raw and RS adsorbent irrespective of

Table 3
Kinetics parameters for the removal of emulsified oil from wastewater

	Parameters	Adsorbents			
		Raw	RS	MW	US
Kinetics model	$q_{e,cal}$	1.398	1.237	1.148	0.612
	K_1	0.017	0.020	0.018	0.008
	R^2	0.880	0.836	0.720	0.865
Pseudo-second-order	$q_{e,cal}$	1.769	1.748	1.589	1.607
	K_2	0.0002	0.027	0.178	0.171
	R^2	0.977	0.978	0.997	0.998
Intra-particle diffusion	I	0.243	0.407	1.271	1.272
	K_{id}	0.115	0.104	0.027	0.027
	R^2	0.978	0.963	0.978	0.947

surface area, pore volume and pore size. MW supported data in Table 2, but US assisted adsorbent shows the least of all the four adsorbent, but in case of oil uptake, the US is almost nearer to MW because *I* value is close to the MW assisted adsorbent. Similarly, RS adsorption capacity is higher than raw, and *I* values support the results.

3.8. Isotherms study

In fact, the dynamic separation of solute from solution depends on the equilibrium separation between two phases. The equilibrium is established when the amount of solute adsorbed is equal to the amount being desorbed. The quantity of solute taken by an adsorbent is a function of concentration of adsorbate and temperature. The amount of adsorbate is determined as the function of the concentration at constant temperature, and the resulting function is adsorption isotherms. Based on the assumption of monolayer adsorption, Langmuir isotherm is derived where there is no interaction between molecules adsorbed on adjacent site and expressed in Eqs. (6) and (7)

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \tag{6}$$

$$R_L = \frac{1}{1 + K_L C_0} \tag{7}$$

The Freundlich isothermal model is expressed as multilayer adsorption where interaction of adjacent molecules is possible on heterogeneous surface and given in Eq. (8).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{8}$$

where C_e is the concentration of adsorbate at equilibrium in mg/g, and q_0 and q_e are maximum amount of adsorbent adsorbed and at equilibrium in mg/g. K_L is the Langmuir's adsorption constant (L/mg). The R_L value of Langmuir isotherms confirms that the adsorption is in the favourable range if it lies between 0 and 1. K_F and n are the Freundlich constants if $n > 1$ indicate the favourability of the adsorption model.

Dubinin–Radushkevish (D–R) model [37,38] is used to estimate the adsorption energy and is shown in Eq. (9)

$$\ln q_e = \ln q_0 - K_{DR} \varepsilon^2 \tag{9}$$

where K_{DR} is sorption mean free energy mol^2/J^2 and ε is Polanyi potential derived from Eq. (10) and plot of ln q_e vs. ε^2 gives slope K_{DR} and intercept ln q_0.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

where R is gas constant (8.314 J/mol K) and T is the temperature in K. The mean free energy of adsorption is calculated by Eq. (11):

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{11}$$

Flory–Huggins model [38] estimates the degree of surface coverage of adsorbent by Eqs. (12) and (13):

Table 4
Isotherm parameters for the removal of emulsified oil from wastewater

		Adsorbents			
Isothermal model	Parameters	Raw	RS	MW	US
Langmuir	q_e	1.658	1.814	1.988	1.912
	K_L	0.067	0.062	0.057	0.042
	R^2	0.992	0.982	0.974	0.980
	R_L	0.587	0.605	0.626	0.694
Freundlich	n	0.6329	0.458	0.274	0.440
	K_F	−2.253	−1.966	−1.692	−1.650
	R^2	0.990	0.978	0.974	0.947
Dubinin–Radushkevish	K_{DR}	−0.049	−0.060	−0.067	−0.049
	q_0	0.359	−0.294	−0.238	−0.244
	R^2	0.961	0.947	0.946	0.947
	E	0.03	0.042	0.047	0.034
Flory–Huggins	α_{FH}	−1.332	−1.342	−1.445	−1.373
	K_{FH}	0.478	0.527	0.591	0.543
	R^2	0.998	0.997	0.996	0.997

Table 5
Error analysis for pseudo-second-order kinetics

Kinetics model	$q_{e,exp}$ mg/g	$q_{e,cal}$ mg/g	K_2	r^2	γ^2
Raw	14.57	17.85	0.002	11.758	0.603
RS	14.98	17.54	0.002	7.554	0.374
MW	15.53	15.87	0.221	1.116	0.007
US	15.80	16.12	0.017	1.102	0.006

$$\log\left(\frac{\theta}{c_e}\right) = \log k_{FH} + \alpha_{FH} \log\,(1-\theta) \tag{12}$$

$$\theta = \left(1 - \frac{C_e}{C_i}\right) \tag{13}$$

where θ is degree of surface coverage, α_{FH} is number of adsorbents occupied in adsorption sites, k_{FH} is the equilibrium constant of adsorption, and plot of log (θ/c_e) vs. log ($1-\theta$) gives slope α_{FH} and intercept k_{FH}.

