Environmental Technology & Innovation 24 (2021) 102061

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Green coagulant from *Dillenia indica* for removal of bis(2-ethylhexyl) phthalate and phenol, 4,4'-(1-methylethylidene)bis- from landfill leachate

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ARTICLE INFO

Article history:
Received 8 July 2021
Received in revised form 26 October 2021
Accepted 26 October 2021
Available online 29 October 2021

Keywords:
Bisphenol A
Bis(2-ethylhexyl) phthalate
Coagulation–flocculation
Dillenia indica seed extracts
Leachate treatment
Natural coagulant

ABSTRACT

This study was aimed to develop a green, effective, non-toxic, and eco-friendly natural coagulant. Novel extract from *Dillenia indica* seed powder were used as a primary coagulant for the removal of selected persistent organic pollutants (POPs) from landfill leachate using the coagulation–flocculation process. The influence of operating variables (dosage of extracts from *D. indica*, pH, and mixing speed) on the coagulation–flocculation process was analysed to optimize the POPs removal. Response surface methodology coupled with Box–Behnken design was employed to determine the optimum conditions. The seed extracts of *D. indica* contain carbohydrate 19.47%, proteins 12.78%, phytic acid 6.98%, and total phenolics 8.23%. At the optimal conditions, 60% phenol, 4,4'-(1-methylethylidene)bis- (Bisphenol A), and 55% bis(2-ethylhexyl) phthalate (DEHP), removal of POPs were achieved at pH 8.5 and dosages of 1066 mgL $^{-1}$ and 958 mgL $^{-1}$, respectively. Results obtained showed that pH and dosage have a substantial impact on the removal of pollutants. The model indicates high R^2 values of 0.948 and 0.982 for Bisphenol A and DEHP, respectively. The specific surface area of the *D. indica* seed was found to be 1.6734 m^2/g The FESEM micrograph indicated fibrous netlike structures, which is an indication of aggregation of the pollutant particles during coagulation–flocculation process suggesting adsorption and interparticle bridging. FTIR studies showed that *D. indica* seed contains hydroxyl, carboxyl, and amino groups, which are the preferred functional groups for the flocculation process. It was concluded that the extract from *D. indica* is a promising natural coagulant for POPs removal from landfill leachate.

1. Introduction

The fast pace of population growth, high living standards, rapid urbanization, industrialization, economic, and commercial growth have led to an increase in the complexity and amount of solid wastes worldwide. In 2016, 2.01 billion

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https://doi.org/10.1016/j.eti.2021.102061

tonnes of MSW was generated worldwide and is expected to increase by roughly 70 percent to 3.40 billion tonnes by 2050 (Kaza et al., 2018). More than 70% of this waste is disposed of in open dumpsites or landfills (Kaza et al., 2018). Despite several advanced technologies such as recycling, composting, and incineration, solid waste disposal practices in many developing countries depend on landfilling due to its relatively simple procedure, low investment and low operating cost (Abdel-Shafy and Mansour, 2018; Ferronato and Torretta, 2019).

The major drawback of landfills is the generation of leachate that not only contaminates the ground and surface water, but also affects soil and air (Rana et al., 2018). Leachates are highly toxic and contain heavy metals, hydrocarbons, chlorinated organic and inorganic matters, xenobiotic organic compounds, persistent organic pollutants (POPs), and other recalcitrant organic pollutants (Boonyaroj et al., 2017; Eggen et al., 2010). Among POPs, phthalic acid esters and phenolic compounds have been commonly reported in the landfill leachate (Boonyaroj et al., 2017; Dan et al., 2017). DEHP and Bisphenol A are hazardous organic compounds that are highly persistent and possess endocrine-disrupting chemicals, besides being extremely toxic and carcinogenic to human health and wildlife (Michałowicz, 2014). DEHP is widely used as a plasticizer in PVC products to enhance the softness and flexibility of the material (Boonyaroj et al., 2017). Bisphenol A is a monomer and is extensively used in the production of polycarbonate plastics, epoxy resins, lacquer coatings, and paper products (Björnsdotter et al., 2017). Therefore, the removal of these pollutants from landfill leachate is crucial prior to their release in the watercourses. This would prevent the deterioration and/or severe toxicity of the ecosystem and aquatic life.

Among various advanced technologies, coagulation–flocculation has been widely employed for the treatment of leachate produced by young and stabilized landfills. It is also applied as pre or post-treatment, either prior to physicochemical or biological methods (Amor et al., 2015; Martínez-Cruz et al., 2021). Experimental variables such as pH, coagulant concentration, and mixing speed are crucial for performance optimization (Kee et al., 2015). Inorganic-based chemical coagulants including alum, ferric chloride, ferrous sulphate, poly aluminium sulphate, poly aluminium chloride, poly alkylene, and poly amine are well-recognized and used for leachate treatment (Freitas et al., 2018). Nonetheless, there are numerous drawbacks associated with their excessive and prolonged usage, such as high procurement costs, ineffectiveness in low-temperature water, detrimental effects on human health, huge amount of production of toxic sludge, and significant fluctuation of pH of the treated water (Ang et al., 2020; Freitas et al., 2018; Oladoja et al., 2017a). The additional hazards include detrimental effects to the environment as some of the derivatives/residues are non-biodegradable. These can also cause neurodegenerative diseases such as Alzheimer's, and have carcinogenic as well as neurotoxic impacts on humans (Pal et al., 2011). Therefore, it is desirable to replace inorganic coagulants with alternative natural coagulants owing to their eco-friendliness, high degradability, and cost-effectiveness. These are also non-toxic, result in less and compact sludge production, possess renewable products character, are highly efficient, and low-cost coagulants. Natural coagulants generally possess a large number of surface charges which may enhance the effectiveness of the coagulation process (Freitas et al., 2018; Oladoja et al., 2017a).

In recent years, various plant-based coagulants have been used for water and wastewater treatment but the most widely known are from *Moringa oleifera*, guar gum, *Mustard* seeds, *nirmali* seeds, *Cereus peruvianus*, *Ocimum basilicum*, Genus *Cassia*, *Plantago* species, *fava* bean seeds, tannin, cactus, chestnut and acorn (Tawakkoly et al., 2019; Oladoja et al., 2017a; Yin, 2010). In this study, *Dillenia indica L.* (*Dilleniaceae*) (*D. indica*) seed extract is introduced as a primary new natural coagulant.

D. indica, is a small to medium-sized evergreen tree that grows up to 10–15 m in the tropics. *D. indica* was selected based on the fact that it is non-edible, and it is widely distributed in moist and evergreen forests of the Indian Subcontinent such as (India, Bangladesh, and Sri Lanka), Indo-China (Thailand, Vietnam), Malesia (Indonesia, Malaysia), and is native to China (Yunnan). The literature revealed that the juice from stem, bark, leaves, and fruits of this plant have been used as traditional medicine for the treatment of several diseases. To date, there are no reports on the use of *D. indica* seed extracts as a natural coagulant for water and wastewater treatment. The objective of this research was to identify and prepare a novel green coagulant from *D. indica* seed extracts and to study the effectiveness of *D. indica* seed extracts for the removal of POPs in the landfill leachate.

