Research Article

Potato Peels as an Adsorbent for Heavy Metals from Aqueous Solutions: Eco-Structuring of a *Green* Adsorbent Operating Plackett–Burman Design

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Received 2 November 2018; Revised 19 February 2019; Accepted 28 February 2019; Published 22 April 2019

Academic Editor: Yuangen Yang

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Treatment of wastewater is becoming a concern of an increasing prominence. Trace amounts of toxic metalloids and heavy metals (HMs) would contaminate large volumes of water. Being present as traces, removal of these ultratrace contaminants from wastewater is challenging. Adsorption of HMs onto raw (RPP) and burnt (BPP) potato peels (PP) is presented in the current treatise. Both adsorbents (RPP and BPP) proved to be efficient in removing Cd(II), Co(II), Cu(II), Fe(II), La(III), Ni(II), and Pb(II) from aqueous solutions. BPP was a more efficient adsorbent compared to RPP. Ecodesign of a *model, green* adsorbent was structured executing a multivariate approach, design of experiments (DoE). The purpose of using DoE is to maximize the efficiency of BPP (carbonaceous biomass) as a versatile adsorbent. Plackett–Burman design (PBD) was used as a screening phase. Four factors were considered: pH, contact time (CT), heavy metal concentration (HMC), and the adsorbent dose (AD). The Pareto chart of standardized effects shows that the most influential factor is the HMC. These data were confirmed by analysis of variance (ANOVA). Derringer's function was operated to find the best factorial blend that maximizes the adsorption process. The percentage (%) removal of Cd(II), for example, was maximized hitting 100%. Adsorbent surface characterization was performed using FTIR, BET, SEM, TGA/dTG, and EDX analyses. Adsorption was found to be physisorption that follows Temkin isotherm with sorption energy 66 kJ/mole. Adsorption kinetics was found to be pseudo-first-order. Adsorption capacity (q_m) for BPP was 239.64 mg/g. The diffusion inside the particles was very limited, while the initial rate of the adsorption was extremely high as shown by the Elovich plot.

1. Introduction

With the progress in human life and the consequent conversion to industrialization, water pollution is becoming a worldwide concern. Many heavy metals (HMs), such as cadmium, lead, copper, and mercury, which originate from anthropogenic activities, were detected in industrial wastewaters. Existing as traces, being hazardous to the ecosystem and human health and being non-biodegradable and difficult to remove even at low concentrations, HMs represent an ecological burden that has attracted great attention. Moreover, the annual toxicity of all metals exceeds

the combined total toxicity of the radioactive and organic wastes generated annually [1, 2].

According to the US Environmental Protection Agency (EPA), the most toxic HMs are mercury, lead, aluminum, cadmium, arsenic, chromium, and nickel [3]. Cadmium (II) is a water contaminant transferred mainly by discharge from metal refineries, galvanized pipes corrosion, and natural deposits erosion as well as smoking. Having a long half-life, a capability to harm the DNA, and consequently a cumulative toxic effect, exposure to Cd(II) as per many regulatory agencies is associated with cancer. Other toxic effects associated with Cd(II) include osteoporosis, height loss in

men, kidney damage, elevated blood pressure, and cardiovascular diseases [3–6].

Removal of HMs from contaminated samples has been performed by a variety of approaches. Examples for these techniques include ion-exchange, reverse osmosis (RO), chemical precipitation, electrolysis, and sorption [7–9]. Yet, most of these techniques are time, cost, chemical, and energy consuming. Moreover, most of these procedures are not efficient for HM traces and might cause production of secondary pollutants [10–12]. Adsorption, on contrary, is not only simple but also cost-effective and efficient. Modelling a *standard* adsorbent that possess all these profitable criteria becomes an exacting task [13, 14].

In 2016, around 376 million tons of potatoes were produced globally. Processing industries are one of the fates of potatoes, where nearly 14% of the harvested crop worldwide is predestined to produce chips, starch, and crisps. It is probably understood that the rest of the crop would be domestically used. For either fates, peeling of potatoes is usually the preprocessing approach commonly followed. The world production of potato peels (PP) is estimated to be 70–140 thousand tons/year [15–19]. The produced peels might be used for a variety of purposes, including production of biogases, feedstock, and fertilizers [16].

Yet, accumulation of these peels would represent an environmental burden. Recycling of these wastes into a low-cost, versatile adsorbent for the removal of HMs, dyes, drugs, etc. would be a solution to get rid of these wastes and simultaneously clean wastewater. Being rich in high-value constituents, specially polysaccharides and lignin [16, 20], which can be converted into carbonaceous material by burning, PP would be an elegant green adsorbent.

Few studies have been reported in the literature employing PP as an adsorbent. Moreover, to the best of our knowledge, none of these approaches was chemometrics-assisted, and factors usually affecting the adsorption process, e.g., pH, dose of adsorbent (AD), heavy metal concentration (HMC), and contact time (CT) of the adsorbent with the contaminant were rather investigated using the traditional univariate-based procedure [21–27]. Though being the approach commonly used by researchers, univariate analysis (UVA), with exhaustion of capitals, time, and efforts, unenviably affects the method greenness. A comparison between the present approach and the reported studies employing PP as an adsorbent is shown in Table 1.

Modelling of a *green* adsorbent from PP using a facile, cost-effective, and efficient procedure, optimization of the adsorption process, and maximizing the removal efficiency of PP were the tasks undertaken in the current approach. A multivariate platform exploiting Plackett–Burman design (PBD) was the maneuver of choice [28, 29]. A comparison between the RPP and BPP was carried out. Surface characterization of adsorbents was performed using SEM, EDX, BET, and TGA/dTGA. FTIR together with TGA/DTG were used to decide on the functional groups on the adsorbent surface that might be responsible for the adsorption process. Prepared adsorbent samples (BPP) were further used for equilibrium and kinetics studies.

