



Removal of solids from surfactant wastewater through synergetic utilization of *Strychnos potatorum* and *Colocasia esculenta*

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ABSTRACT

The presence of surfactants typically found in laundry discharge poses a serious threat to aquatic niche when let out in open water bodies. In the present study, activated carbon produced from a novel source, *Colocasia esculenta* has been suggested as adsorbent to trap turbid colloids present in the surfactant wastewater. A synthetic wastewater was prepared by spiking kaolin in aqueous solution for different concentrations and the adsorption studies have been conducted. The carbon has been modified into carbon – sodium alginate bead complex and the operating parameters like pH, adsorbent dosage and its contact time under different concentrations have been optimized. The maximum equilibrium uptake capacity of 2.067 mg/g was achieved at 60 min with adsorbent dosage of 1.5 g conducted in neutral pH. Langmuir and Freundlich models were used to predict the reaction kinetics and it was hypothesized that multi-layer physisorption is predominant at higher concentrations. *Strychnos potatorum*, a common household bio-coagulant has been suggested in the continuous mode process designed specifically to treat the discharge form laundry. The total dissolved solids present in the wastewater has been reduced from 168 ppm to 12 ppm with a total reduction of 92.86%, while the turbidity has been reduced from an average 132 NTU to 10 NTU.

Keywords: *Strychnos potatorum*; *Colocasia esculenta*; Surfactant wastewater; Adsorption; Turbidity

1. Introduction

Water is the most essential component of life and is vital for sustenance. Even though oceans cover about 71% of the earth's surface, very less quantity of water is available to meet daily needs of nearly seven billion people and millions of other species. Purity of water directly affects health, hence it is essential to consume potable water. In the rustic areas of various countries, people use groundwater as a source of drinking water as it only requires slight treatment. In the case where no appropriate aquifer is available, clean water from water bodies like lakes are consumed. With growing industrialization, urbanization and water scarcity, it has become necessary to treat wastewater and use it. There are many industrial processes that

utilize huge amount of water for its processing needs. Nowadays, the stringent environmental regulations envisaged by the pollution control boards helps in combating the usage of clean water and its reuse [1]. Often the industrial plants have in-house recycling plants thereby reducing the dependence of clean surface water for their consumption. On the other hand, domestic utilization of clean water for day-to-day needs have a phenomenal impact if goes unchecked. Utilization of clean water for laundry is one such area where the water consumption is high with no real in-situ treatment methodologies available at present. The contaminants which are present in the laundry discharge wastewater are in the colloidal form and do not settle immediately [2]. These particles provide color and turbidity to the water sample, and cannot be removed by sedimentation process [3]. Some of the

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common compounds present in the laundry discharge are alcohol ethoxylate – removes greasy stains, alkyl/benzene sulfonate – removing stains, carboxymethyl cellulose – prevents relapse of stains, citric acid – removes bad odor from clothes, hydrogen peroxide – bleaching agent, monoethanol amine – neutralization agent and poly ethylene glycol /oxide – lubricant and surfactant [4]. The presence of these compounds pose a serious risk to the ecological niche if let out without prior treatment. Apart from surfactants, recent development in the detergent industry is the utilization of micro-plastics to combat oil and grease stains. The micro plastics are non-biodegradable and difficult to treat due to its microstructure [5]. These plastics pose a serious hazard to the aquatic life if consumed. Micro-plastics have low specific gravity and no residual charge around them, hence difficult to devise a coagulation and sedimentation process. But, the pertinent problem that exists in surfactant water treatment is the turbidity variation. Turbidity is proportional to the amount of total suspended solids in the water [6]. Greater the quantity of suspended solids in water, higher will be the turbidity. The presence of phosphates in the water bodies promotes eutrophication thereby blocking the dissolution of atmospheric oxygen in to the stream. This also leads to blockade of sunlight thus restricting the growth of aquatic life. Therefore, it is imperative that the turbidity in the wastewater be treated before letting out in open water stream.

The efficiency of any treatment process depends on the cost, availability and applicability of chemicals and re-utilization of effluent. Chemical coagulants like alum, ferric chloride and poly aluminum chloride are extensively used in the water treatment plants which generate huge amount of sludge and quite expensive [7]. Sludge dewatering, handling and disposal become difficult if the daily operating volume is high. In recent studies, plant based bio-coagulants are being reported for their high coagulation capacities. The 4 major plant-based coagulants that are studied extensively are - *Strychnos potatorum*, *Moringa Oleifera* [8], Tannin and Cactus. To completely comprehend on how to utilize natural coagulants, it becomes essential to understand the coagulation mechanisms of these coagulants. Coagulation mechanism can be broadly classified into four types. The 4 types are double layer compression, sweep flocculation, adsorption and charge neutralization, and adsorption and inter-particle bridging. In the first type, coagulants compress the double layer which leads to suspended particulate destabilization, whereas in the second type, coagulants enclose the suspended flocculates in a colloidal floc. In the third type, simultaneous absorption and adsorption of particulates with oppositely charged ions take place, whereas in the fourth type, coagulant provides polymeric chain. In the inter-particle bridging mechanism, polymeric coagulants play a fundamental role. Since polymeric coagulants with high molecular masses are long chained structures, they greatly increase the number of adsorption sites. These two adsorption mechanisms coupled with charge neutralization and inter-particle bridging mechanism help in understanding the working of natural coagulants. Moreover, the dependence and utilization of activated carbon in water

treatment has grown in manifold [9]. The raw materials required for activated carbon always decide the efficiency of the carbon produced apart from the activation atmospheric conditions. Even though there have been many activated carbon sources, identifying a local yet cheap raw material is a constraint. In the present study, *Colocasia esculenta* is selected as the source for activated carbon for which the adsorption parameters are studied.

The main objective of this study is to devise a continuous method of treatment for the removal of sulfates from surfactant rich laundry wastewater by using *Strychnos potatorum* seeds and activated carbon from *Colocasia esculenta*. The operating parameters like pH, dosage, contact time and turbid concentrations were varied and optimized for maximum removal efficiencies for synthetic wastewater. The kinetic parameters were established using Langmuir and Freundlich models. A low-cost continuous mode system was developed to treat the turbidity and reduce TDS levels from the surfactant wastewater.

2. Materials and methods

2.1. Preparation of activated carbon beads

The stem of *Colocasia esculenta* plant was chosen as the raw material for the preparation of activated carbon. The collected stem was dried in sunlight for 7 days and the top epidermal layer was scrapped, cleaned and cut in to pieces of 1.5–3 cm length. Concentrated H_2SO_4 (1:1 w/v) was used as charring agent for a contact time of 30 min. Subsequently, the charred stems were washed with distilled water until the pH of wash water becomes neutral. The stems were oven dried at $110^\circ C$ for 48 h to remove the surface and interstitial moisture [10]. They were then crushed and sieved through 100 micron size to present a homogenous blend. The powdered material was preheated in muffle furnace at $450^\circ C$ for 2 h and finally activated at $800^\circ C$ for 1 h. The activated carbon thus produced was utilized for the preparation of alginate - carbon beads through ionic polymerization route. 2.4 g of sodium alginate powder and 1.8 g of the prepared powdered activated carbon were mixed in 100 mL of distilled water and rapidly homogenized to present a clear suspension. The mixed solution was then dropped into a beaker containing 2% $CaCl_2$ solution from a height of 500 mm to form droplets of alginate beads. The beads were then separated from the decanted $CaCl_2$ solution and washed with distilled water [11]. The activated carbon beads were stored in double distilled water to prevent the time bound degradation of alginate complex.