2. Methods and materials

2.1. Chemicals

Standards of bis-(2-ethylhexyl) phthalate (DEHP) and Phenol, 4,4′-(1-methylethylidene)bis- (Bisphenol A) with purity >98%, potassium alum, Gallic acid monohydrate, Folin Ciocalteu reagent, sodium carbonate, phytic acid sodium salt, 2,2′-bipyridine, sodium phosphate monobasic, bovine serum albumin, and Coomassie Brilliant Blue G-250 were obtained from Sigma Aldrich (Malaysia, Bhd. Sdn). Dichloromethane, Ethyl acetate, Hydrochloric acid, and Ethanol solvents were obtained from Merck Chemical Co. (Malaysia). All other chemicals and reagents used in the study were of analytical grade and were used without further purification.

2.2. Site description and leachate sampling

Leachate samples were collected from Jeram Sanitary Landfill (JSL), which is located 50 km northwest of Kuala Lumpur (3°11′20″N and 101°21′50″E). It has been operating since 2007 and is presently receiving 2500 metric tons of waste every day which is comprised of 95% domestic waste while rest is non-hazardous and industrial waste (Agamuthu and Fauziah, 2011). The total area of JSL is approximately 65 hectares including six phases for waste disposal with an expected lifespan of 16 years. It is estimated that 0.375 million L/day of leachate is generated from JSL (average leachate production is estimated at 150 L/tonne), based on 2500 tonne/day of MSW dumped into the landfill (Kamaruddin et al., 2017). Landfill leachate was collected according to Aziz et al. (2021) using a grab sampling method from the outlet of the leachate pond into high-density polyethylene (HDPE) bottles and stored at 4 °C prior to further use. Physicochemical parameters of the leachate were immediately measured after collection. The characterization of the landfill leachate was done in triplicates.

2.3. Physico-chemical characterization of raw landfill leachate

The physicochemical characterization of the raw leachate was carried out according to APHA (2012) together with other commonly used methods. All analyses were carried in triplicates. The total dissolved solids (TDS), pH, and specific conductivity were analysed using a multi-parameter model (YSI Pro Plus, 16B101281, USA). Ammoniacal nitrogen (NH_3–N) was measured according to USEPA 3050B. Chemical oxygen demand (COD), total suspended solids (TSS), and turbidity were analysed using HACH DR/4000 Spectrophotometer HACH programme. The determination of BOD_5 was performed in accordance with the 5210 D (APHA, 2012).

2.4. Preparation of natural coagulant from D. indica seed extracts

D. indica fruits were collected from the garden of University of Malaya and rinsed thoroughly with distilled water to remove dirt. The extraction of natural coagulants from the seeds of *D. indica* was done in accordance with the method used by Bodlund (2013) with slight modification. The seeds of the fruits were separated manually from the peels and then air-dried at room temperature for 15 days. The seeds were grounded to powder using an electronic blender and the powder was kept in an air-tight glass container after sieving through a 250 μm sieve. For the process of extraction, the seed powder was defatted with ethanol by using electrothermal Soxhlet apparatus. This was done by weighing 10 gm of seed powder and setting it in the thimbles of the electrothermal Soxhlet extraction chamber followed by the addition of 170 mL ethanol in the heating chamber. The ethanol was then evaporated through three 30 min cycles, to ensure the extraction of oil from the seeds until the ethanol became colourless, and then the seed cake was removed from the Soxhlet thimbles. The collected *D. indica* seed cake residue was later dried at room temperature and used throughout this study.

2 g of cake residue was dissolved in 100 mL distilled water and mixed with a magnetic stirrer for 30 min. The mixture was filtered with a fivefold muslin cloth to remove seed fibres and solid residues and the extract was termed as a crude coagulant. *D. indica* seed extracts were prepared on daily basis for each experiment to avoid microbial contamination. Fig. 1 shows the process flow chart for producing green coagulant from *D. indica* seed.

2.5. Coagulation–flocculation test

The jar test used in this experiment was conducted using a programmable apparatus (Velp Scientifica JLT6 Flocculation tester) equipped with six- paddled blender. *D. indica* seed extracts were tested, and potassium alum was used as a control in the coagulation–flocculation test. Treatment was carried out to evaluate the effect of pH, coagulant dosage, and mixing speed by using *D. indica* seed extracts for determining the optimum experimental conditions for the removal of POPs. The ranges and the levels of the operating variables were selected based on our preliminary experiments. 250 mL of leachate sample was poured into 1 L beaker and varying amounts of *D. indica* seed extracts ranging between 200 to 1200 mg/L were used individually for each test at room temperature (25 °C). To obtain the desired pH condition, the sample was adjusted by using 1N NaOH/H_2SO_4 solutions. Multiple Probe (YSI Pro Plus, 16B101281, USA) was used to measure the pH value. The experimental procedure was conducted in three stages, initial mixing was operated at rapid 200 rpm for 1 min to obtain homogeneity. Extract of *D. indica* seed was added to the leachate after 1 min of rapid mixing which was then continued for another 4 min. Afterwards, two slow mixing stages were performed at 70 rpm and 50 rpm for 10 min each. The samples were left undisturbed for 45 min and after settling, the supernatant was collected and used for quantification and measurement of POPs.

2.6. Extraction of POPs and instrumental analysis

The leachate sample was analysed using GC–MS/MS. The extraction and quantification of POPs in the sample was done based on the procedure proposed by Kee et al. (2015) with slight modification. 100 ml of leachate sample was applied to Liquid–liquid extraction (LLE) process. Sample extraction was repeated three times using 50 mL of dichloromethane (DCM) into a separating funnel and shaken vigorously for 3 min. The bottom organic layer was mixed and dried over anhydrous sodium sulphate. The organic solution was concentrated using a rotary evaporator until dryness and rinsed with 3 mL of

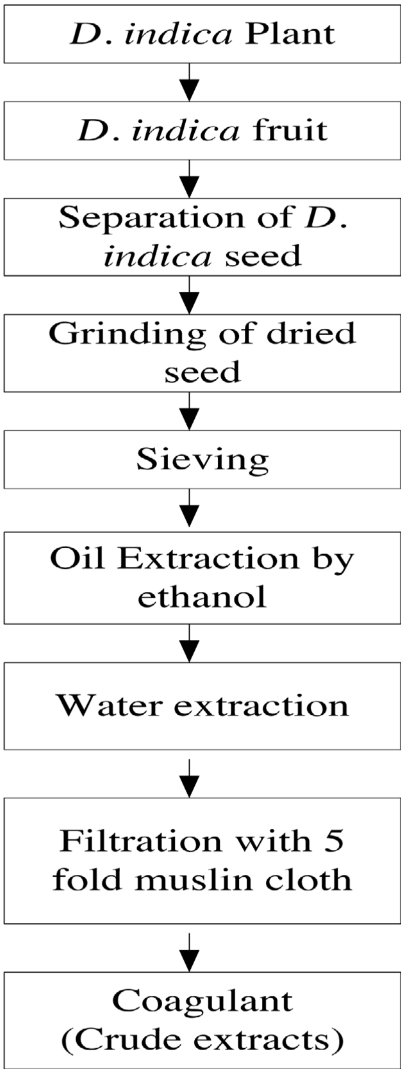

Fig. 1. Schematic of processing of *D. indica* seeds used in coagulation studies.