2. Experimental

2.1. Materials and Reagents. All chemicals used in the current investigation were analytical grade reagents and solvents. Potatoes were purchased from local markets (Doha, Qatar). All solutions were prepared using ultrapure deionized water (18.2 M Ω). A stock solution of a mixture of 250 ppm of HMs (Cu, Zn, Ni, Cd, Fe, Pb, Co, and La) was used as the artificially contaminated water. Dilutions of the previous stock were initially tested to find the HM that is most adsorbed by either adsorbent using inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo Scientific-iCAP 6500). Cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; MW 308.48 g/mol, Sigma-Aldrich, USA) was used to prepare the single-element solution (a stock solution of 500 ppm) for flame atomic absorption spectrometric (FAAS, Shimadzu 6800) measurements. Nitric acid (5%, BDH, USA) solution was used to wash all the glassware (pipettes, volumetric flasks, beakers, and watch glasses) followed by deionized water (DIW). Hydrochloric acid and sodium hydroxide (2% solution, Sigma-Aldrich) were prepared to adjust pH of the solution. A Thermo Scientific centrifuge (SL8) was used to centrifuge the samples after treatment with the adsorbent at 4200 rpm and for 30 min. Sterilized Whatman syringe filters (0.45 μm) were used to filter the desired samples.

2.2. Methodology

2.2.1. Adsorbent Preparation and Characterization. Collected potatoes were washed using DIW to remove dirt and impurities, and then peels were soaked in DIW for 3 h. Clean peels were placed in ovens (Thermolyne furnace 48000) at 100°C until dryness. Dry PP (10 g) was grinded using a non-metallic blade mill operated at the maximum speed for 15 min and divided into two portions. The first portion was labelled raw potato peels (RPP) and was kept in a sealed container in the desiccator. The second portion was burned in furnace at 500°C for 30 min and labelled burnt potato peels (BPP).

Topographic features of the prepared adsorbent were determined using a field emission scanning electron microscopy (SEM) (FEI, Quanta 200, USA). Energy-dispersive X-ray spectroscopy (EDX) was used for the elemental analysis. Disintegration of the adsorbent with respect to temperature was studied using a thermal gravimetric analyzer (TGA, PerkinElmer-TGA 400). Fourier-transform infrared spectroscopy (FTIR, PerkinElmer Spectrum BXII, USA (transmission mode), PerkinElmer Spectrum 400, USA (ATR unit, reflection mode, Central Lab Unit, Qatar University), and Bruker Alpha, USA (ATR unit, reflection mode)) were used to determine the functional groups in both RPP and BPP. Spectra of samples were reported in the range of 4000–400 cm^{-1} , with a resolution of 4 cm^{-1} and implementing KBr pellets.

Brunauer–Emmett–Teller (BET) surface area and pore size distribution for the prepared samples were determined using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry system. Degassing of the sample was first performed at 100°C followed by the nitrogen

TABLE 1: Comparison between the performance of PP prepared in the current approach and PP as reported in the literature. Adsorbent (PP) given name and abbreviations are as mentioned in the corresponding reference.

Adsorbent (PP)	Modification method	Analytical approach used	HM removed	BET surface area and pore volume	Adsorption capacity (mg/g)	Adsorption/removal (%)	Ref.
Potato residues	No chemical modification. Peels are washed and dried in an air oven at 80°C, 24 h, then grinded and sieved.	Univariate analysis	Cd (II) Cu (II) Ni (II) Zn (II) Mn (II) Fe (II)	ND	41–90 mg/g	ND	[21]
Untreated potato peel	No chemical modification. Peels washed, dried, and sieved, then dried in an air-circulating oven at 50°C for 7 days.	Univariate analysis	Cu (II)	ND	84.74 mg/g	ND	[22]
Activated carbon of potato peels; ACPP40 ACPP70 ACPP110 ACPP160	Peels were washed and dried for 24 h then impregnated by ratios of 40, 70, 110, and 160 wt.% of ZnCl ₂ and dried at 823 K for 4 h.	Univariate analysis	Cu (II)	ACPP40: 620 m ² /g, V _{microp} 0.18 cm ³ /g, ACPP70: 810 m ² /g, V _{microp} 0.20 cm ³ /g, ACPP110: 958 m ² /g, V _{microp} 0.24 cm ³ /g, ACPP160: 1078 m ² /g, V _{microp} 0.26 cm ³ /g	62–74 mg/g	ND	[23]
Po PoP400 PoP600 PoP800	Potato peels were washed, dried for 24 h at 393 K and then impregnated with H ₃ PO ₄ (75% w/w) for 24 h. Prepared samples were heated at different temperatures (400–800°C).	Univariate analysis	Co (II)	PoP400: 904.56 cm ² /g, and 0.726 cm ³ /g PoP600: 1041.43 cm ² /g, and 2.96 cm ³ /g PoP800: 0.91 cm ³ /g, and 0.004 cm ³ /g	373 mg/g 405 mg/g ND	87.5% 92% ND	[24]
Activated carbon of potato peels (ACP)	Chemical activation using H ₃ PO ₄ in the presence of N ₂ at 600°C.	Univariate analysis	Pb (II)	498 m ² /g, and 2.960 cm ³ /g	171 mg/g	ND	[25]
Potato peels charcoal (PPC)	Thermal activation. Peels are washed and dried in an air oven at 283 K, for 2 h, burned at 973 K for 2 h, then grinded and sieved.	Univariate analysis	Cu (II)	ND	0.3877 mg/g	99.8%	[26]
<i>Current approach</i>							
RPP BPP	See the Experimental section.	Multivariate analysis	Cd(II)	RPP: 4.075 m ² /g and 0.008 cm ³ /g BPP: 13.430 m ² /g and 0.017 cm ³ /g	ND 239.64 mg/g	64.09% 99.19%	

adsorption-desorption processing. Surface area was thereafter calculated based on the nitrogen isotherms measured at 77°K and implementing the BET equation. Pore volume was obtained using the t -plots and the Barrett–Joyner–Halenda (BJH) equation. The total pore volume was evaluated at a relative partial pressure of 0.99 cm³/g.

2.2.2. Design of Experiments (DoE). Experimental design was built up using Minitab® 17 software. Four factors with their upper and lower boundaries were fed to the software, and Plackett–Burman design (PBD) was executed. Factors, their codes, and their real values at the three levels (low, mid, and high) are displayed in Table 2.