2.2. Preparation of kaolinite clay

Homogenous powdered kaolin clay was procured from Loba to prepare kaolinite blocks. Double distilled water was added to the kaolin powder (1:2 w/v) so that a consistent paste was obtained. Small blocks of size 25 mm × 10 mm × 10 mm were made and dried in oven for 12–24 h so that moisture is removed (preheated). The blocks were subjected to a process called glazing which prevents the rehydration of clay when it comes in contact with water during

adsorption. The kaolinite blocks weighing 160 g were then kept in an Ashing furnace with high temperature and abrasion resistant silica crucible and the temperature was set at 900°C with heating rate of 16°C/min. The kaolinite blocks were held at this temperature for 1 h. The final weight of sample was measured to indicate a 31.81% of weight reduction which was attributed to the evaporation of surface and interstitial moisture. This step is carried out to prevent the rehydration of clay when it comes in contact with water during adsorption.

2.3. Preparation of *S. potatorum* seeds

The *S. potatorum* seeds used in this present study were procured from local agricultural stores in Tiruchirappalli, India. The seeds were primarily washed to remove any pre-existing dirt and impurities on the surface. The Sp. seeds were then dried in sunlight for three days and oven dried at 110°C for 24 h to remove any interstitial moisture present. The seeds were subsequently crushed using proctor compaction equipment and sieved under various sieve sizes of 10 mm, 4.75 mm, 2.36 mm, 1.18 mm and 600 micron to estimate the overall gradation of the Sp. seeds under impact loading. Since the effect of Sp. powder over turbidity removal has already been studied [2], the present study incorporates the utilization of Sp. seeds as a whole and it is suspended in wastewater. The seeds are tied and wrapped in a muslin cloth and suspended in the contact time wherein the biomass is leached in to the turbid wastewater housed in an earthen clay pot. The perception of utilizing earthen clay pot was derived from ancient water treatment techniques employed in the rural villages wherein the Sp. seeds were scratched in the interior portion of the clay pot and the drinking water is collected and stored. Upon sufficient contact time, the impurities settle at the bottom of pot and thus the turbidity is removed. A similar hypothesis is delineated in this experiment to remove partial turbidity from the washing machine wastewater with the help of Sp. seeds suspended in the sedimentation chamber.

2.4. Washing machine water discharge collection

An 8-kg semi-automatic washing machine generating around 50–60 L of wastewater was used as the single point source for sampling. The average turbidity varied

around 128–136 NTU due to the fluctuation of parameters like type and number of clothes, dosage of detergent and influent water characteristics. The cloudy precipitate-like effluent from the machine can be attributed to the surfactants reaction with the chloride-ions present in the water thus requiring a pre-treatment like adsorption, coagulation and sedimentation for removing turbidity. The wastewater was subjected to a range scan in the UV spectrophotometer (Lambda 45, Perkin Elmer) to determine the dominant wavelength.

2.5. Preparation of synthetic turbid wastewater

To determine and optimize the removal efficiency of activated carbon and Sp. seeds, varying concentrations turbid water samples are required. Therefore synthetic samples were prepared at different concentrations viz. 50, 80, 110, 125 and 145 NTU as per the procedures laid out in previous studies [2].

2.6. Sorption experiments

The removal of turbidity by Sp. seeds has been optimized between 65–84% for both synthetic and washing machine effluent in the pH range 6–7 [2]. The present study focuses on utilizing Sp. seeds as whole within the same range of synthetic water as per previous studies. The water absorption of Sp. seeds was tested under varying pH conditions from 2 to 12 to determine their stability under corrosive environment. The zero point charge (pH_{zpc}) of the seeds were also computed which helps in identifying the surface charge of the seeds. The adsorption on CEAC (*Colocasia esculenta* activated carbon) has been optimized by varying pH, dosage of the carbon and contact time with synthetic turbid water. The sorption experiments were conducted in 100 mL Erlenmeyer flasks by taking 25 mL of synthetic turbid wastewater at room temperature i.e. $30 \pm 2^\circ\text{C}$. The adsorbent dosages were varied through 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g. The pH was varied from 2 to 11 while the contact time of the adsorbent was varied till 120 min. the adsorbate was subsequently removed from the industrial grade shaker and transferred in a 50 mL centrifuge tubes and centrifuged at 5400 rpm for 10 min so as to separate the carbon from the solution. The absorbance values were measured through spectrophotometer at λ_{max} - 301 nm and the removal efficiency was computed as per Eq. (1). The final

Table 1
FTIR Spectra of adsorbent before and after adsorption

Functional groups	Bands (cm^{-1})	FTIR Spectrum			
		SP	SSP	AC	SAC
Alcohol O-H stretch	3500–3150	3306	3341	–	–
C=C alkene, N-H amide	1675–1625	1618	1636	1577	1566
	1600–1550				
	1500–1450				
Alkoxy C-O	1150–1000	1019	1035	1105	1109
Aromatic sp^2 C-H bend	920–600	–	–	665	668

turbidity values were computed using the calibration curve (not shown) plotted with respect to the absorbance values and the optimized values were reaffirmed by measuring the supernatant with the nephelometer.

2.7. Continuous mode setup

A continuous mode was designed to remove the turbidity of the surfactant containing washing machine wastewater. The powdered activated carbon prepared from *Colocasia esculenta* was filled for 1/3 of the total length of the glass column. A layer of glass wool was kept on either side so as to prevent leaching of carbon. A microprocessor based peristaltic pump with variable flow rate of 100 to 5000 ml/min operating at 5–75 RPM is used to pump the influent wastewater to the glass column of 20NB dia and 300 mm long. The treated supernatant is passed through kaolinite blocks filled up to 1/5th height of the filter column. This column has two different filter media consisting of the alginate beads prepared from the CEAC activated carbon and a rapid sand filter column. The carbon - alginate beads are imperative to the continuous mode operation: a) the turbid and carbon leaching are blocked and absorbed b) the flow into the sand filter is equalized. The rate of filtration is kept at 10–25 ml/min and the filter sand conforming to Appendix 7.8, CPHEEO manual - Water supply and treatment. The beads and the filter sand were separated with a layer of glass wool to prevent contamination of the beads. The filtrate from the sand filter is allowed to collect in a bio-coagulation chamber where the *Strychnos potatorum* seeds are suspended in the muslin cloth till 2/3rd the depths of the chamber. A 2 LPM aerator is operated in the bio-coagulation chamber for continuous contact of the Sp. Seeds with the wastewater. Since the detergent wastewater is highly odour in nature, a high rate homogenizer was operated at 11000 RPM in a separate ORC - odour removal chamber. The supernatant from the ORC is pumped to a glass filter column of 50 NB dia and 1000 mm long. The column is filled with diatomaceous earth for height of 200 mm with glass wool at the bottom to prevent clogging of the pump. The filtrate is passed through a helical glass column of 20NB dia and length 250 mm fitted in a photo-degradation chamber of 300 mm × 450 mm × 400 mm. The chamber is designed to produce a luminous intensity 4000–7000 lux with the help of CFL bulb. The photo-degradation chamber aims in removing bacterial and other pathological microbes thereby sterilizing through concentrated photons. The heat generated due to tight constricted nature of the coils also helps in disinfecting the filtered water. The collected final effluent is tested for different physico-chemical parameters and the results are compared with previous studies to draw comparison on the efficiency of the treatment process.