DCM. 1 mL of organic phase solution was transferred into vials for GC–MS/MS analysis. The POPs were determined with gas chromatograph Agilent 7890 A coupled with Tandem Mass Spectrometry Agilent 7000 (Agilent Technologies, USA). The column used was HP-5MS fused capillary operated with nitrogen carrier gas with the following description: 30.0 m x 0.25 mm i.d x 0.25 μm film thickness. The inlet temperature was 230 °C with a split less injector and the injection volume was 2 μL. The GC column operating condition was programmed as follow: preliminary oven temperature was 70 °C maintained for 2 mins, then raised from 25–150 °C per min and maintained for 0 min, then increased to 200 °C at 3 °C per min, and maintained for 0 min, and ramped to 280 °C at 8 °C per min and maintained for 15 min.

2.7. Experimental design and statistical analysis

The design of the experiment, mathematical modelling, optimization, and statistical technique were employed using Design Expert 8.0.6 software. Response surface methodology (RSM) fixed with Box–Behnken design (BBD) were used for the optimization of the removal of POPs. BBD is an independent quadratic design and known as an effective design tool to fit second-order polynomial quadratic models. Because of its spherical design, it has good predictability and requires a fewer experimental runs to estimate the factors. Three significant operating variables (Coagulant dosage, pH, and mixing speed) were optimized to predict the best responses. The ranges and levels of the operating variables were selected based on the preliminary experiments. The ranges and the levels of the operating parameters examined by using BBD are illustrated in Table 1.

Table 1
Experimental range and levels of the independent parameters.

Factor	Variables	Type	Low actual value	Central values (zero level)	High actual value
A	pH	Numeric	4	7.5	11
B	*D. indica* seed extract dosage	Numeric	800	1000	1200
C	Mixing speed	Numeric	150	200	250

In this study, the operating variables include dosage, pH, and mixing speed with the range of 800–1200 mg/L, 4–11, and 150–250 rpm, respectively. The BBD consists of 17 runs with repeated five central points used to increase the accuracy of the prediction. The POPs removal was analysed as responses in the experiment. A second-order polynomial quadratic model was used to evaluate the effects of different variables on the responses using the Eq. (1):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i \leq j}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{1}$$

where, y = observed response, β_0 = constant term, βi = represents the regression coefficients of the linear variable, βii = represents the regression coefficients of the quadratic variable, βij = represents the regression coefficients of the interaction variable. Whereas Xi and Xj indicate variables, k denotes the number of factors studied and optimized in the experiment and ε indicates a random error.

An analysis of variance (ANOVA) was carried out to estimate the interaction among the experimental factors and process responses. The statistical significance of the results of the coefficient of determination R^2, polynomial model, and Fisher F-test were evaluated using the same program. The model terms were selected or rejected based on the P-value (probability) with a 95% confidence level (Rasool et al., 2016). Three-dimensional (3D) contour plots explained the relationship between the experimental variables and process responses. The plots of predicted versus actual values and the contour plots were analysed to observe the impact of the interactions of the operating factors on POPs removal. Optimization was carried out by the Design Expert 8.0.6 software using the numerical optimization process.

2.8. Physiochemical characteristics of the flocs

The physiochemical characteristics of the samples and flocs obtained after the treatment with *D. indica* seed extracts or alum were examined using FTIR, FESEM, and BET. FESEM was applied to examine the micro-scale changes on the flocs surface. The molecular structure and functional groups of the flocs were analysed using attenuated total reflectance-Fourier transform infrared spectroscopy, ATR-FTIR (Perkin-Elmer 400 FT-IR/FT-FIR), from 400–4000 cm^{-1} at resolution 2 cm^{-1}. Simultaneous thermal analysis (STA) was conducted for melting point, prior to the determination of the surface area of the samples. The properties of adsorption and specific surface area of the *D. indica* seeds were determined by BET method with Micromeritics TriStar II 3020 model using nitrogen adsorption–desorption isotherms at 77.35 K. The total pore volume and pore size was determined by Barrett–Joyner–Halenda (BJH) method. *D. indica* sample was degassed at 90 °C for 1 h and then at 100 °C for 4 h prior to the analysis. The Zeta potential of the supernatant and leachate samples was measured using Malvern Zetasizer Nano ZS and performed at 25 °C in triplicates.

2.9. Chemical analysis of Green coagulant

The following procedures were carried out on crude extracts of *D. indica* seed and *D. indica* seed powder. The content of protein was determined using Bradford assay (1976) with bovine serum albumin as standard. Carbohydrate content was determined by the colorimetric method (Dreywood et al. 1946). Folin–Ciocalteau method was used to measure the total phenolic content (Singleton and Rossi, 1965), while phytic acid was evaluated according to Haug and Lantzsch (1983). All experiments were carried out in triplicates and the average values are reported.

2.10. Statistical analysis

The statistical analysis of all the data was performed using Microsoft Excel 2013 and IBM SPSS Statistics version 20.0. Means, standard error, and standard deviation values were computed for each experiment. For POPs concentration, the unit used was milligramme per litre (mg/L) in leachate samples and experiments.

3. Results and discussions

3.1. Leachate characteristics

The physiochemical properties of the landfill leachate sample are summarized in supplementary materials (Table S1). The pH of the landfill leachate sample was slightly alkaline, that is, 8.3, corresponding to a typical mature landfill

(Aziz et al., 2021). The strong ammonia odour was due to the ammoniacal (NH_3-N) concentration (423 mg L^{-1}), which resulted from hydrolysis and fermentation of proteins, amino acids, and other nitrogenous substances of the biodegradable fractions (Aziz et al., 2021). The level of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in the leachate was 1,036 mg L^{-1} and 9,638 mg L^{-1}, respectively. This is fairly high which could be due to the dominant humic-acid substances that are yet to be stabilized by microorganisms (Scandelai et al., 2018). The BOD_5/COD ratio was determined to be 0.128 which indicates a partially stabilized landfill. These values are in line with (Aziz et al., 2012) who established that leachate from intermediate landfills has a BOD_5/COD ratio between 0.1–0.5. While the BOD_5/COD ratio of young landfill leachate may be up to 0.85 which shows the presence of biodegradable organic matter and equally corresponds to the acid phase of anaerobic degradation (Hassan et al., 2021). However, a typical BOD_5/COD ratio is less than 0.1 which denotes a low concentration of biodegradable organic matter in the leachate sample (Rana et al., 2018). The total suspended solids (TSS), total dissolved solids (TDS), and turbidity value of the leachate was 378 mg L^{-1}, 16 638 mg/L, and 632 FAU, respectively, indicating a high amount of dissolved organic matter and inorganic salts. It also showed the presence of humic substances formed during organic matter decomposition (Scandelai et al., 2018).