2.2.3. Procedure

(1) ICP-OES Measurements. A preliminary study was performed to test the ability of PP in removing HMs from a multielement aqueous solution. Accordingly, different amounts of RPP (0.1–0.5 g) and a volume of 10 mL of a 1 ppm multielement HM solution were mixed into a 15 mL centrifuge tube. On the other hand, blanks (no HMs or untreated HM solutions) were similarly prepared and centrifuged at 4200 rpm for 30 min. The supernatant was then separated and filtered using a syringe filter and transferred to a new set of 15 mL tubes. A similar procedure was followed employing BPP. All filtered solutions were analyzed using ICP-OES, and the % removal of each metal by the RPP and BPP (Y) was calculated using equation (1), where C_i and C_f are the initial and final concentrations of the HM.

$$Y (\% \text{ removal}) = \frac{C_i - C_f}{C_i} \times 100. \quad (1)$$

(2) FAAS Measurements. A stock solution, 500 ppm of Cd (II), was prepared by dissolving the respective amount of Cd(NO₃)₂·4H₂O in ultrapure DIW. Serial dilutions to obtain solutions with concentrations of 10–200 ppm were prepared in the same solvent. FAAS was calibrated by using Cd(II) solutions of 10, 20, 26, 30, 40, and 50 ppm with $R^2 = 0.9969$. A Cd(II) hollow cathode lamp was operated at 228.8 nm and 8 mA, while the burner is completely in a cross position. The planned PBD design was executed as shown in Table 3, where 13 base runs, with one added central point (Ct.Pt.), were generated. As shown in this table, a specific amount of Cd(II) and the stated adsorbent dose (AD) of BPP were added to each tube and left to react for the set out contact time (CT). The pH of all samples was varied between 3.00 and 9.00 ± 0.20 using small aliquots of 2% solutions of HCl/NaOH. Samples were centrifuged at 4200 rpm, filtered into a new set of labelled tubes using a Whatman syringe filter, and analyzed using FAAS.

(3) Adsorption Kinetics and Isotherms Using BPP. A series of Cd(II) solutions (5–500 ppm) were prepared in 15 ml tubes using DIW without adjusting the pH at the room temperature. An amount of 0.1 g BPP was added to each tube. Prepared solutions were kept in a shaker for 3 h at 150 rpm at

TABLE 2: Variables and their domains for a Plackett–Burman design (PBD) for both RPP and BPP.

Variables and their codes	Level 1 (low, −1)	Level 2 (central point, 0)	Level 3 (high, +1)
pH (pH, A, pH unit)	3	6	9
Heavy metal concentration (HMC, B, ppm)	10	105	200
Adsorbent dose (AD, C, g/L)	0.1	1.550	3.0
Contact time (CT, D, min)	5	32	60
Response “Y”	Maximum % of heavy metal removal		

room temperature. Following this treatment, samples were kept aside for 30 min, and then the supernatant was decanted and filtrated using a 0.2 μm syringe filter. Samples were then analyzed by FAAS. For the kinetics study, 300 mL of a 100 ppm solution of Cd(II) was prepared. Solution was then divided into three equal portions, and an exact amount of 0.506 g of BPP was added to each beaker when the solution reaches the assigned temperature (20, 31, and 41°C). The reaction medium was kept under stirring at 280 rpm, while 2 mL were withdrawn every 5 min, filtrated with 0.2 μm syringe filter, completed to 15 mL with DIW, and finally analyzed by FAAS.

3. Results and Discussion

3.1. Preliminary Results of ICP-OES for Both RPP and BPP. The main goal of this study was to test the efficiency of as-prepared PP for removal of HMs from artificially contaminated water samples. As shown in Figure 1, BPP seems to be a more efficient adsorbent compared to RPP. The later, in turn, showed a reasonable adsorption efficiency in case of Cd(II) and Pb(II), with a % removal of 64.09 and 77.34%, respectively. This superior capability of BPP will be explained later when it comes to the surface characterization.

3.2. Screening and Structuring of a Regression Model. The efficiency of PP as an adsorbent was optimized using a multivariate approach. As the purpose was to develop an ecodesign-based adsorbent, it was necessary to acquire the needed data by performing the lowest number of experiments. Multivariate analysis (MVA), in addition to its competency in diminishing the waste in experimentations, chemicals, and resources, serves to produce a top-notch data which can be further exploited with a great degree of inevitability.

In the current investigation, Plackett–Burman design (PBD) was implemented as a screening approach. PBD, in comparison to other screening and response surface methodologies (RSM), is one of the commonly operated approaches in robustness tests used for analytical method validation [28, 29]. Running this design would guarantee a low number of trials, where only the key effects are measured. Variable-variable interactions, on the other hand, are profoundly confounded with these key effects.

TABLE 3: PBD matrix for coded and uncoded variables. Response is shown as observed and predicted % of removal of Cd (II) using BPP.

Run	Coded levels of variables				Uncoded variables				Response (Y, %)		
	A ^a	B ^b	C ^c	D ^d	A ^a	B ^b	C ^c	D ^d	*Obs.	**Pred.	***Pred.
1	+1	-1	+1	-1	9	10.0	3.00	5.00	34.82	45.39	52.50
2	+1	+1	-1	+1	9	200	0.10	60.0	98.50	87.54	98.65
3	+1	+1	+1	-1	9	200	3.00	5.00	97.00	88.66	96.49
4	-1	+1	-1	-1	3	200	0.10	5.00	90.00	97.14	99.19
5	-1	-1	-1	-1	3	10.0	0.10	5.00	70.00	67.66	69.63
6	0	0	0	0	6	105	1.55	32.5	95.65	85.65	86.60
7	+1	-1	+1	+1	9	10.0	3.00	60.0	40.00	41.06	42.57
8	-1	-1	+1	+1	3	10.0	3.00	60.0	40.00	46.32	42.57
9	+1	+1	-1	+1	9	200	0.10	60.0	98.40	100.0	98.65
10	-1	+1	+1	+1	3	200	3.00	60.0	96.14	85.59	95.89
11	-1	+1	+1	-1	3	200	3.00	5.00	97.00	93.93	96.49
12	-1	-1	-1	+1	3	10.0	0.10	60.0	74.30	63.32	67.28
13	+1	-1	-1	-1	9	10.0	0.10	5.00	71.43	62.39	69.64

A^a is the pH of the solution, B^b is the heavy metal concentration (HMC, ppm), C^c is the adsorbent dose (AD, g/L), and D^d is the contact time between adsorbent and HM solution (CT, min). *Obs.: experimental values; **Pred.: predicted values before response transformation: $Y = 68.99 - 0.877 \text{ pH} + 0.2277 \text{ HMC} - 5.86 \text{ AD} - 0.0789 \text{ CT} + 9.66 \text{ Ct Pt}$; ***Pred.: predicted values after response transformation: $(Y^{\lambda-1})/(\lambda \times g^{(\lambda-1)}) = 9.47 + 0.30893 \text{ HMC} - 3.148 \text{ AD} - 0.0347 \text{ CT}$.

FIGURE 1: A Comparison of BPP and RPP in the adsorption of HMs from aqueous multielement samples.