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR) studies

The functional groups present in the activated carbon - CEAC, Sp. seeds before and after contact with the surfactant wastewater have been identified through FTIR - Perkin Elmer in the range 4000–400 cm⁻¹. The functional

groups present in the biomass were categorized based on their respective peak positions in the spectrum [12]. A broad range of functional groups can be associated with specific peak bandwidths hence it is important to identify the groups based on the raw material biomass [13]. The variation in the peak intensity and the peak positions of the adsorbent can substantiate the underlying complexion of the adsorption process [14]. The FTIR was performed for *Strychnos potatorum* seeds before and after contact with the washing machine water. The FTIR spectrum for the Sp. seeds reflects peak resolved at 3306 cm⁻¹, 2923 cm⁻¹, 1618 cm⁻¹ and 1019 cm⁻¹ as shown in Fig. 1a. The peak at 3306 cm⁻¹ corresponds to the hydroxyl group while the peak at 1019 cm⁻¹ conforms to presence of alkoxy C-O based compound. Now, the peak at 1618 cm⁻¹ can reflect either the presence of C=C alkene group or an N-H amide related compound. Similarly the spectrum of seeds that were in contact with the wastewater showed peaks at 3341 cm⁻¹, 1636 cm⁻¹ and 1035 cm⁻¹. It can be understood that the shift in the peak positions were minimal and belonging to the same functional groups indicating that the surface morphology of the seeds have not been altered post contact with the wastewater. Similarly, the FTIR peaks (Fig. 1b) resolved for the activated carbon at 1577 cm⁻¹, 1109 cm⁻¹, 665 cm⁻¹ and 594 cm⁻¹ indicated the presence of N-H amide, an alkoxy C-O and an aromatic sp² C-H bond type organic hydrocarbon in them. The turbid fragments present in the wastewater gets attracted towards the surface of the activated carbon through physical adsorption and it is reflected in the reduction in peak intensities with virtually no changes in the peak position. This illustrates that physical adsorption is predominant with the activated carbon. From the FTIR peaks of the activated carbon after its contact with the wastewater, it was also evident that only the sodium and sulfonate salts present gets adsorbed in their interstices and the bigger turbid like particles gets clogged in between the carbon powder.

The Sp. seeds and the activated carbon were analyzed for the morphological changes on their surface by JEOL Model JSM - 6390LV make scanning electron microscopy (SEM) under different limit of resolutions. The SEM image of Sp. seeds (Fig. 2a) show fragmented surface while the spectroscopic image of activated carbon (Fig. 2b) shows the presence of pores that are required for the adsorption of turbid particles. The SEM images of both Sp. seeds (Fig. 2c) and the carbon (Fig. 2d) after contact with the wastewater shows appreciable morphological change through the presence of disintegrated particles over the surface. It is noted that the SEM images can only indicate the visible changes in the morphology in case of any chemical or biological metamorphosis due to the contact with wastewater and therefore should be studied and analyzed along-with IR spectrums to understand the nature of sorption.

3.2. Physical characteristics of Sp. seeds

The efficiency of the seeds in turbidity removal is studied by virtue of their innate physical characteristics. The surface ruggedness, durability of the seed's core cellulosic structure and the water holding capacity of the seeds illustrate the ability of its bio-coagulation. The crushing strength determines the rigidity thereby indicating that the seeds

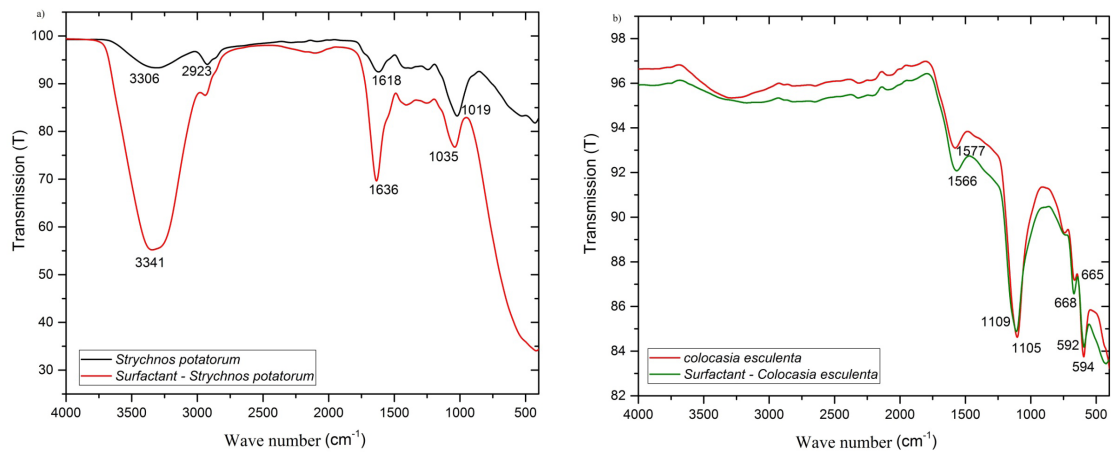


Fig. 1. FTIR peaks for: (a) *Strychnos potatorum* seeds and surfactant wastewater (b) *Colocasia esculenta* activated carbon and surfactant wastewater.