3.2. Analyses of the extracts of *D. indica* seed

Active compounds were extracted from *D. indica* seeds using distilled water. The extracts were analysed, and the contents obtained were carbohydrate 19.47%, proteins 12.78%, phytic acid 6.98%, and total phenolics 8.27%. According to Jung et al. (2018), the active components in seed extracts of *M. oleifera* are dimeric cationic proteins. While few other researchers reported that the active coagulating agent is neither protein, polysaccharide nor lipid, but some other organic polyelectrolytes (Kukić et al., 2015); however, it is not clear that which constituent among all of them is the active coagulant agent. The chemical characteristics of the seed extracts do not provide much evidence about their effectiveness as natural coagulants. Therefore, it is important to carry out coagulation tests. The experiment was conducted using various dosages and different pH to evaluate the efficiency of *D. indica* seed extracts. It can be postulated that the carbohydrates and proteins in *D. indica* seed extracts could be responsible for the coagulation activity, however, other constituents including phenolics and phytic acid might have aided in the coagulation activity as active components. These compounds were previously known as the dominant coagulating agents present in many plants (Kukić et al., 2015).

3.3. Percentage removal of POPs using *D. indica* seed extracts and alum

The average value of Bisphenol A and DEHP found in leachate was 31 mg L^{-1} and 15 mg L^{-1}, respectively. A primary study on *D. indica* seed extracts showed that it was capable to remove POPs from the leachate, thus, it is used as a natural coagulant. The removal efficiency of Bisphenol A and DEHP in the leachate was investigated using *D. indica* seed extracts with various dosages ranging from 200–1200 mg L^{-1}. The variation in coagulant dosage can be observed in Fig. 2. It can be observed that as the dosage of *D. indica* seed extracts was increased, the removal efficiency of Bisphenol A and DEHP gradually increased until it reached an optimal point. The highest amount of removal of Bisphenol A and DEHP was achieved at a pH value of 7.5 using 1000 mg L^{-1} and 800 mg L^{-1}, respectively. Under optimal conditions, it also removed 63% COD, 76% BOD_5, and 81% SS from landfill leachate. The removal efficiency did not meet the allowable discharge limits, and therefore, it requires further treatment prior to release into any watercourse. However, it is always a combination of methods that are employed for a total treatment. The results obtained showed that the addition of more coagulants aids in higher amount of POPs removal by providing more adsorption sites for chelation and physical adhesion via hydrogen bonding to the suspended particulates (Shak and Wu, 2014). The lowest removal was observed at a coagulant dosage of 200 mg L^{-1}. An over-dose of *D. indica* seed extracts was not able to reduce the POPs concentration but instead could increase the residual concentration as the polymer chain of *D. indica* seed extracts that were largely overlapped with each other due to the overcrowding impact and surface saturation (Choy et al., 2016). Therefore, a reverse effect was observed when the optimal concentration was surpassed. Similarly, the surface area for the attachment of segments was reduced following the addition of excess *D. indica* seed extracts which would lead to the resuspension of colloidal particles and may partially develop steric repulsions (Choy et al., 2016). Eventually, this may lead to repulsive energy between POPs and the flocculant, which may reduce the removal efficiency of POPs (Bratby, 2016). By applying alum, the highest removal of Bisphenol A (53%) and DEHP (58%) was achieved at dosage of 1.5 gL^{-1}. Additional alum beyond optimal dosage did not contribute to significant flocculation of suspended particles, this may be due to the fact that it may persist as an impurity in the sample; thereby lowering the pollutant reduction (Mukherjee et al., 2018). Like our current work, Kee et al. (2015) also reported that Guar gum had effectively removed DEHP and phenol,2,4-bis(1,1-dimethylethyl) from farm effluent. It can be concluded that *D. indica* seed extracts have proved to be effective for the removal of Bisphenol A and DEHP from the leachate as compared to alum.

The flocs produced by *D. indica* seed extracts were clustered and were more compact as compared to the flocs of alum, which can minimize the treatment and disposal costs (Aziz et al., 2018b; Bratby, 2016). The quantity of the sludge produced at an optimum dosage of *D. indica* seed extracts was 2.5 mL and 6.8 mL for alum in 250 mL of leachate, respectively. According to Rasool et al. (2016), the higher generation of sludge by alum may be the result of precipitation of metal hydroxide that holds water contents. In contrast, plant-based polymers produced less sludge owing to their physical characteristics and bridging effect.

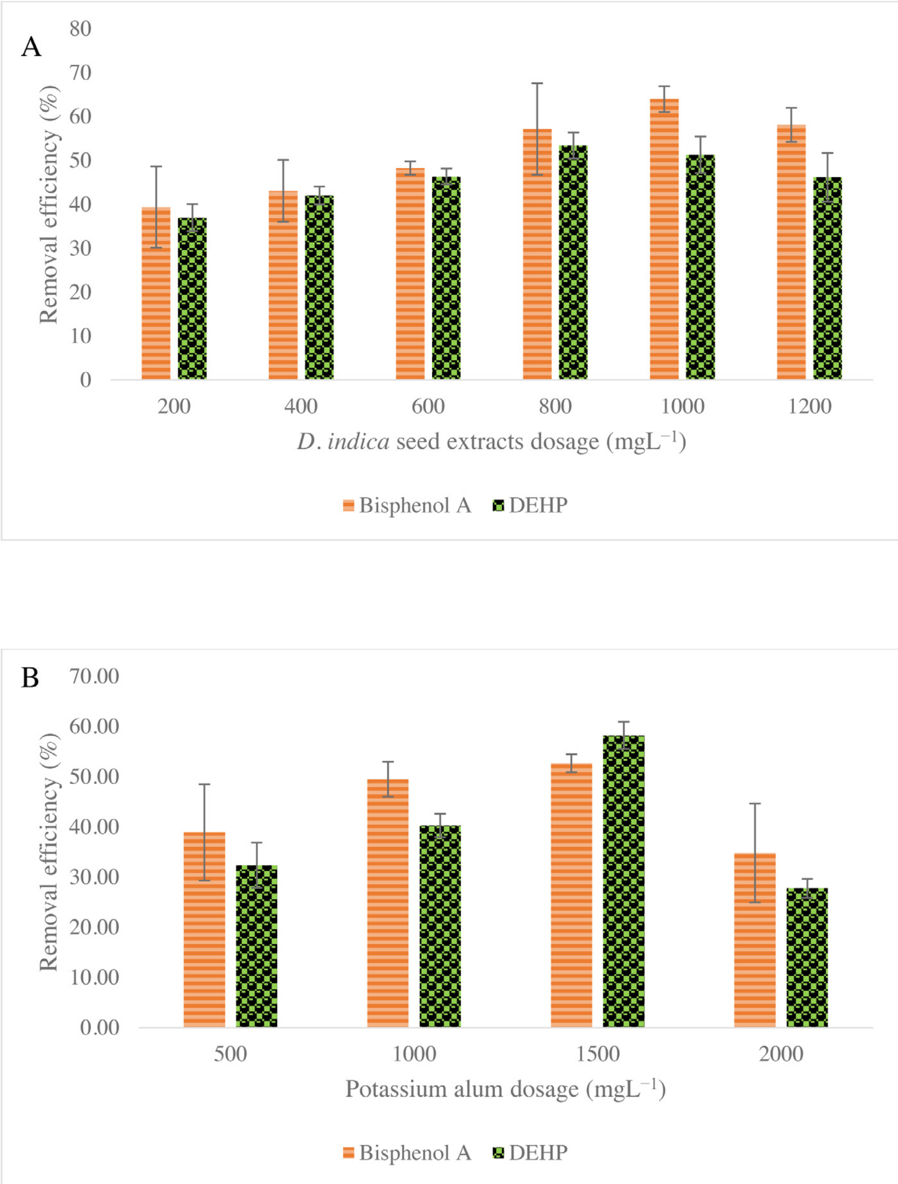

Fig. 2. Bisphenol A and DEHP removal efficiency in landfill leachate using (A) *D. indica* seed extracts and (B) potassium alum, at varying coagulant dosages and at pH 7.5.