3.2.1. Quality Tools

(1) *Pareto Chart and ANOVA*. Quality charts, e.g., Pareto chart (Figure 2), were utilized to signify the “weighty” factors among all investigated variables. As shown in Figure 2, HMC (B) is the most influential factor, followed by the AD (C). The following regression formula was obtained following a response transformation process [30, 31]:

$$\frac{(Y^{\lambda-1})}{(\lambda \times g^{(\lambda-1)})} = 9.47 + 0.30893 \text{ HMC} - 3.148 \text{ AD} - 0.0347 \text{ CT},$$

$$\lambda = 5,$$

$$g = 72.1818 \text{ is the geometric mean of } Y,$$

$$R^2 = 0.9974,$$

$$R^2(\text{adj.}) = 0.9965,$$

$$R^2(\text{pred.}) = 0.9946.$$

(2)

FIGURE 2: The Pareto chart of standardized effects drawn after response transformation. Effectual factors impacting the removal capacity of BPP exceed the reference line.

As shown in equation (2), the value of R^2 (predicted) is relatively high, implying the capability of the proposed model to calculate new observations as appropriately as it fits the current data set. Experimental and predicted values are shown in Table 3. Comparing values predicted after response transformation to the observed data shows an excellent match.

Statistical validation of screening data was performed using ANOVA testing, Table 4. Similar conclusions can be obtained. By and large, the increase in AD corresponds to a consequent elevation in the adsorption surface area and hence an increase in the removal efficiency. However, as shown in equation (2), the AD (C) negatively influences the removal efficiency of BPP. This case was previously reported [32–34]. Many justifications were given, e.g., possible hindrance caused by the interaction of the active sites of adsorbent when the dose is increased. Other elucidations count

TABLE 4: Analysis of Variance (ANOVA) for transformed response.

Source	DF*	Adj. SS*	Adj. MS*	F value	P value
Model	3	10596.6	3532.2	1145.50	0.00
Linear	3	10596.6	3532.2	1145.50	0.00
HMC	1	10335.7	10335.7	3351.88	0.00
AD	1	250.0	250.0	81.06	0.00
CT**	1	10.9	10.9	3.55	0.09
Error	9	27.8	3.1		
Curvature	1	4.0	4.0	1.36	0.28
Lack-of-fit**	7	23.6	3.4	56.40	0.10
Pure error	1	0.1	0.1		
Total	12	10624.4			

*DF is degrees of freedom, SS is sum of squares, and MS is mean of squares.

**Insignificant variables and lack-of-fit appear italic.

on the influence of the blend of experimental conditions employed on the adsorbent itself where aggregates of the adsorbent might form at a high concentration, an issue that hinders the metal uptake. Taking into consideration the large size of Cd(II) and hence existence of possible steric hindrance, HM ions would be adsorbed only on the freely reachable adsorbent sites.

(2) *Main Effects, Cube, and 2D Plots.* To examine the difference between each level means on the response, main effects plot was drawn for all variables (effectual model variables and pH). As shown in Figure 3 there is a main effect when altered levels of the same variable influence the response differently. Thus, HMC (B), which has the steepest line slope (upper right panel), would have the greatest effect on the response. In contrary, CT (D) has a line that is parallel to the x -axis, indicating no main effect.

Cube plots, on the other hand, (Figure 4) show the relation between variables and the % removal (Y). As shown in the graph, two cubes display all the patterns of a variable setting for both significant and insignificant variables. A blend of, for example, CT 5 min, pH 9, AD 3 g/L, and HMC 200 ppm, translates to a % removal of 95.5589.

A 2D view of the relationship between a fitted response and the interaction of two variables is shown in the contour plot (Figure 5); dashed lines are used to represent the contours. Dark purple regions disclose zones with the highest % removal as well as the corresponding factorial setup.

3.3. Response Optimization. One response was considered in this study, % removal (Y), and the goal was to maximize the response. A common approach is the operation of desirability plots. In this approach, factorial settings that can achieve maximum/minimum/target response can be controlled following the determination of the goal. A value of D "composite" or d "individual" desirability close or equal to 1.0000 infers a better optimality and hence a preferentiality to the target [35]. As shown in Figure 6, ideal settings are denoted as "curr." For example, a factorial blend of HMC of 200 ppm, AD of 0.1 g/L, and CT of 5 min. at pH of 6.00 ± 0.2 would achieve 99.19% of removal. Moving the vertical solid

line to the right or the left shows the impact of different factorial setting on the desirability.

3.4. Adsorbent Characterization

3.4.1. ATR-FTIR Analysis and the Proposed Mechanism for the Adsorption Process. FTIR spectra of RPP and BPP are shown in Figure 7. For RPP, a band between 3000 and 3300 cm^{-1} was observed confirming the presence of free and H-bonded -OH stretching vibration of the hydroxyl group in the adsorbent structure (derived from polymers composing the adsorbent, e.g., cellulose, hemicellulose, and lignin). This broad peak may be attributed to the existence of water molecules on the adsorbent surface [36, 37]. Peak observed at 2938 cm^{-1} can be attributed to aliphatic C-H bond stretching of the methyl and methylene groups in the polymers existing in PP [38]. Carbonyl (C=O) stretching vibration of aldehydes at 1632 cm^{-1} reflects the presence of the aromatic compounds in the lignin component of RPP [39, 40]. Peak at 1572 cm^{-1} can be assigned to the aromatic C=C stretching mode. Peaks at 1409 and 1154 cm^{-1} indicate the presence of aryl OH groups. Peaks at 1081 and 1364 cm^{-1} can be attributed to -OH and C-O stretching vibrations of the carboxylate group in lignin, hemicellulose, and cellulose [39, 41]. Yet, the FTIR fingerprint region shows that the main component is hemicellulose [42]. On the other hand, spectrum for BPP shows a very broad band between 2700 and 3600 cm^{-1} and a peak at 1631 cm^{-1} , which can be attributed to aldehydes or carboxylic acids formation. Presence of different carbon-oxygen functional groups is indicated by the peaks at 1631, 1236 and 1364, and 1071 cm^{-1} for C=O, C-O-C, and C-O, respectively.