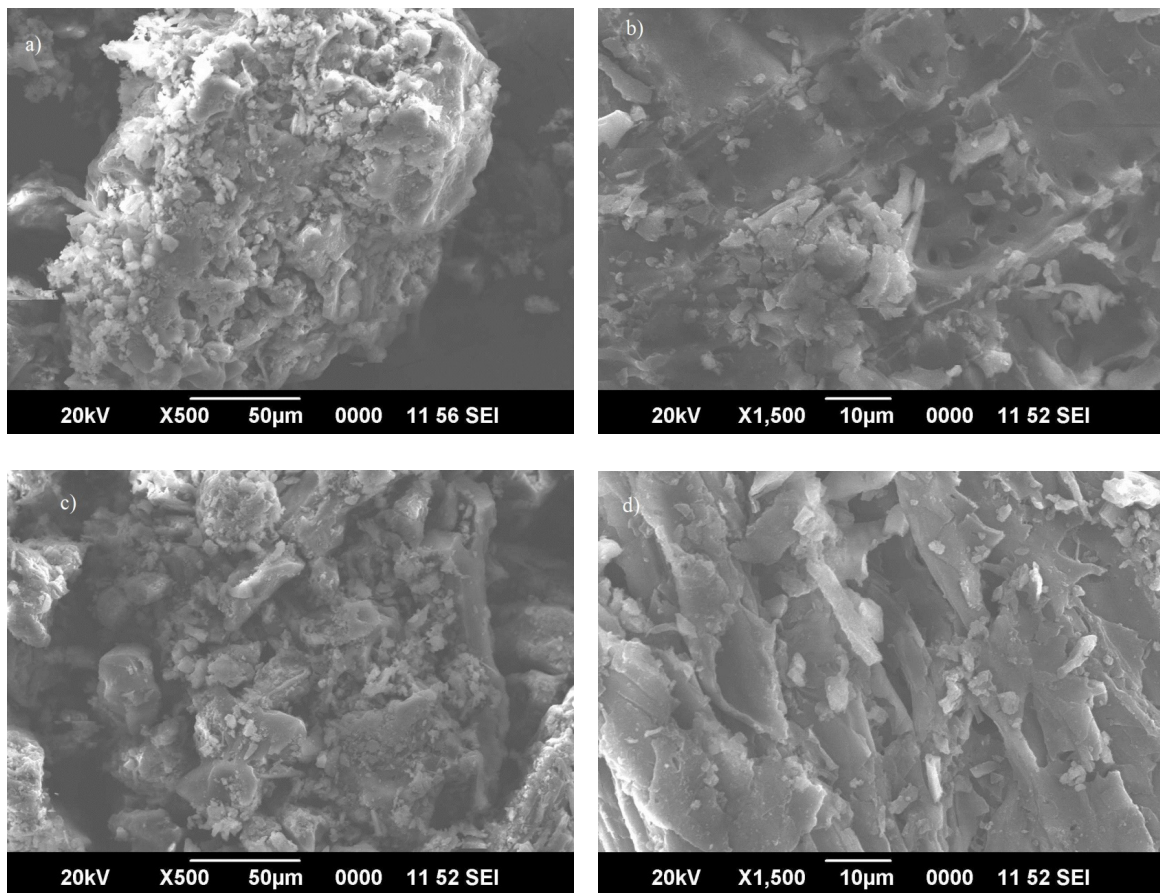


Fig. 2. SEM image of (a) *Strychnos potatorum* (b) *Colocasia esculenta* activated carbon (c) Surfactant – Sp. seeds (d) surfactant activated carbon.

may be tolerable for heavy and rough handling during logistics in the treatment plants. Since the seeds are naturally grown and cannot be controlled for their sizes, a preliminary gradation called particle size analysis is taken up. Prior to the sieve study, the seeds were washed gently and oven dried at 60°C for 24 h. The seeds were then crushed

in impact testing machine which are specifically designed for determining the strength of coarse aggregates in concrete. The crushed seeds were passed in different sieve sizes ranging from 10mm to 600 micron and the weight retained in each sieve is measured and tabulated (Table 2). From the results it can be observed that 10.38% of total weight

Table 2
Particle size analysis of Sp. seeds

Sieve Size	Weight retained (g)	Percentage mass retained (%)	Cumulative percentage retained (%)	Cumulative percentage passing (%)
10 mm	25.1 g	10.38	10.38	89.62
4.75 mm	198.3 g	82.01	92.39	7.61
2.36 mm	2.3 g	0.95	93.34	6.66
1.18 mm	4.9 g	2.03	95.37	4.63
600 micron	6.2 g	2.56	97.93	2.07
Pan	5 g	1.99	99.92	0.08
Total weight	241.8 g	–	–	–

is retained in 10 mm sieve while a maximum of 82.01% is retained 4.75 mm with a cumulative of 93.34% shared between 10 mm, 4.75 mm and 2.36 mm particle sieve sizes. This indicates that the seeds are sturdy in nature thus capable of handling impact loads. The higher retention in 4.75 mm sieve also peripherally indicates that the seeds can be subjected to being suspended in wastewater as a whole. Therefore it is imperative that the seeds are to be tested for their in situ moisture content. This implicates the amount of the moisture that the seeds can trap inside them based on the atmospheric conditions. This data is utilized extensively when calculating the dosage of seeds required per litre of wastewater to be treated so that appropriate weight corrections can be implemented. For the experiment to be carried inconspicuously, 25 seeds of varying dimensions were taken and the initial weight of 15.9 g was noted. Subsequently, the seeds were kept in oven for 24 h to remove the moisture present in them. The dried seeds were again weighed for the final dry weight of 13.7 g with the moisture content computed at 13.8%. It is to be noted that this moisture content is variable based on the surface area of the seeds and the cell wall matrix that absorbs moisture from the atmosphere.

In order to compute the water absorption of the seeds based on the solute characteristics, a pH based water absorption method is devised. 25 mL of pure distilled water is taken in 6 Erlenmeyer flasks and their pH is varied via 2–12. One seed of uniform dimensions are suspended in each flask for 24 h and their final weights are noted after 24 h. The experiments are performed in triplicate and the average values are reported (Table 3). From the results it should be observed that the water absorption increases as a general trend with respect to the increase in pH scale. This suggests that the presence of excess OH⁻ ions in the system aids in increasing the water holding capacity of the seeds. Previous literature studies reveal that the OH⁻ ions in the aqueous solution softens the cell wall surface thereby allowing water to percolate inside the seeds [6]. Therefore, it is essential to find the nature of the surface of the seeds that are suspended in the wastewater. The zero point charge of the seeds based on variable pH helps in understanding its ionic attributes. The surface charge of the seeds and their capacity to attract any specific nature of impurities can be determined through this zero point charge method. Here, 50 ml of 0.01 M NaCl solution was taken in 6 different 100 mL conical flasks and the pH was adjusted from 2–12 using 0.1 M HCl/NaOH solution. One homogenous Sp. seed of uniform dimension

Table 3
Water absorption of Sp. seeds under variable pH conditions

pH	Dry weight (in g)	Wet weight (in g)	Percentage absorption
2	0.611	0.836	36.82
4	0.637	0.770	20.87
6	0.633	0.836	32.06
7	0.630	1.151	45.26
8	0.665	1.232	85.23
10	0.743	1.274	71.47
12	0.724	1.306	80.40

is suspended in each flask and the contents were shaken in temperature controlled incubating shaker at 30±2°C at 150 RPM for 24 h. The final pH of each flask was measured after discarding the Sp. seeds. The pH_{zpc} was then obtained by plotting a graph between the initial and final pH (figure not shown) and the intersection point at 7.8 was interpreted as the pH_{zpc} of the surface of Sp. seeds. The pH_{zpc} indicate the presence of OH⁻ ions more than equilibrium suggests a slight affinity of the seeds for attracting impurities with a mild +ve charge.

3.3. Adsorption studies for CEAC

3.3.1. Optimization of adsorption parameters

The activated carbon beads prepared from *Colocasia esculenta* is studied for its adsorption efficiency by varying the operating parameters involved in the sorption. The synthetic wastewater prepared from kaolin under various concentrations ranging 50, 80, 110, 125 and 145 NTU. The general assumption of utilizing synthetic wastewater is to mimic the turbidity and to study the adsorption of kaolin like colloidal particles onto CEAC beads. The effect of pH on the sorption system was studied in the pH range 2–11 and depicted as shown in Fig. 3a. It can be observed that the amount of the removal of the kaolin colloids from the system increased from 54.6% to 83.2% with respect to increase in pH scale from 2 to 6. Subsequently, the removal dropped to 33.8% at pH=11 indicating the beads' decreased operating efficiency at basic pH scale [15]. The pH_{zpc} of the beads