For the treatment of one million gallons of leachate using *D. indica* seed extracts and alum, the quantity of sludge will be 9.08 m^3 and 52.99 m^3, respectively. The quantity of sludge generated from the use of *D. indica* seed extracts was lower and dense, which greatly reduced the associated treatment and disposal cost. Considering the economic feasibility, the disposal of 52.99 m^3 of sludge generated by alum will cost USD 2100, whereas that of 9.08 m^3 of sludge produced by *D. indica* seed extracts only will cost USD 420.26 (Kee et al., 2015). Therefore, using *D. indica* seed extracts highly reduce the disposal cost. *D. indica* seed extract is eco-friendly and biodegradable; therefore, it is suggested as an alternative to inorganic coagulants for the treatment of landfill leachate for the purpose of POPs removal.

3.4. Experimental design and data analysis

The experimental design matrix with POPs removal percentage is shown in Table 2. The data obtained was fitted into second-order polynomial equations for Bisphenol A and DEHP removal in Eqs. (2) and (3). If the equation fits well, the

Table 2
Bisphenol A and DEHP removal responses for the treatment of landfill leachate by *D. indica* seed extracts.

Run	Independent variables			Bisphenol	DEHP
	pH	Dosage (mg L^{-1})	Agitation (rpm)	a removal %	removal %
1	4.00	1000	250	47.37	42.05
2	4.00	1200	200	52.06	39.55
3	7.50	800	250	53.92	52.87
4	7.50	1000	200	59.86	55.27
5	7.50	1000	200	58.4	54.12
6	7.50	1200	150	54.97	39.17
7	7.50	1000	200	60.44	53.17
8	7.50	800	150	46.11	36.98
9	11.00	1000	250	49.87	42.67
10	11.00	1000	150	47.65	35.00
11	4.00	800	200	41.28	40.98
12	7.50	1000	200	57.33	55.32
13	11.00	800	200	45.22	46.27
14	11.00	1200	200	49.6	43.91
15	7.50	1000	200	63.76	53.07
16	4.00	1000	150	43.14	35.33
17	7.50	1200	250	52.66	42.24

Table 3
ANOVA results for two responses.

Responses	R-square	Adj R-squared	Pred R-squared	Std. Dev.	C.V. %	Adeq precision	PRESS
Bisphenol A	0.9482	0.8817	0.6842	2.24	4.31	10.72	214.72
DEHP	0.9822	0.9593	0.7903	1.812	3.90	17.83	270.923

lack of fit should be insignificant. The validity of the model was tested by analysis of variance (ANOVA).

$$\textbf{Bisphenol A removal}\ (\%) = -240.62 + 14.09A + 0.28B + 0.95C - 2.29AB - 2.86AC - 2.53BC - 0.73A^2 - 1.00B^2 - 1.62C^2 \tag{2}$$

$$\textbf{DEHP removal}\ (\%) = -364.60 + 12.51A + 0.35B + 1.95C - 3.32AB + 1.35AC - 3.20BC - 0.80A^2 - 1.45B^2 - 3.89C^2 \tag{3}$$

The regression analysis of ANOVA for the model indicates that quadratic polynomial models were statistically significant for the prediction of Bisphenol A and DEHP removal. The models showed *F*-values of 14.25 and 42.93, respectively, with *P*-values 0.0010 and <0.0001, respectively, shown in supplementary materials (Table S2), indicating that the model was significant at a 95% confidence interval. There is only 0.01% and 0.10% chance that a "Model *F*-Values" of this large quantity could occur due to noise. Table 3 shows high R^2 values of 0.948 and 0.982 for Bisphenol A and DEHP, respectively, which indicates the aptness of the quadratic model and is representing the relationship between the process variables (Subramonian et al., 2015). According to Rasool et al. (2016), the coefficient R^2 value should be greater than 0.75 implying a good fit of the model. In the case of Bisphenol A and DEHP removal, the predicted R^2 values of 0.684 and 0.790 were in good agreement with the adjusted R^2 values of 0.882 and 0.959, respectively. According to Mukherjee et al. (2014), less than 0.20 difference between the predicted and adjusted R^2 values denotes the accuracy of the quadratic model to the experimental data. The adequate precision recorded was 10.72 and 17.83 which showed adequate precision for Bisphenol A and DEHP removal, respectively. A signal-to-noise ratio higher than four indicates that the developed model can be used to navigate the design space (Long et al., 2017).

The "lack of fit *F*-values" obtained were 0.64 and 0.14, respectively, which are greater than 0.05 and it implied that the lack of fit was not significant, which in turn indicated the aptness of models for precise prediction of the responses (Rasool et al., 2016). Also, the coefficient of variance (CV%) recorded was 4.31 and 3.90, respectively, where less than 10% shows a good reproducibility of the model (Long et al., 2017). The developed model indicates satisfaction of the quadratic model for Bisphenol A and DEHP removal efficiencies.

The graph of the predicted values versus actual experimental values depicted that the values were uniformly distributed at 45° line, indicating a satisfactory agreement between the observed data and predicted data values of the model (Fig. 3).

Perturbation analysis was carried out to examine the impact of operating parameters on the process responses. In this case, coagulant dosage and mixing speed had a lesser impact on Bisphenol A, while pH had more impact as observed from the steepness of the response curve shown in supplementary materials (Fig. S1a). However, all three variables were sensitive for DEHP removal, which showed a steep slope shown in supplementary materials (Fig. S1b).