3.4.2. BET and TGA Analysis. Porosity of prepared adsorbent is an important variable that impacts the performance of the adsorption process. Nitrogen adsorption-desorption measurements would portray a picture on the surface area readily available to the HM. The BET surface area and pore volume of both adsorbents were determined and shown in Table 1. The BET surface area of the RPP was around 3 times smaller than that of BPP, whereas the single point total pore volume was about 2 times smaller in case of RPP compared to BPP. Pore size distribution, another important feature, exemplifies the physical heterogeneity of the adsorbent surface [43–45]. Figure 8 shows that BPP has type V isotherm, indicating that BPP is porous and that as the concentration increases; adsorption of N_2 gas occurs via multilayer adsorption followed by capillary condensation. Referring to IUPAC guidelines (microporous: pore size <2 nm, mesoporous: pore size = 2–50 nm, and macroporous: pore size >50 nm), RPP is mainly micro-mesoporous where peaks are mainly observed at a pore diameter <2 nm and between 2 and 50 nm, while BPP showed mainly mesopores with fewer macropores and much less micropores. These data show the thermal activation of PP is essential for enhancing the porosity and hence the adsorption process.

FIGURE 3: Main effects plots acquired subsequent to response transformation. A gray background represents a term not in the model.

FIGURE 4: Cube plots for the model terms and pH.

TGA graph shown in Figure 9 characterizes the % weight loss of RPP against temperature in the range of 30–800°C. Decomposition of RPP is shown where the dashed line represents TGA curve, while the solid line represents differential TGA curve ($dTGA$). According to the obtained data, the first decomposition peak at ~60°C (4.65%) is probably due to water vapor or humidity in the sample. The second clear sharp peak at ~300°C (64.37%) can be attributed to the decomposition of hemicellulose, starch, and cellulose content of the peels, which are decomposed at 263, 296, and 354°C, respectively. In addition, the TGA curve shows that the peel consists mainly of hemicellulose and

starch with little amount of cellulose. These findings agree with FTIR data in the finger print region. The remaining undecomposed peels (~30.9%) can be attributed to the carbon content which is necessary for the adsorption process [5, 42, 46].

3.4.3. Surface Topography. SEM micrographs for both RPP and BPP are shown in Figures 10(a) and 10(b), respectively. The RPB (Figure 10(a)) appears to have a smooth surface. On the other hand, BPP surface looks to have more pores that appear as dark cavities. Presence of these cavities infers

FIGURE 5: 2D plots (contours) of model variables.

FIGURE 6: Optimization plots. Optimal values are represented by the vertical solid lines.

the capability of BPP to uptake the metal ions [21, 47]. Consolidating the findings of FTIR and TGA and in agreement with previous studies, the burning process of agricultural wastes results in increasing the carbon content in the prepared samples due to the destruction of cellulose and organic materials. In addition, FTIR analysis of the burnt material shows the formation of carbonyl, ether, ketones and carboxylic function groups and the

disappearance of hydroxyl group [48, 49]. This also would explain the improved capability of BPP to remove HMs compared to RPP, as is shown in Figure 1.

3.4.4. EDX Analysis. EDX was used for the elemental analysis of RPP and BPP. Attained data, Figure 11, show that the % of carbon in RPP and BPP is 55.85 and 74.76, respectively. On the other hand, oxygen content decreased

FIGURE 7: FTIR spectra of (a) RPG and (b) BPG.

FIGURE 8: Nitrogen adsorption-desorption isotherms at 77 K for RPP and BPP. Insets show the relation between pore volume and diameter for both adsorbents.

from 37.30% in RPP to 16.65% in BPP. These data confirm that most oxygen functional groups were eliminated by burning of PP and converted to mainly carbon which is responsible for the high adsorption efficiency of Cd(II). EDX shows also the presence of small concentrations of other elements, e.g., Mg, P, S, Cl, K, and Ca, and their concentrations before and after burning were less than 2%.

3.5. Equilibrium, Isotherms, and Kinetics Studies of Cd(II) Adsorption on BPP. Two factors should be considered when designing a good sorbent: (i) the adsorbent should be porous and with a reasonable surface area and (ii) adsorption rate should be high with more preference given to chemisorption [50].

FIGURE 9: TGA analysis of the as-prepared RPP sample.

3.5.1. Adsorption Isotherms. Adsorption can be described using different isotherms. Yet, a suitable isotherm is the one that can basically replicate the experimental data. Four isotherms have been considered in the current approach: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R). It is noteworthy to mention that the capacity of the adsorption isotherm is crucial in determining the adsorption efficiency of the investigated adsorbent [50].

As shown in Figure 12(a) and Table 5, the Langmuir isotherm reveals that adsorption has three regions: (i) unfavorable region where C_0 ranges from 0 to 0.78 mg/L, (ii) the second region 0.78–200 mg/L in which the favorability increases with increasing the concentration, and (iii) the third region >200 mg/L, where the dimensionless constant becomes close to zero and therefore the adsorption becomes irreversible and precipitation occurs. Adsorption capacity (q_m) was calculated, Table 5, and found to be 239.64 mg/g, which is higher than the previously reported values for adsorbents prepared from PP [21–23, 25, 26], or other adsorbents, e.g., sweet potato [5] where loading capacity of Cd(II) was 18 mg/g.

Freundlich isotherm, Figure 12(b), shows two regions, where in both the reciprocal of the exponent of nonlinearity (n) is > the unity. Therefore, there is a competition between adsorbate (Cd (II)) and water molecules on adsorption sites.

Although most of the conducted investigations on the adsorption of Cd(II) refer to Langmuir [51] and Freundlich [52] models as proposed isotherms, the adsorption curve is well fitted to the Temkin isotherm as shown in Figure 12(c). Temkin constant b_T has a value of 66 kJ/mole (less than 80 kJ/mole) [53], so the interaction between adsorbate and adsorbent is physical. R-D isotherm confirms that the adsorption is physical adsorption with energy 5 kJ/mole (less than 8 kJ/mole) [54].

3.5.2. Kinetics Studies. More than 95% of Cd(II) were consumed within 5 min of the contact time. The consumption then slows down until the equilibrium was reached within 3 h

FIGURE 10: SEM micrographs at 5000x magnification power for (a) RPP and (b) BPP.

FIGURE 11: EDX analysis of (a) RPP and (b) BPP.

FIGURE 12: Adsorption isotherms of Cd(II) on BPP: (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) D-R isotherms.

TABLE 5: General and used linear form equations of the adsorption isotherms with the extracted parameters from Figures 12(a)–12(d) as described [53–55].