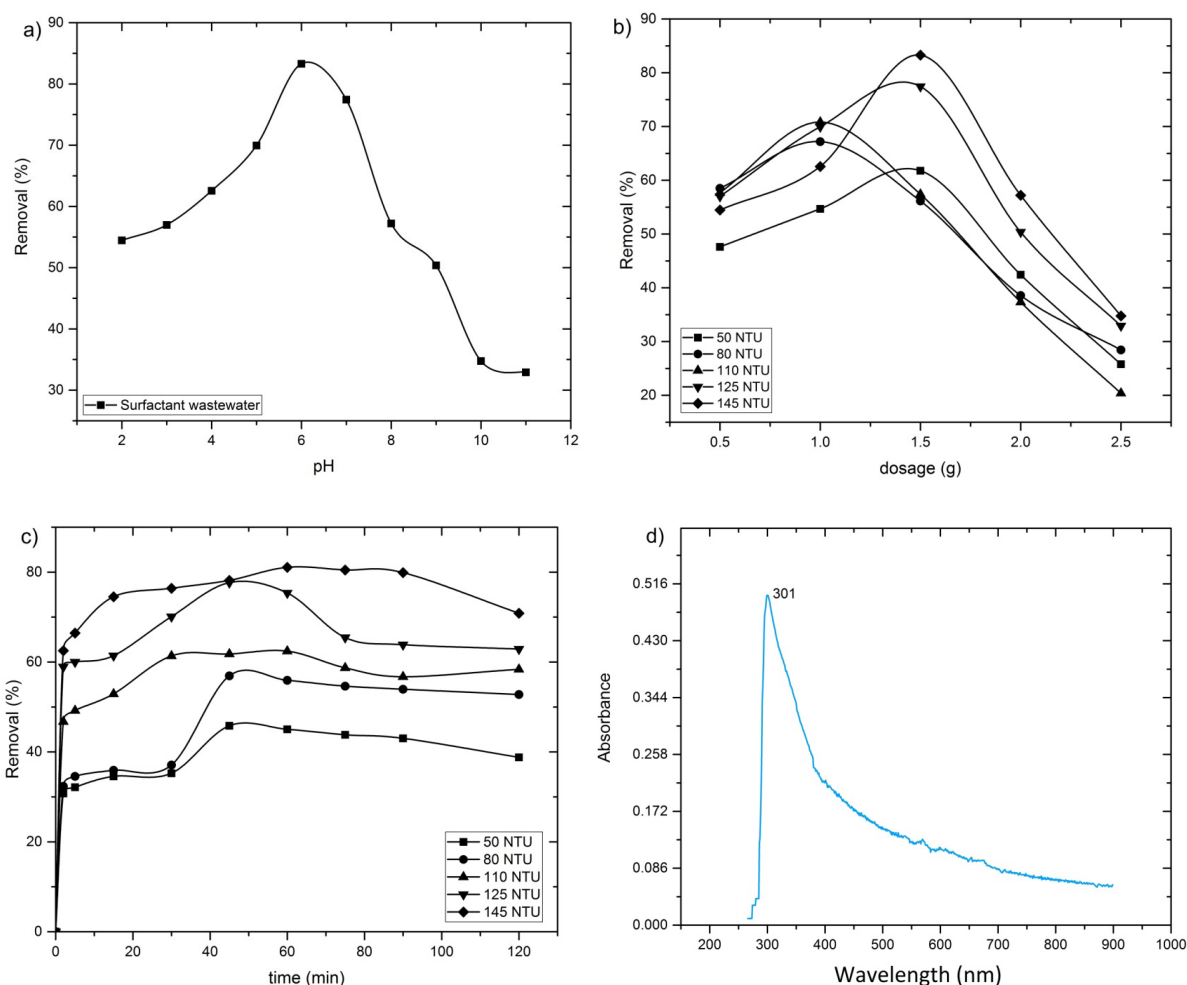


Fig. 3. Optimization of adsorption parameters (a) Effect of pH (b) Effect of adsorbent dosage (c) Effect of contact time (d) Range scan of washing machine wastewater.

were computed to be 8.2 indicating the presence of slight negative charge in the surface and capable of attracting positively charged colloids [16]. But kaolinite being a heterogeneous surface [17] with the basal presence of $\text{Al}_3^+/\text{Si}_4^+$, the protonation/deprotonation on the surface strictly depends on the surface OH groups and thus the solution's pH. The amphoteric nature of the kaolin presents [17] an edge – to – face interactions commonly found in aromatic hydrocarbons and higher derivatives of benzene [18] often resulting in agglomerate formation. With the raise in pH, the surface of kaolin attains a negative charge leading to electrostatic repulsion with the activated carbon beads. Therefore it is imperative that the pH of the system is to be maintained at 6.7–7.2 for further optimization studies and continuous mode operation. The neutral pH of the system also prevents setting up of neutralization tanks separately that requires handling of salt precipitates due to fluctuating pH at every stage of treatment process.

The dosages of the wet beads were varied from 0.5–2.5 g and the adsorption was studied for various concentrations of synthetic wastewater (Fig. 3b). It can be ascertained that the effect of beads dosage has a direct physical relationship with the removal percentages of the colloids. The basal removal

percentage for 0.5 g is varied between 46.2–58.4% while it decreased drastically to 20.8–37.4% for 2.5 g. This can be substantiated with the fact that the increase in presence of negatively charged beads with pH_{zpc} of 8.2 has an adverse effect on the sorption system [19]. The adsorption was found maximum for concentrations 80 and 110 NTU for 1 g of beads dosage while concentrations 50, 125 and 145 NTU displayed their maximum removal percentages for 1.5 g adsorbent dosage. The maximum removal percentages found in the lower adsorbent dosages reflect the fact that at higher dosages, the adsorbent sites are scattered making the kaolin particles difficult to agglomerate due to weak van der Waal's forces. From the experimental studies, 1.5 g was chosen to be the optimum adsorbent dosage for removal of turbid colloids from aqueous solution.

The effect of contact time of the beads was also studied by varying the interaction time of the carbon beads with the varying concentrations of the synthetic wastewater. The removal percentage peaked for 145 NTU at a maximum of 79.8% while the removal efficiencies were found to be the lowest for 50 NTU at 30.4–32.8%. Comprehensively, the sorption for all concentrations was achieved in 45–60 min time frame and thereafter saturation was maintained in and

around the same removal percentages till 120 min (Fig. 3c). Albeit the equilibrium time can be postulated at 100–120 min time range, there could be possibility of kaolin colloids losing their electrostatic attraction with carbon beads. Therefore, 60 min was fixed as the optimum time for equilibrium studies for the sorption using CEAC carbon beads. Since the initial colloids concentration affects the maximum equilibrium uptake capacity [20], it is derivative to determine the optimum concentration under which the beads can efficiently adsorb. From Fig. 3c, it can be observed that as the concentration increase the uptake by the beads increase and hence the removal percentage increase. The higher uptake at higher concentrations can be associated with the presence of significant energy to break the mass transfer barrier leading to sorption of adsorbate on to the carbon beads adsorbent [21]. Moreover, during the initial characterization of the laundry discharge, the turbidity was measured in the range 128–136 NTU and hence the optimum concentration was fixed at 145 NTU. There have been similar trends reported in selecting optimum concentrations at this turbidity range for their sorption onto Sp. seed powder [9].