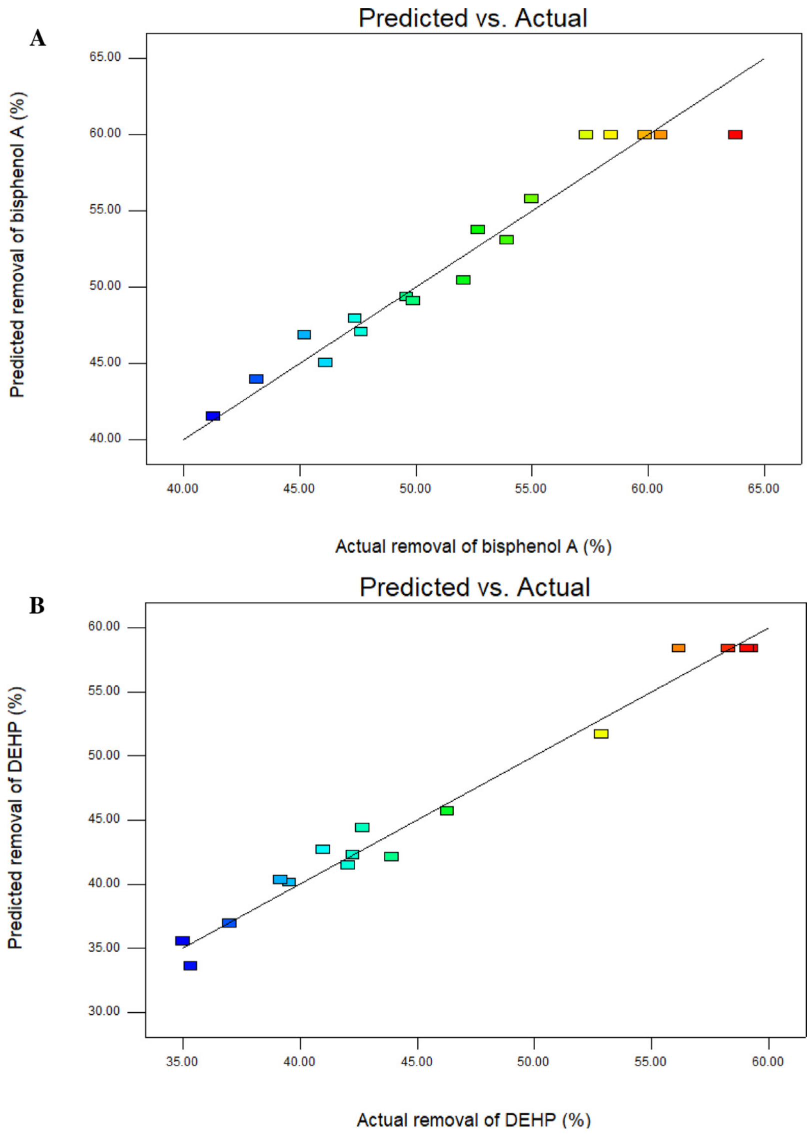

Fig. 3. Predicted versus actual values plots (A) Bisphenol A and (B) DEHP.

3.5. The impact of pH on Bisphenol A and DEHP removal

The pH is an important factor that may affect the nature of the functional groups of pollutants and existing forms of coagulants (Aziz et al., 2018a). Fig. 4 shows the three-dimensional response surface plot about the influence of pH and coagulant dosage and their interactions on the responses. The contour plots showed that after increasing the pH of the leachate, the removal of Bisphenol A and DEHP was initially increased and then started to decrease. Beyond the optimal pH conditions, the efficiency of POPs removal was also slightly decreased. The highest POPs removal efficiencies were obtained under slightly alkaline conditions from pH 8–9 whereas the lowest POPs removal was achieved at pH 4. This phenomenon could be attributed to the fact that the pH of the leachate affects the surface charge of *D. indica* seed extract in the solution. In slight alkaline condition, more adsorption and bridging occurred, which may be due to the availability of more adsorption sites (Shak and Wu, 2014). Under the slight alkaline condition, most probably the –COOH group present in *D. indica* seed extract would be ionized into –COO–, and the quantity of –OH would be increased. This produces electrostatic repulsion energies between polymer chains and the adjacent ionized groups. This results in the formation of ionic complexes between the POPs molecules and the *D. indica* seed extract networks, resulting in a higher POPs removal. However, at a higher pH level, the carbohydrate bone of *D. indica* seed extract could be fragmented into complex particles that might not effectively interact with the pollutant particles that probably resulted in lower POPs removal. The results agreed well with Kee et al. (2015), who indicated that natural polymers effectively removed POPs

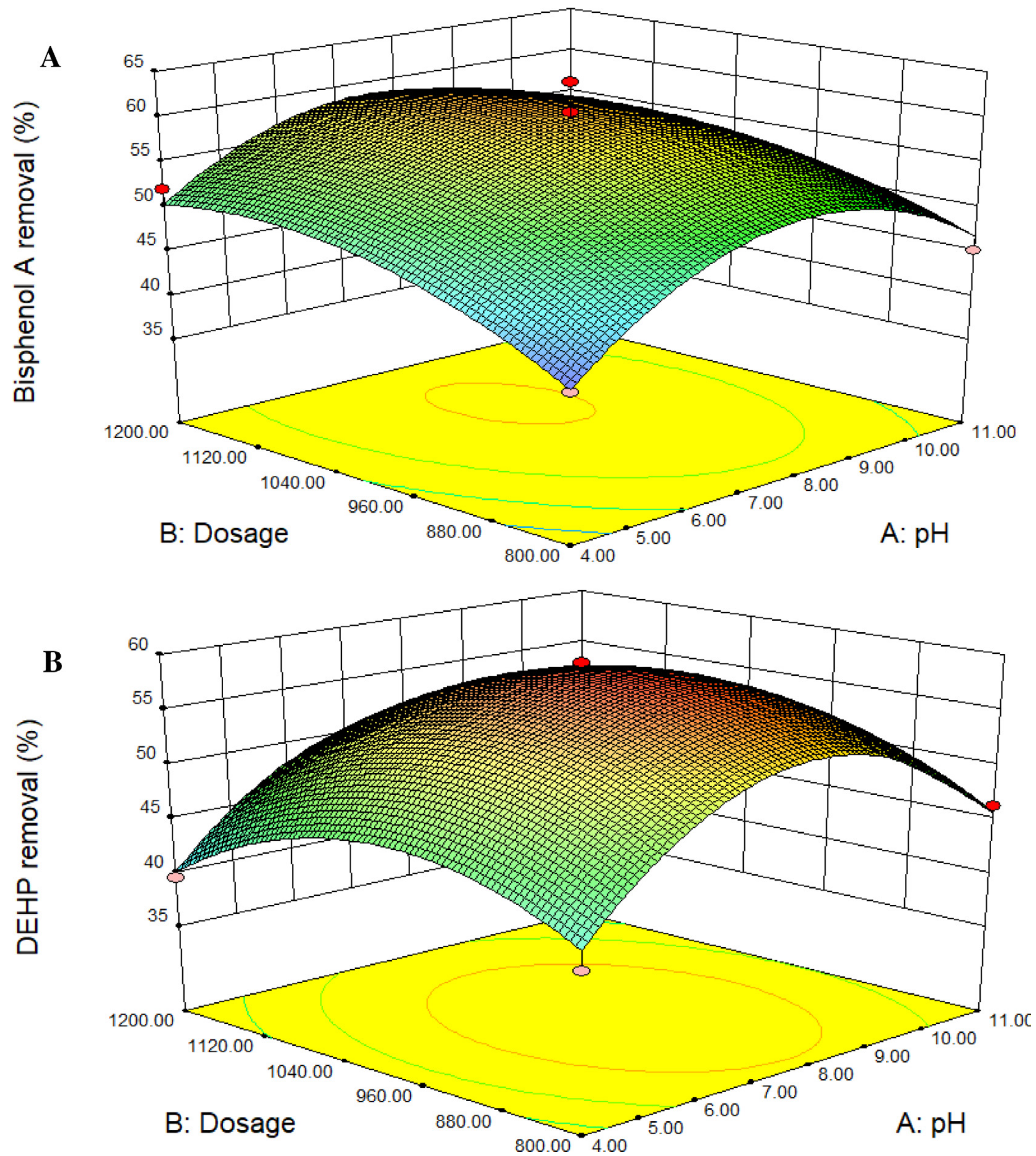

Fig. 4. Response surface 3D plot of (A) Bisphenol A and (B) DEHP removal by using *D. indica* seed extracts.

from farm effluents at an optimum pH of 8.5. Similar research conducted by Mukherjee et al. (2013) also asserted that plant-based flocculants efficiently removed pollutants from rubber mill wastewater at pH 8.24. In another study, Sanghi et al. (2006) found that *Ipomeoa dasysperma* seed gum and guar gum were more effective at optimal pH 9.5. Perng and Bui (2015) found that high pH values were more appropriate for pollutant removal using *Cassia fistula* gum. In addition, Yin (2010) and Bratby (2016) also found that plant-based coagulants are most effective at a pH range of 7 to 10.