Item	Langmuir	Freundlich	Temkin	Dubinin–Radushkevich
General equation	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$	$q_e = K_F C_e^{1/n}$	$q_e = RT/b_T \ln A_T C_e$	$q_e = q_m \exp(-k_{ad} \epsilon^2)$
Linear form	$(q_e/C_e) = q_m K_L - K_L q_e$	$\ln q_e = \ln K_F + (1/n) \ln C_e$	$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e$	$\ln q_e = \ln q_m - k_{ad} \epsilon^2$
Parameters	Region (I): $q_m = 0.25 \text{ mg/g}$ $K_L = -1.386 \text{ L/mg}$ $R_L = 1.45$ Region (II): $q_m = 239.64 \text{ mg/g}$ $K_L = 0.1326 \text{ L/mg}$ $R_L = 0.03$	$K_F = 16.77 \text{ L/g}$ $(1/n) = 1.714$ $n = 0.583$	$b_T = 66 \text{ kJ/mole}$ $A_T = 1.85 \text{ L/g}$	$k_{ad} = 5.689 \times 10^{-7} \text{ M}^2 \text{ J}^2$ $E = 0.937 \text{ kJ/mole}$ $(C_e \text{ in mg/L})$ $E = 5.00 \text{ kJ/mole}$ $(C_e \text{ in M})$

q_e : adsorbed amount at equilibrium; q_m : maximum adsorbed amount; C_e and C_0 : equilibrium and initial concentrations, respectively; K_L : Langmuir rate constant; R_L : dimensionless constant $R_L = (1/1 - K_L C_0)$; K_F : Freundlich rate constant; n : exponent of nonlinearity; R and T : ideal gas constant and temperature in Kelvin, respectively. b_T : Temkin isotherm constant; A_T : Temkin isotherm equilibrium binding constant; ϵ : Polanyi potential; $\epsilon = RT \ln(1 + 1/C_e)$; E : adsorption energy $E = (1/\sqrt{-2k_{ad}})$; k_{ad} : sorption energy constant.

FIGURE 13: Arrhenius plots of (a) adsorption process (first order), (b) Cd(II) consumption (second order), (c) Weber-Morris, and (d) Elovich plots.

at room temperature. The order of the adsorption reaction employing the integration method is not clear; however, Arrhenius' plots show that the reaction could be pseudo-second-order with respect to Cd(II) consumption and pseudo-first-order with respect to adsorption of Cd(II) on BPP (Figures 13(a) and 13(b)). These findings align with many reported investigations and as shown by Ho et al. [56]. The activation energies are found to be 34.46 and 46.63 kJ/mole, while the pre-exponential factor is $4100 \text{ L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ and 2479853 min^{-1} , for Cd(II) consumption and adsorption processes, respectively. Moreover, the reaction order of the adsorption confirms that the process is physical adsorption.

Intraparticle diffusion (Weber–Morris plot Figure 13(c)) shows that there are two segments with coefficient constants of 5.2×10^{-2} and $2.6 \times 10^{-2} \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, while the barrier thickness is 19.07 and 19.16 $\text{mg}\cdot\text{g}^{-1}$ for first and second steps, respectively. In addition, the adsorption is not controlled only by intraparticles diffusion, where and as shown by Weber–Morris diffusion plot, a thick layer is formed around the particle limiting the diffusion. Figure 13(d) shows Elovich plot, where desorption constant (β) is 0.0561 g/mg and initial sorption rate (α) equals $0.135 \times 10^{150} \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$, which is extremely high.

Findings of equilibrium, BET surface area, porosity, and kinetics studies are in alignment with each other. Type V N_2 adsorption isotherm, confirming the porosity of BPP, together with Langmuir isotherm, where the adsorption of Cd(II) on BPP is unfavorable at low concentration, then becomes irreversible with increasing Cd(II) content, which are indicative of physisorption. Freundlich isotherm shows that there is a competition between adsorbate and water molecules, while Temkin and D-R isotherms show the adsorption sites are heterogeneous and the adsorption is endothermic and physical. Kinetics studies confirm the adsorption is physical due to the pseudo-first-order of the reaction.

From the above, the suggested mechanism is physical adsorption, where Cd(II) is attracted to the particles under the influence of negative charges on the BPP surface that is rich with oxygen-groups. The Cd(II) fill the pores of BPP in extremely high adsorption rate to form multilayers around the particles.

4. Conclusion

The aim of this study was to optimize the efficiency of potato peels as a natural and green adsorbent for Cd(II) from contaminated aqueous samples. Two achievements were gained: cleaning of the contaminated water samples from toxic HMs and getting-rid of the peels that would accumulate and act as a source of pollution. Burning of potato peels into a char (carbonaceous biomass) was done through a simple process with no use of chemicals. Obtained results show that BPP is more efficient as an adsorbent compared to RPP. To ensure the method greenness, data were acquired through a minimal usage of efforts and resources using the DoE and in specific, Plackett–Burman design PBD as an approach. Four factors were investigated: pH, adsorbent dose, contact time, and heavy metal concentration.

Optimum conditions were decided upon after three stages: screening, optimization, and then verification using ANOVA and quality tools. A regression model was generated, and three variables were proved to be significant. Adsorbent characterization was done using FTIR, where several functional groups were proved to exist on the adsorbent surface. SEM analysis revealed the existence of pores on the surface of BPP. Furthermore, the equilibrium, BET, and kinetic studies indicate that the BPP is a porous and Cd(II) are adsorbed physically on the BPP surface as multilayers, which is well fitted by Temkin isotherm.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was made possible by UREP award (UREP 20-116-1-020) from the Qatar National Research Fund (a member of the Qatar Foundation). The statements made herein are solely the responsibility of the authors.

References

- [1] P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, and D. J. Sutton, "Heavy metal toxicity and the environment," *Experientia Supplementum*, vol. 101, pp. 133–164, 2012.
- [2] A. Jan, M. Azam, K. Siddiqui, A. Ali, I. Choi, and Q. Haq, "Heavy metals and human health: mechanistic insight into toxicity and counter defense system of antioxidants," *International Journal of Molecular Sciences*, vol. 16, no. 12, pp. 29592–29630, 2015.
- [3] United States Environmental Protection Agency, *Risk Assessment Forum, Framework for Metals Risk Assessment, Environmental Protection, EPA. 120/R-07/001*, United States Environmental Protection Agency, Washington, DC, USA, 2007.
- [4] M. A. A. Wijayawardena, M. Megharaj, and R. Naidu, "Chapter 3: exposure, toxicity, health impacts, and bio-availability of heavy metal mixtures," in *Advances in Agronomy*, D. L. Sparks, Ed., vol. 138, pp. 175–234, 2016.
- [5] E. D. Asuquo and A. D. Martin, "Sorption of cadmium (II) ion from aqueous solution onto sweet potato (*Ipomoea batatas* L.) peel adsorbent: characterisation, kinetic and isotherm studies," *Journal of Environmental Chemical Engineering*, vol. 4, no. 4, pp. 4207–4228, 2016.
- [6] G. J. Fournié, M. Mas, B. Cautain et al., "Induction of autoimmunity through bystander effects. Lessons from immunological disorders induced by heavy metals," *Journal of Autoimmunity*, vol. 16, no. 3, pp. 319–326, 2001.
- [7] A. Dąbrowski, Z. Hubicki, P. Podkościelny, and E. Robens, "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method," *Chemosphere*, vol. 56, no. 2, pp. 91–106, 2004.