3.3.2. Adsorption isotherm and kinetics

The existing equilibrium models utilize the influent and effluent concentrations to analyze the synergy between adsorbent and adsorbate [22]. It can be visualized that beyond a certain saturation range the carbon beads would not be able to take part in the adsorption as there may not be sufficient sorption sites. In some cases even though the adsorption sites are saturated, the adsorbate molecules adhere along themselves by virtue of any resident electrostatic forces with the adsorbent, ionic or covalent bonds with the adsorbent's surface. The isotherm models were developed to identify reaction parameters that take part in the sorption and present an opportunity to optimize considering different parameters like reaction kinetics, influent concentrations and dosage of adsorbents. In the present study, two isotherms namely, Langmuir [23] and Freundlich [24] were selected to forecast and scrutinize the nature of sorption of kaolin colloids on to activated carbon beads. Since the Langmuir model hypothesizes monolayer adsorption, the availability of free sites does not necessarily ensure adsorption beyond its equilibrium uptake capacity. As the zero point charge of the bead indicates the presence of resident negative charge, the isotherm model provides a tangible idea as to whether the kaolin colloids negate their intrinsic amphoteric nature and gets adsorbed on the beads' surface. The non-linearized form of Langmuir model is presented in Eq. (1).

$$q_e = \frac{q_m k_a C_e}{1 + K_a C_e} \quad (1)$$

where, q_e is the quantity of kaolin colloids adsorbed per unit mass of CEAC beads, q_m is the maximum equilibrium uptake capacity and C_e is the unadsorbed effluent concentration. To determine the Langmuir constant k_a , the non-linearized form of the Langmuir isotherm is modified into a linear form and is expressed as in Eqs. (2) and (3).

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{k_a q_m} \quad (2)$$

$$\frac{1}{q_e} = \left(\frac{1}{k_a q_m} \right) \frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

The Langmuir-1 model is linearized to determine the maximum dye adsorption capacity and the Langmuir affinity constant by using the plot between C_e/q_e and C_e (Fig. 4a). In order to determine the concordance of the isotherm's hypothesis, Langmuir-2 model is developed as in Eq. (3) with a plot between $1/q_e$ and $1/C_e$ (Fig. 4b). The kinetic parameters and the regression coefficients are computed from the slope and intercepts of the two Langmuir plots and are presented in Table 4. It can be noted that the maximum equilibrium capacity, q_m increase linearly with respect to the increase in colloids concentration for both the Langmuir plots with a maximum of 1.454 mg/g for 145 NTU and minimum of 0.113 mg/g for 50 NTU. A slight variation in the k_a values can be noticed but also present an increasing trend as the concentration progresses. On the other hand, the Freundlich isotherm hypothesizes that the maximum uptake capacity is relative to the concentration of the adsorbent [25]. This suggests that the adsorption can be controlled by breaking the driving force between the sorbent molecules and the adsorbate by increasing its concentration. The following equation represents the isotherm model, assuming that the system follows a single-solute adsorption.

$$q_e = k_f C_e^{1/n} \quad (4)$$

where, the intensity of adsorption $1/n$ is proportional to the effluent concentration and is governed by Freundlich isotherm's constant - k_f . The above expression is linearized and expressed as in Eq. (5).

$$\log(q_e) = \log(k_f) + \frac{1}{nF} \log(C_e) \quad (5)$$

The isotherm parameters were determined from the slope and intercepts of the plot between $\log q_e$ vs $\log C_e$ and the values are tabulated (Table 4). From the results, it can be deduced that as the concentration of the kaolin in aqueous solution increase, the dependency of reaction constants with respect to its applicability decrease. This is evident with the decrease in the $1/n$ and k_f values with respect to the increase in turbidity concentrations. Both Langmuir and Freundlich model's applicability not only depend on the regression coefficients but also on the surface morphology, configuration matrix of the beads and the adhesion methodology of the kaolin colloids. For low dosages of the beads at neutral pH, there exists a basal negative charge over the aqueous solution which may not interfere against the kaolin sorption. But as the concentration of the colloids increases, the aqueous solution becomes basic and hence the interpretation of these isotherms becomes essential. If physical adhesion of kaolin colloids along with a monolayer adsorption is prevalent at low concentrations, then the applicability of Langmuir models can be considered [26]. In the same system, at higher concentrations, multi-layer sorption is predominant due to the fact that the colloids form an electrostatic attraction with the beads thereby presenting an increased removal efficiency in the system.

It can be observed that the sorption kinetics range decrease as the turbidity concentration increases irrespec-

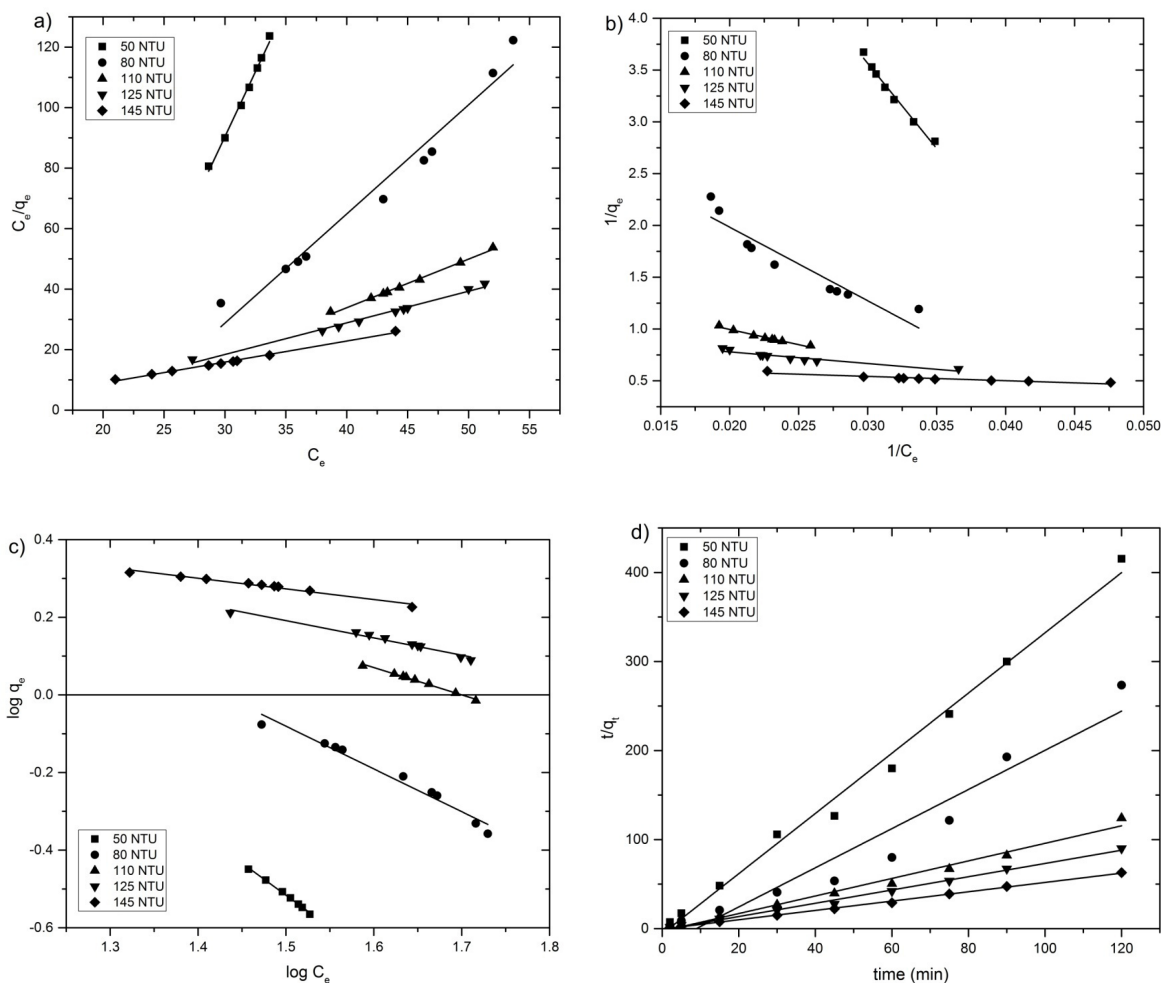


Fig. 4. Determination of adsorption kinetic parameters through (a) Langmuir-1 plot (b) Langmuir-2 plot (c) Freundlich isotherm (d) Pseudo-second order model.