3.6. The impact of coagulant dosage on Bisphenol A and DEHP removal

Coagulation dosage is an essential parameter during the coagulation–flocculation process for determining the optimal conditions for the performance of the treatment process and also for the reduction of sludge formation as well as dosage cost (Aziz et al., 2018b; Bratby, 2016). As depicted in Fig. 4, the response surface plots for DEHP and Bisphenol A removal by *D. indica* seed extracts are shown in contours. The response plots indicated that the removal percentage of Bisphenol A and DEHP slightly increased with an increase in the coagulant dosage. The highest removal of Bisphenol A and DEHP was obtained at 1066 mg L^{-1} and 958 mg L^{-1}, respectively. The lowest removal of Bisphenol A and DEHP was obtained at 800 mg L^{-1}. However, further addition of dosage leads to restabilization of the suspended particles, which is due to the repulsive energy between the flocculants at a higher dosage to inhibit the formation of the flocs (Mukherjee et al., 2018). These results agreed with the previous work conducted by Choy et al. (2016) who asserted that increase in the coagulant dosage would increase the removal efficiency of pollutants by green coagulants. In a study performed by Oladoja et al. (2017b), it was found that pollutants removal increased with increasing coagulant dosage. The destabilization of suspended particles occurs due to the chemical interactions and dehydration between functional groups on the colloids surface and applied coagulants (Bratby, 2016). This phenomenon indicates that bridging flocculation could be due to the flocculants being adsorbed on the surface of the pollutant particles and their interaction with others to form two or more particle aggregates (Ramavandi, 2014). When flocculant adsorbed on the pollutants particles that could extend out into the solution, it then tends to form loops and tails and may attach itself with another adjacent pollutant particle promoting the flocculation (Shak and Wu, 2014). These complexes formed a particle–polymer–particle, while the flocculant acts as a bridge. This leads to the formation of huge flocs via the bridging process (Kee et al., 2015). According to Subramonian et al. (2015), natural polymers generally destabilized pollutants particles via adsorption and inter-particle bridging.

3.7. Optimization of experimental variables

Optimization of operating variables (flocculant dosage, pH, and stirring speed) for POPs removal using *D. indica* seed extract was carried out by applying RSM. The aim was to reduce the operating cost by decreasing the flocculants dosage, keeping pH at neutral condition, and stirring speed within the range to achieve maximum Bisphenol A and DEHP removal. The maximum removal efficiency of 60% and 55% for Bisphenol A and DEHP, respectively, were achieved under optimal treatment conditions of pH 8.5 and dosage 1048 mg L^{-1}. The experimental model results were very close to the predicted data, with little marginal error of 4%–6%. These results proved the validity of the model test and the existence of an optimal point. It can be said that BBD is a powerful tool to determine the optimum points of the individual parameters.

3.8. FTIR and FESEM analysis of flocs

The functional groups present in *D. indica* seed extract and the respective flocs produced from the treatment of leachate with *D. indica* seed extract and alum, and leachate sample were analysed using FTIR (Fig. 5). For *D. indica* seed extract, an intensive broadband around 3300 cm^{-1} was attributed to -OH stretching of intermolecular hydrogen bonding and the N–H vibrations of amino-group (Mukherjee et al., 2018). The medium infrared band at around 2921 cm^{-1} and 2852 cm^{-1} implied CH_2 stretching and bending of carbohydrate and fatty acid in *D. indica* seed extract. The characteristic IR band at 1622 cm^{-1} and 1533 cm^{-1} was assigned to the C=O stretching of the amide group (amide-1 and II, respectively) which indicated the appearance of protein in *D. indica* seed extract. Meanwhile, the relatively strong peak at 1035 cm^{-1} referred to the stretching of the C-O-C group, which indicated the appearance of polysaccharides. The appearance of these active groups may serve as active sites on *D. indica* seed extracts for the absorption or attachment of pollutant particles. According to Zhang et al. (2010), the most preferred groups for the flocculation activity are carboxyl (C=O), hydroxyl (O–H) and amino or amide (–NH_2) groups, and hydrogen bonding, which can serve as a bridge between the pollutant particles and flocculants. It can be postulated that these active groups were responsible for the removal of POPs from the leachate. The FTIR spectra of the flocs produced from the treatment of the leachate with *D. indica* seed extracts were identical with those of the raw leachate with relatively intense transmittance as observed by peaks at 3300, 1622, and 1035 cm^{-1} which corresponded to vibrations of –OH, C–C, and C–O, respectively. This indicated the physicochemical interaction between leachate sample and active functional groups in *D. indica* seed extract coagulant. Alum produced flocs from the treatment of leachate had peaks around 3347, 2893, 1622, and 1074 cm^{-1} which can be attributed to the presence of O–H, C–H, C–C, and C–O, respectively. *D. indica* seed extract had similar peaks with raw leachate, but with a slight shift in the position of the peaks. This phenomenon indicated the chemical interactions between the polymer chain and pollutant particles, which enabled the removal of selected POPs.

Fig. 6 shows the FESEM micrographs of the dried flocs treated with *D. indica* seed extracts and alum. The flocs generated by *D. indica* seed extract exhibited fibrous network patterns on the surface revealing relatively clustered and more compact nature (Fig. 6b), which is the indication of agglomeration of the pollutant particles during coagulation–flocculation processes. This phenomenon could be attributed to the effective adsorption and inter-particle bridging of the *D. indica* seed extract onto the surface of the pollutant's particles. The adsorption and interparticle bridging revealed the inter-connection and wrapping structures that resulted in destabilization and aggregation (Smoczyński et al., 2014). This led to the formation of aggregates through the coagulation–flocculation process with the aid of *D. indica* seed extract particles. In addition, it provided a large surface area (1.6734 m^2/g) as there were abundant absorption sites available. Lek et al. (2018), found a similar fibrous structure after treatment of POME with chickpea. Based on the research, Shak and Wu (2015) reported that the porous and rough surface offers a better adsorption process. The results of this study are in agreement with the findings of Subramonian et al. (2015), who observed similar morphological structures for raw industrial effluent, raw pulp and paper mill effluent using *Cassia obtusifolia* seed gum. According to Beltran-Heredia et al. (2009), natural polymers act as a bridge and form a net-like structures via coagulation activities.