- [8] L. Charerntanyarak, "Heavy metals removal by chemical coagulation and precipitation," *Water Science and Technology*, vol. 39, no. 10-11, pp. 135-138, 1999.
- [9] S. E. Bailey, T. J. Olin, R. M. Bricka, and D. D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Research*, vol. 33, no. 11, pp. 2469-2479, 1999.
- [10] X. Niu, L. Zheng, J. Zhou, Z. Dang, and Z. Li, "Synthesis of an adsorbent from sugarcane bagass by graft copolymerization and its utilization to remove Cd (II) ions from aqueous solution," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 5, pp. 2557-2564, 2014.
- [11] A. Heidari, H. Younesi, and Z. Mehraban, "Removal of Ni(II), Cd(II), and Pb(II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica," *Chemical Engineering Journal*, vol. 153, no. 1-3, pp. 70-79, 2009.
- [12] U. Garg, M. P. Kaur, G. K. Jawa, D. Sud, and V. K. Garg, "Removal of cadmium (II) from aqueous solutions by adsorption on agricultural waste biomass," *Journal of Hazardous Materials*, vol. 154, no. 1-3, pp. 1149-1157, 2008.
- [13] D. Sud, G. Mahajan, and M. Kaur, "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review," *Bioresource Technology*, vol. 99, no. 14, pp. 6017-6027, 2008.
- [14] L. S. Bădescu, D. Bulgariu, L. Ahmed, and L. Bulgariu, "Valorisation possibilities of exhausted biosorbents loaded with metal ions—a review," *Journal of Environmental Management*, vol. 224, pp. 288-297, 2018.
- [15] M. J. H. Keijbets, "Potato processing for the consumer: developments and future challenges," *Potato Research*, vol. 51, no. 3-4, pp. 271-281, 2008.
- [16] M. Hijosa-Valsero, A. I. Paniagua-García, and R. Díez-Antolínez, "Industrial potato peel as a feedstock for bio-butanol production," *New Biotechnology*, vol. 46, pp. 54-60, 2018.
- [17] FAOSTAT, *Statistics of the Food and Agriculture Organisation of the United Nations*, FAOSTAT, Rome, Italy, 2018.
- [18] A. Schieber and M. D. A. Saldana, "Potato peels: a source of nutritionally and pharmacologically interesting compounds—a review," *Food*, vol. 3, no. 2, pp. 23-29, 2009.
- [19] K. C. Chang, "Polyphenol antioxidants from potato peels: extraction, optimization and application to stabilizing lipid oxidation in foods," in *Proceedings of the National Conference on Undergraduate Research (NCUR)*, Ithaca College, NY, USA, 2011.
- [20] K. B. Jeddou, F. Chaari, S. Maktouf, O. Nouri-Ellouz, C. B. Helbert, and R. E. Ghorbel, "Structural, functional, and antioxidant properties of water-soluble polysaccharides from potatoes peels," *Food Chemistry*, vol. 205, pp. 97-105, 2016.
- [21] M. Feizi and M. Jalali, "Removal of heavy metals from aqueous solutions using sunflower, potato, canola and walnut shell residues," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 54, pp. 125-136, 2015.
- [22] E.-K. Guechi and O. Hamdaoui, "Evaluation of potato peel as a novel adsorbent for the removal of Cu(II) from aqueous solutions: equilibrium, kinetic, and thermodynamic studies," *Desalination and Water Treatment*, vol. 57, no. 23, pp. 10677-10688, 2016.
- [23] J. C. Moreno-Piraján and L. Giraldo, "Activated carbon obtained by pyrolysis of potato peel for the removal of heavy metal copper (II) from aqueous solutions," *Journal of Analytical and Applied Pyrolysis*, vol. 90, no. 1, pp. 42-47, 2011.
- [24] G. Z. Kyzas, E. A. Deliyanni, and K. A. Matis, "Activated carbons produced by pyrolysis of waste potato peels: cobalt ions removal by adsorption," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 490, pp. 74-83, 2016.
- [25] G. Z. Kyzas, G. Bomis, R. I. Kosheleva et al., "Nanobubbles effect on heavy metal ions adsorption by activated carbon," *Chemical Engineering Journal*, vol. 356, pp. 91-97, 2019.
- [26] T. Aman, A. A. Kazi, M. U. Sabri, and Q. Bano, "Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent," *Colloids and Surfaces B: Biointerfaces*, vol. 63, no. 1, pp. 116-121, 2008.
- [27] Z. Zhang, X. Luo, Y. Liu et al., "A low cost and highly efficient adsorbent (activated carbon) prepared from waste potato residue," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 49, pp. 206-211, 2015.
- [28] K. Vanaja and R. H. Shobha Rani, "Design of experiments: concept and applications of Plackett Burman design," *Clinical Research and Regulatory Affairs*, vol. 24, no. 1, pp. 1-23, 2007.
- [29] S. L. C. Ferreira, A. O. Caires, T. d. S. Borges, A. M. D. S. Lima, L. O. B. Silva, and W. N. L. dos Santos, "Robustness evaluation in analytical methods optimized using experimental designs," *Microchemical Journal*, vol. 131, pp. 163-169, 2017.
- [30] R. Bruns, I. Scarminio, and B. Neto, *Statistical Design—Chemometrics*, Elsevier, Vol. 25, Amsterdam, Netherlands, 2006.
- [31] G. E. P. Box and D. R. Cox, "An analysis of transformations," *Journal of the Royal Statistical Society: Series B (Methodological)*, vol. 26, no. 2, pp. 211-243, 1964.
- [32] J. Xie, Y. Lin, C. Li, D. Wu, and H. Kong, "Removal and recovery of phosphate from water by activated aluminum oxide and lanthanum oxide," *Powder Technology*, vol. 269, pp. 351-357, 2015.
- [33] S. Iftekhhar, D. L. Ramasamy, V. Srivastava, M. B. Asif, and M. Sillanpää, "Understanding the factors affecting the adsorption of lanthanum using different adsorbents: a critical review," *Chemosphere*, vol. 204, pp. 413-430, 2018.
- [34] A. Esposito, F. Pagnanelli, A. Lodi, C. Solisio, and F. Vegliò, "Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations," *Hydrometallurgy*, vol. 60, no. 2, pp. 129-141, 2001.
- [35] G. Derringer and R. Suich, "Simultaneous optimization of several response variables," *Journal of Quality Technology*, vol. 12, no. 4, pp. 214-219, 1980.
- [36] M. Madhavarao, A. Ramesh, G. Purnachandrarao, and K. Seshiah, "Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls," *Journal of Hazardous Materials*, vol. 129, no. 1-3, pp. 123-129, 2006.
- [37] M. J. K. Ahmed, M. Ahmaruzzaman, and R. A. Reza, "Lignocellulosic-derived modified agricultural waste: development, characterisation and implementation in sequestering pyridine from aqueous solutions," *Journal of Colloid and Interface Science*, vol. 428, pp. 222-234, 2014.
- [38] U. Farooq, M. A. Khan, M. Athar, and J. A. Kozinski, "Effect of modification of environmentally friendly biosorbent wheat (*Triticum aestivum*) on the biosorptive removal of cadmium(II) ions from aqueous solution," *Chemical Engineering Journal*, vol. 171, no. 2, pp. 400-410, 2011.
- [39] R. Bodirlău, C. A. Teacă, and I. Spiridon, "Preparation and characterization of composites comprising modified hardwood and wood polymers/poly(vinyl chloride)," *Bioresources*, vol. 4, no. 4, pp. 1285-1304, 2009.