Table 4
Adsorption isotherm kinetics and dynamic parameters

Isotherm plot	Parameter	Synthetic wastewater concentrations (NTU)				
		50	80	110	125	145
Langmuir 1	q_m	0.113	0.260	0.607	0.921	1.400
	k_a	0.050	0.043	0.051	0.074	0.129
	r^2	0.992	0.965	0.995	0.988	0.994
Langmuir 2	q_m	0.114	0.275	0.615	0.964	1.454
	k_a	0.051	0.045	0.052	0.082	0.146
	r^2	0.981	0.873	0.967	0.890	0.875
Freundlich	$1/n$	1.697	1.173	0.727	0.472	0.292
	k_F	7.611	5.403	3.435	2.467	2.035
	r^2	0.995	0.967	0.992	0.971	0.967
Pseudo 2nd order 1	$q_e - exp$	0.360	0.840	1.189	1.628	2.067
	k_2	-0.951	-0.897	-0.199	-0.234	-0.299
	$q_e - cal$	0.286	0.415	0.974	1.308	1.881
	r^2	0.991	0.931	0.986	0.994	0.998

tive of the nature adsorbent [27]. Moreover a significant observation can be made for 145 NTU where the k_a value is distinctively more compared to other concentrations. This phenomenon occurring in the present study validates the Langmuir model's preliminary assumption which is as the concentration increases [28] the equilibrium uptake capacity of the adsorbent increases so long that all the available adsorption sites are saturated. This underlying principle is also substantiated with the r^2 values which are significantly higher than that for the Freundlich isotherm [29,30]. Although the objective for *Strychnos potatorum* treatment prior to adsorption is to remove the suspended solids through coagulation [31], the adsorption of dissolved solids is also would be enhanced by creating an attraction for the linear alkyl sulfonates (LAS), alkylbenzene sulfonates (ABS) present in the grey laundry effluent. The chemisorption occurring in the system is minimal and the same can be observed through the $1/n$ values of the isotherm. The Freundlich constant k_f values decrease as the NTU concentration increase which symbolizes that the adsorbent could not attract solids at their higher concentration [32].

The structural framework of the pores and their surface morphology of the biosorbent helps in deciding the efficiency of the adsorption system. Predicting the rate of adsorption for the present study depends on two factors: the contact time with the adsorbate and the physical properties of both the adsorbate and the adsorbent. In order to design an adsorption system, the reaction kinetics has to be studied. The synergy between the adsorbate molecules when in contact with the adsorbent are represented using two predominantly existing mathematical expressions via, Lagergren's modified pseudo-first order [33] and Ho-Mckay's pseudo second order [34] models. The following mathematical expression represents the Lagergren's linearized pseudo first order model for the present study.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

The relationship between the first order rate constant, k_1 and the equilibrium concentration q_e , helps in distinguishing the reaction kinetics of the present study. The kinetic parameters were determined from slope and intercept of the graphical plot between $\log(q_e - q_t)$ vs t (figure not shown). Since the model showed poor compatibility with pseudo first order model it was concluded that the adsorption's dynamics cannot be represented through this model.

$$\frac{dq}{dt} = k_2(q_e - q_t) \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The pseudo-second order model derived from the Ho-Mckay's postulation on the adsorption kinetics are expressed as in Eqs. (7) and (8). The underlying principle of the pseudo second order model is that the predominant forces are chemical in nature [35] and the adsorption is adapted and transfigured due to the sharing of valence electrons between the adsorbent and the adsorbate molecules. The second order kinetic constant k_2 was calculated through the plot between t/q_t and time - t (Fig. 6d), where q_t is the uptake quantity at given time. The plot's applicability to the current sorption data was validated through the comparison of the regression coefficients as presented in Table 4. Moreover, the uptake capacity increases from 0.360 mg/g for 50 NTU to 2.067 mg/g as the synthetic wastewater's concentration increases to 145 NTU, which suggest a predominant physisorption. From the table, a subtle variation between the calculated and theoretical values of the maximum equilibrium uptake capacity can be noted. Similar trend can also be observed in previous reports for treatment of surfactants using *Sp.* seeds and *Moringaolifera*.

3.4. Continuous mode studies

A continuous mode setup was devised to treat detergent wastewater generated from washing machines through uti-

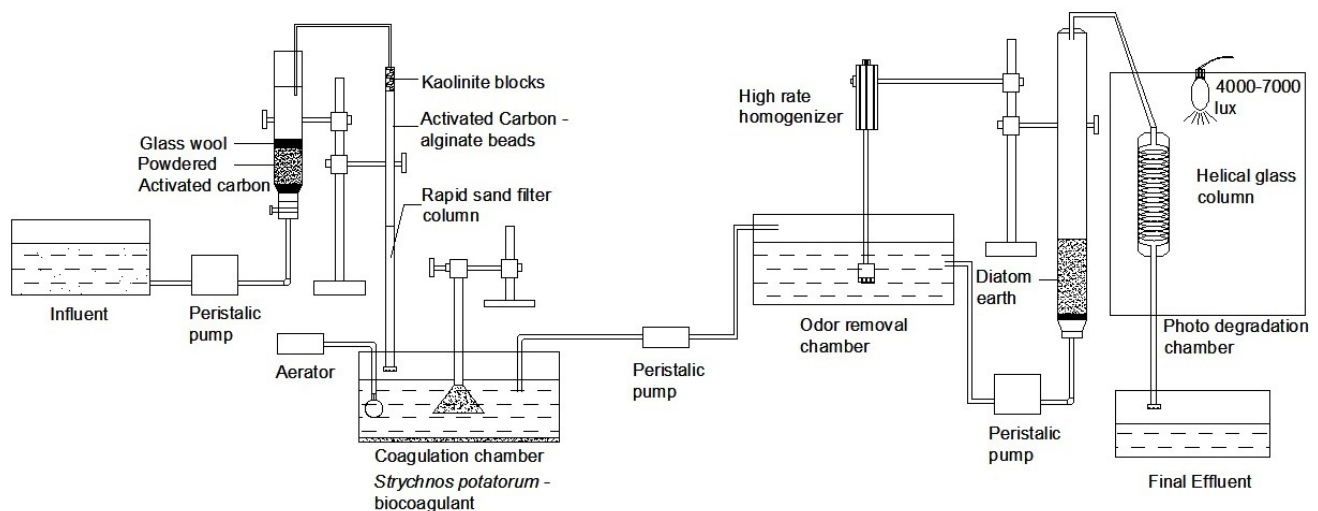


Fig. 5. Continuous mode setup for the removal of turbidity from washing machine wastewater using *Strychnos potatorum* seeds and activated carbon prepared from *Colocasia esculenta*.