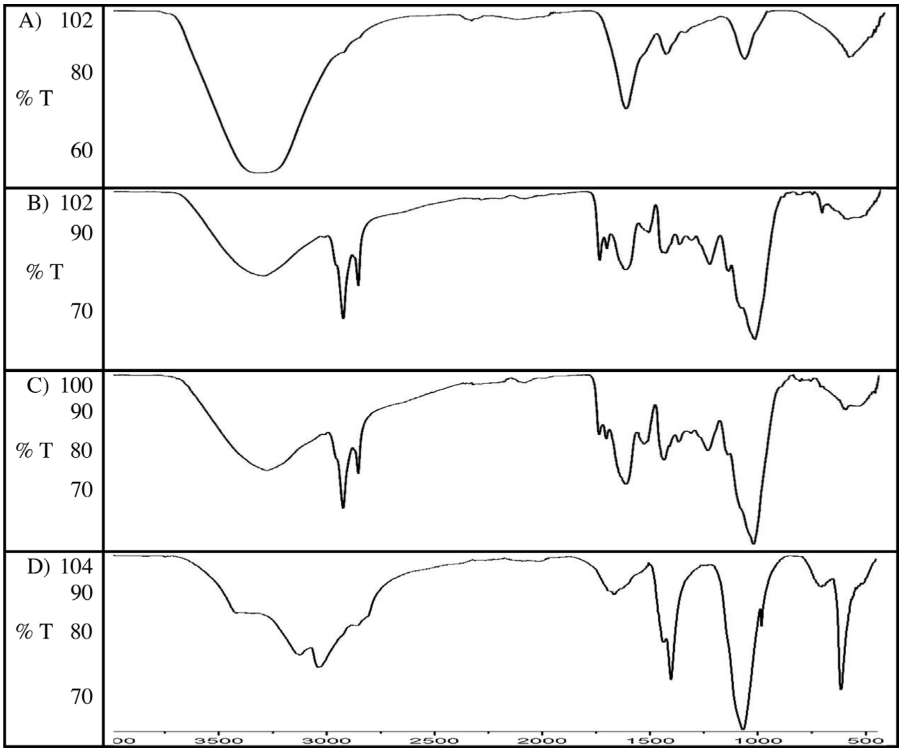

Fig. 5. FTIR spectra of (A) leachate (B) raw *D. indica* seed (C) *D. indica* seed extracts treated flocs (D) Alum flocs.

3.9. BET analysis of D. indica seeds

The BET analysis was carried out to investigate the adsorption properties and specific surface area of the *D. indica* seeds. The characteristics were determined by nitrogen (N_2) adsorption/desorption curve with aids of BET. The results obtained from the N_2 adsorption–desorption isotherm are summarized in supplementary materials (Table 3).

D. indica seeds had a surface area of 1.6735 m^2/g and pore volume of 0.0022 cm^3/g. The BET surface area of *D. indica* seeds was significantly higher when compared with the surface area of chickpea powder 0.0577 m^2/g and *Moringa oleifera* seeds powder 0.3965 m^2/g (Lek et al., 2018; Zakaria et al., 2018). This signifies the superiority of *D. indica* seeds compared to chickpea in terms of adsorption properties and effective surface area. The higher BET surface area may provide porous and irregular morphology, which could enhance the bridging mechanism in coagulation–flocculation activities (Shak and Wu, 2014). The average pore diameter was found to be 54.2663 nm, suggesting that the *D. indica* seeds are mainly macroporous. From (Fig. S2) shown in supplementary materials, it is evident that nitrogen adsorption–desorption isotherms can be classified as type IV curve according to the IUPAC classification (Carmody et al., 2007) with hysteresis generally related to macropores.

4. Conclusion

The performance of novel coagulant from *D. indica* seed extract was investigated to treat landfill leachate. Extract of *D. indica* seeds contained a higher amount of carbohydrates and proteins than phenolic constituents and phytic acid and was found to be an effective biopolymer for POPs removal in the landfill leachate. Box Behnken experimental design was performed for optimization and modelling of the treatment variables. Results showed that *D. indica* extract effectively removed at least 60% of Bisphenol A and 55% of DEHP from landfill leachate at the optimal pH 8.5 and dosages of 1066 mg L^{-1} and 958 mg L^{-1}, respectively. FTIR analysis showed that *D. indica* seeds contain hydroxyl, carboxyl, amide groups, and hydrogen bonding, which are the active groups for the coagulation and flocculation activity. The FESEM images indicated fibrous netlike structures, which confirmed the adsorption and interparticle bridging between pollutant particles to form flocs during coagulation–flocculation processes. The sludge volume index values of *D. indica* seeds extract and alum were 52 mL/g and 180 mL/g, respectively. From the economic point of view, for treating one million gallons of leachate using *D. indica* seeds extract (at 1000 mg/L dosage) would cost 0.6 USD while alum (at 1.5 g/L dosage) would cost 3.6 USD. The quantity of sludge produced by *D. indica* was small and compact which can reduce the disposal and treatment costs. This study confirmed that *D. indica* seeds extract could be applied for the treatment of POPs in the landfill leachate.

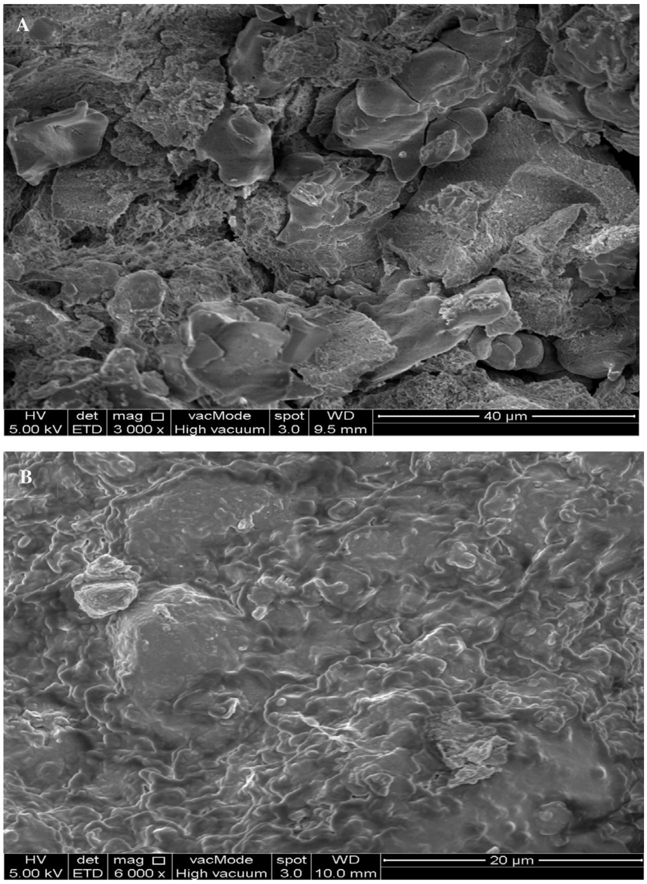

Fig. 6. FESEM images of (A) Alum treated flocs and (B) *D. indica* seed extracts treated flocs.

CRediT authorship contribution statement

A. Aziz: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **P. Agamuthu:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration. **A. Hassan:** Formal analysis, Investigation, Writing – review & editing. **H.S. Auta:** Methodology, Formal analysis, Editing, Investigation. **S.H. Fauziah:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by University Malaya Research Grant (RP011A-14SUS), FRGS Project (FP052-2013B), and Lasbela University of Agriculture, Water and Marine sciences, Uthal, Balochistan, Pakistan.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2021.102061.

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