- [40] K. Johari, N. Saman, S.-T. Song, and H. Mat, "Adsorption equilibrium and kinetics of elemental mercury onto coconut pith," *Journal of Environmental Science and Technology*, vol. 8, no. 2, pp. 74–82, 2015.
- [41] M. Bansal, U. Garg, D. Singh, and V. K. Garg, "Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk," *Journal of Hazardous Materials*, vol. 162, no. 1, pp. 312–320, 2009.
- [42] H. Yang, R. Yan, H. Chen, D. H. Lee, and C. Zheng, "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel*, vol. 86, no. 12–13, pp. 1781–1788, 2007.
- [43] W. C. Conner, J. F. Cevallos-Candau, E. L. Weist, J. Pajares, S. Mendioroz, and A. Cortes, "Characterization of pore structure: porosimetry and sorption," *Langmuir*, vol. 2, no. 2, pp. 151–154, 1986.
- [44] O. Altin, H. Ö. Özbelge, and T. Dogu, "Effect of pH in an aqueous medium on the surface area, pore size distribution, density, and porosity of montmorillonite," *Journal of Colloid and Interface Science*, vol. 217, no. 1, pp. 19–27, 1999.
- [45] Y. Chen, S.-R. Zhai, N. Liu, Y. Song, Q.-D. An, and X.-W. Song, "Dye removal of activated carbons prepared from NaOH-pretreated rice husks by low-temperature solution-processed carbonization and H₃PO₄ activation," *Bioresource Technology*, vol. 144, pp. 401–409, 2013.
- [46] L. Sanchez-Silva, D. López-González, J. Villaseñor, P. Sánchez, and J. L. Valverde, "Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis," *Bioresource Technology*, vol. 109, pp. 163–172, 2012.
- [47] H. J. Park, S. W. Jeong, J. K. Yang, B. G. Kim, and S. M. Lee, "Removal of heavy metals using waste eggshell," *Journal of Environmental Sciences*, vol. 19, no. 12, pp. 1436–1441, 2007.
- [48] A. E. Ogungbenro, D. V. Quang, K. Al-ali, and M. R. M. Abu-zahra, "Activated carbon from date seeds for CO₂ capture applications," *Energy Procedia*, vol. 114, pp. 2313–2321, 2017.
- [49] A. E. Ogungbenro, D. V. Quang, K. A. Al-ali, L. F. Vega, and M. R. M. Abu-zahra, "Physical synthesis and characterization of activated carbon from date seeds for CO₂ capture," *Journal of Environmental Chemical Engineering*, vol. 6, no. 4, pp. 4245–4252, 2018.
- [50] É.C. Lima, M. A. Adebayo, and F. M. Machado, "Chapter 3: kinetic and equilibrium models of adsorption," in *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*, C. P. Bergmann and F. M. Machado, Eds., pp. 33–43, Springer International Publishing, Cham, London, UK, 2015.
- [51] A. Agrawal and K. K. Sahu, "Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue," *Journal of Hazardous Materials*, vol. 137, no. 2, pp. 915–924, 2006.
- [52] M. Torab-Mostaedi, M. Asadollahzadeh, A. Hemmati, and A. Khosravi, "Equilibrium, kinetic, and thermodynamic studies for biosorption of cadmium and nickel on grapefruit peel," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 44, no. 2, pp. 295–302, 2013.
- [53] A. R. Kaveeshwar, S. K. Ponnusamy, E. D. Revellame, D. D. Gang, M. E. Zappi, and R. Subramaniam, "Pecan shell based activated carbon for removal of iron(II) from fracking wastewater: adsorption kinetics, isotherm and thermodynamic studies," *Process Safety and Environmental Protection*, vol. 114, pp. 107–122, 2018.
- [54] V. d. O. S. Neto, G. S. C. Raulino, P. d. T. C. Freire, M. A. Araujo-Silva, and R. F. d. Nascimento, "Equilibrium and kinetic studies in adsorption of toxic metal ions for wastewater treatment," in *A Book on Ion Exchange, Adsorption and Solvent Extraction*, M. Naushad and Z. A. AlOthman, Eds., Nova Science Pub Inc, Hauppauge, NY, USA, 2013.
- [55] K. Y. Foo and B. H. Hameed, "Insights into the modeling of adsorption isotherm systems," *Chemical Engineering Journal*, vol. 156, no. 1, pp. 2–10, 2010.
- [56] Y. S. Ho and G. McKay, "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents," *Process Safety and Environmental Protection*, vol. 76, no. 4, pp. 332–340, 1998.