lization of Sp. seeds and activated carbon prepared from *Colocasia esculenta*. The physical characteristics of the Sp. seeds used in the process have been determined and carbon beads have been optimized for high turbid conditions by spiking synthetic wastewater. The continuous mode setup involves an activated carbon column, bio-coagulation chamber bearing Sp. seeds, a double column filter (DCF) of CEAC beads and uniformly graded rapid gravity sand. Peristaltic pumps are used to mimic an up-flow system to the reactors. A constant flow rate of 6.35 mL/min was achieved at the outlet of activated carbon column. The surfactant colloids and turbid salt precipitates that are present in the wastewater come in contact with the activated carbon column. The activated carbon column was provided with effluent collection depth of 50 mm and a freeboard depth of 25 mm in case of rapid percolation due to fluctuation in influent concentrations. The kaolin blocks present in the DCF aims in regularizing the flow and in sorption of trace metal salts through electrostatic attraction. The amphoteric nature of the kaolin helps in creating a miniature agglomeration of salt precipitates thereby reducing the salt concentration load in the sand filters.

The equilibrium data generated from the batch studies were used to determine the contact time of the beads with the wastewater. A flow rate of 1.221 mL/min was maintained in the DCF that provided sufficient contact time for the wastewater with the filter media. The intent of the treatment process is to remove surfactants and sulfate salts like alcohol ethoxylate, benzene sulfonate and polyethylene glycol that cause significant odor when let out in the open stream due to degradation. A specific odour removal chamber (ORC) is provided with a high rate homogenizer operating at 10000–12000 rpm. Since the volume of ORC is higher, the hydraulic flow was designed in such a way that for every 6 runs of influent to AC and DCF column for 5 min each, a single run of water from the coagulation chamber will be pumped for 5 min to ORC at a flow rate of 172 mL/min. During the idle time of 30 min, the wastewater comes in contact with the Sp. seeds suspended inside the coagulation chamber at 2/3 of its total depth. A small scale 2LPM bubble aerator is operated at the bottom of the coagulation chamber to provide complete mixture during pumping of water from coagulation chamber to ORC. The idle time in the chamber also facilitates sedimentation of turbid particles present in the wastewater thus creating a clari-flocculator mechanism. Subsequently, the water from the coagulation chamber is pumped to ORC at flow rate of 33.2 mL/min. The flow in ORC is aligned with respect to that of the coagulation chamber and hence the high rate homogenizer is operated for 30 min. The ORC is provided with a goal to remove odor and diffuse oxygen into the wastewater thereby oxidizing remnant organic contaminants. The flow from the ORC is directed to a diatomaceous earth column at a flow rate of 1.2 mL/min. The diatomaceous earth helps in trapping trace metal salts and biotic organics that are otherwise left out in primary treatment stages. The diatom column is provided with a water board depth of 700 mm that aims in collecting filtered water from the ORC. The column also has a freeboard depth of 100 mm in case of irregular flow. The filtered water is passed into a helical condenser coil enclosed in a photo degradation chamber illuminated at 4000–7000 lux. Previous stud-

ies indicate that pathogens and other biotic components are destroyed due to the concentrated photons and heat generated due to the high luminous intensity. Since the removal of total dissolved solids from the wastewater is regarded as the prime objective, TDS is measured at every outlet stage of the setup and are tabulated in Table 5. The dissolved solids at the influent were measured at 168 ppm with an average turbidity of 128–136 NTU. A decrease of 41 ppm was observed due to the contact with activated carbon with a total reduction of 24.40% at the filter's outlet. The turbidity was further reduced at the DCF due to the combined interaction of activated carbon beads and rapid sand filter thereby reducing the solids concentration to 87 ppm suggesting a decrease of 48.21% in total TDS. The Sp. seeds in the coagulation chamber created a competitive destabilizing effect over the colloidal particles thereby generating an electrostatic attraction. The flocs generated were made to settle and sediment in the coagulation chamber by providing a sedimentation period designed based on the stokes' law [36].

The supernatant was pumped to the ORC where odor is removed through high speed mixer. A combined reduction of 31.55% in TDS was observed between the coagulation chamber and the ORC thereby suggesting that the Sp. seeds are an integral part of the treatment of laundry discharge wastewater. A final reduction of 22 ppm was computed after the diatom column with total reduction of 92.86% from the initial TDS value. Negligible reductions in TDS were found after the photo-degradation chamber as the dissolved solids were seldom affected. The physio-chemical parameters were determined before and after the continuous mode treatment process and are tabulated in Table 6. Since sulfates are predominant in the laundry discharge, the corresponding hard-

Table 5
TDS Removal percentages after different stages of treatment

Stage	TDS value (PPM)	Removal (%)
Initial - Influent	168	–
After activated carbon column	127	24.40
After AC + GSF column	87	48.21
After Sp. Coagulant chamber	56	66.67
After ORC	34	79.76
After Diatomaceous Earth - final Effluent	12	92.86

Table 6
Physio-chemical parameters of wastewater before and after treatment

Parameters	Initial	Final
pH	8.4	6.8–7.4
Chlorides	27.49 mg/L	12.36 mg/L
Hardness	245 mg/L	118.2 mg/L
Alkalinity	267.5 mg/L	84.36 mg/L
Sulphates	323.14 mg/L	86.6 mg/L
Turbidity	128–136 NTU	8–11 NTU

ness and alkalinity were also computed. The concentration of the sulfates and chlorides at the influent were measured at 323.14 mg/L and 27.49 mg/L. The hardness and alkalinity of the influent wastewater was found to be high at 245 mg/L and 267.5 mg/L due to the presence of alkyl sulfonates. The initial pH of 8.4 was brought down to 6.8–7.4 by virtue of removal of salts in the wastewater. After numerous stages in the treatment process, the concentration of sulfates and chlorides were reduced to 86.6 mg/L and 12.36 mg/L respectively. Similarly, the hardness and alkalinity caused due to these salts were reduced to 118.2 mg/L and 84.36 mg/L respectively thus implying that the removal of turbidity and salts precipitates from the influent wastewater has a direct lineage with the reduction of physico-chemical parameters. More importantly, the trapping of colloids in the activated carbon column and in the rapid sand filter aided in reduction of turbidity from a higher range of 128–136 NTU to 8–11 NTU with a total reduction of 92.8%.

4. Conclusion

A continuous mode process for the treatment of laundry discharge wastewater was designed to remove solids generated due to the interaction between detergent salts and the laundry clothes. The adsorption studies were carried in synthetic wastewater prepared from kaolin with activated carbon prepared from *Colocasia esculenta* and the operating parameters were optimized at a maximum equilibrium uptake capacity of 2.067 mg/g achieved at 60 min with adsorbent dosage of 1.5 g in neutral pH. Langmuir and Freundlich models were checked for its applicability by plotting the equilibrium data and it was found that physisorption is predominant in the system at higher concentrations of colloids. *Strychnos potatorum* with pH_{zpc} 8.2 was used as a bio-coagulant in order to make the turbid particles agglomerate thereby creating a novel clari-flocculator design. A 92.86% reduction in TDS and turbidity was achieved while the sulfates were reduced from 323.14 mg/L to 86.6 mg/L.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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