The parameters of Langmuir, Freundlich, Dubinin–Radushkevish and Flory–Huggins are given in Table 4. The R^2 value of the isotherms is near unity. The R_L value of Langmuir for raw, RS is between 0 and 1 which represents the favourability. In Freundlich model, value shows the heterogeneity of the adsorbent surface, and it is less for MW reformed adsorbent than US and RS reformed adsorbent. The adsorption energy K_{DR} is estimated using Dubinin–Radushkevish, and it lays below 40 (for all the four adsorbent) indicating that physic-sorption process has taken place. In Flory–Huggins model estimates, the degree of surface coverage of adsorbent is in the order of MW < US RS < raw, which supported experimental data, α_{FH} represents the occupied molecules on the surface, which shows that high value for MW and the adsorption capacity is also higher for MW assisted adsorbent.

3.9. Error Analysis

The error analysis test [39] is used to compare the adequacy of model quantitatively by coefficient of determination (r^2) and the chi-square value (γ^2), and it is given in Eqs. (14) and (15):

$$r^2 = \frac{(q_{e,mea} - \overline{q_{e,cal}})^2}{(q_{e,mea} - \overline{q_{e,cal}})^2 + (q_{e,mea} - q_{e,cal})^2} \tag{14}$$

$$\gamma^2 = \sum \frac{(q_{e,mea} - q_{e,cal})^2}{q_{e,cal}} \tag{15}$$

where $q_{e,mea}$ and $q_{e,cal}$ are measured and calculated adsorbent concentration at equilibrium in mg/g and

$\overline{q_{\mathrm{e,cal}}}$ is average of calculated $q_{\mathrm{e,cal}}$ values. Table 5 shows the error analysis for pseudo-second-order kinetics which supports $q_{\mathrm{e,exp}}$. The r^2 values are used to select the best-fit and γ^2 for comparison. When r^2 is considered, MW, RS and raw follow US adsorbent. Among the adsorbent chosen, MW shows more fitness. When compared with γ^2 values, MW and US are very less, indicating more competence. Therefore, r^2 and γ^2 found to go hand in hand. In case of assessment of $q_{\mathrm{e,exp}}$ and $q_{\mathrm{e,cal}}$ values, MW shows 99.66% adjacency and sustains the pseudo-second-order kinetics model more than other adsorbent.

4. Conclusion

The investigation on the removal of emulsified oil from water was carried out using reformed adsorbent techniques. The investigation exhibited the following promising results:

(1) The MW assisted cornhusk shows higher adsorption capacity than US, RS assisted and raw cornhusk. However, under selective condition of 120 min, neutral pH, 10 g/L, 140 rpm and 313 K, the emulsified oil uptake efficiency improvement is noticed for raw, RS, US and MW assisted adsorbent.

(2) The experimental data fit the pseudo-second-order kinetics and favour Freundlich isotherms. The boundary layer thickness value of intraparticle diffusion and degree of surface coverage of the adsorbent of Flory–Huggins model supported the order of experimental adsorption capacity: AC < MW < US < RS < raw. The adsorption taken place is physi-sorption is confirmed through Dubinin–Radushkevish model.

(3) The error analysis for MW and US is found to be closer in pseudo-second-order kinetics model.

List of symbols

C_0 — initial concentration of emulsified oil (mg/L)
C_{t} — concentration of emulsified oil at time t (mg/L)
v — volume of oil-in-water (L)
m — mass of the adsorbent (gm)
q_{e} — amount of emulsified oil adsorbed at equilibrium (mg/g)
q_t — amount of emulsified oil adsorbed at time t (mg/g)
K_1 — Pseudo-first-order rate constant (L/min)
K_2 — Pseudo-second-order rate constant (g/mg min)
k_{id} — intra-particle diffusion rate constant (mg/g min^2)
I — thickness of the boundary layer (mg/g)
K_{L} — Langmuir's adsorption constant (L/mg)
R_{L} — equilibrium parameter or separation factor
K_{F} — multilayer adsorption capacity (mg/g)
$1/n$ — arbitrary constant
K_{DR} — sorption mean free energy (mol^2/J^2)
ε — Polanyi potential
R — gas constant (J/mol K)
T — temperature (K)
E — mean free energy (KJ/mol)
θ — degree of surface coverage
α_{FH} — number of adsorbents occupied on adsorption sites
k_{FH} — Flory–Huggins equilibrium constant
r^2 — coefficient of determination
γ^2 — chi-square
$q_{\mathrm{e,mea}}$ — measured adsorbate concentration at equilibrium (mg/g)
$q_{\mathrm{e,cal}}$ — calculated adsorbate concentration at equilibrium (mg/g)

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