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Screening of Significant Parameters Affecting Zn (II) Adsorption by Chemically Treated Watermelon Rind

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ABSTRACT

In recent years, agricultural wastes and biomass have been extensively investigated as low cost adsorbents in heavy metal removal owing to the facts that they are relatively cheap and exhibit high adsorption capacities. Watermelon rind is a natural and rich source of the non-essential amino acid citrulline, containing abundant amino and carboxyl groups, which have been proven to have great capability of binding heavy metals in aqueous solutions. In the present study, various chemical solvents were utilized to pre-treat watermelon rind in enhancing its Zn^{2+} ions adsorption performance. Improvement in the physical and chemical properties of chemically treated watermelon rind was evidenced through SEM and FTIR characterization results. Drastic improvement in the adsorption efficiency was observed compared to non-treated watermelon rind that resulted that at only 52.4 % removal percentage. NaOH solution was found to be the best pre-treatment solvent compared to $Ca(OH)_2$, H_2SO_4, and $C_6H_8O_7$, with the highest Zn^{2+} removal percentage attained up to 90.2 % using NaOH treated watermelon rind. The Zn^{2+} ions adsorption process using NaOH treated watermelon rind was then further investigated using a statistical tool. Fractional factorial design (FFD) was applied to evaluate the effects of 7 process parameters, namely solution pH, adsorption temperature, biosorbent dosage, initial metal ions concentration, contact time, concentration of pre-treatment solvent and stirring rate. Contribution of every parameter in influencing the adsorption efficiency was evaluated and factors that significantly affected the adsoprtion were elucidated by employing experimental design and analysis of variance in FFD. The result of factorial design revealed that solution pH, adsorption temperature, biosorbent dosage, initial metal ions concentration and the interaction effect between biosorbent dosage and initial metal ions concentration imposed significant effect ($P < 0.05$) to the removal percentage of Zn^{2+} ions at the end of the adsorption process. Effects of these process factors on the adsorption efficiency were investigated and discussed in detail.

Keywords:
Adsorption, Chemically treated, Fractional factorial design, Watermelon rind, Zinc

1. Introduction

With advancement in the global economic development and growing industrialization, wastewater treatment is becoming an important factor to be considered [1]. This is to prevent deterioration of current pollution conditions and minimization of adverse effects to the environment. Industrial effluent

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discharged from various industries such as dye, fertilizer, electroplating, paint, battery, piping, and steel contains different types of heavy metal ions [2]. Generally, metals with density higher than 5 g/cm^3 and atomic number above 20 are regarded as 'heavy' [3]. According to Angelakis and Snyder [4], discharge of such heavy metals into the environment without proper treatment or monitoring are often associated with environmental problems, particularly water pollution. Among all, water pollution due to the presence of Zn (II) ions in water streams is one of the major problems nowadays. The applications of zinc are wide in many industries. Its applications diversify from the manufacture of negative plate in electrical batteries to the galvanization of steel, and also the preparation of specific alloys [5]. Moreover, zinc can be also used as catalyst and heat dispenser in the final product of rubber industry [6]. Hence, traces of Zn (II) ions in the wastewater stream originating from these industries are common. Sud et al. [7] reported that contamination of water bodies due to the presence of Zn (II) ions caused harmful effects to both human health and environment. The negative impacts included breakdown of immune system, causing human body system to act like an open gateway for all kind of diseases and also imposing damages to the nervous system. As such, its presence at even a very low concentration is expected to result in various health problems to mankind and potential damage to the environment [8].

To date, various wastewater treatment methods had been developed, which were categorized as physical, chemical, and biological approaches. Different methods such as coagulation-flocculation, membrane separation, electrochemical oxidation, ion exchange, microbial biodegradation, and adsorption had been reported as successful ways to remove heavy metals from the wastewater [9]. Among all, adsorption was recognized as the most effective method compared to others due to its operational simplicity, high efficiency with low energy requirements, low cost, biodegradability, and ability to treat concentrated pollutants as well as good control over the Biochemical Oxygen Demand [9, 10]. Apart from cost effectiveness and competitive performance, regeneration of adsorbent at low cost, availability of known process equipment, sludge free operation, and possible recovery of sorbate are the prominent advantages offered by adsorption method [10]. As of now, activated carbon is one of the most widely researched adsorbents for adsorption process in wastewater treatment. The effectiveness of activated carbon was proven to be excellent in terms of heavy metals, dyes and other pollutants removal from wastewater. Nevertheless, its utilization was highly debated due to the high energy consumption and cost incurred in the synthesis of activated carbon [11]. Therefore, the emphasis is gradually shifting to biosorbent, an alternative inexpensive and more environmentally friendly adsorbent that would drastically reduce the cost of an adsorption system.

As a result, many approaches had been attempted to produce alternative adsorbents including the utilization of waste materials capable of removing significant quantity of dyes from wastewater [12–14]. The use of renewable sources of low cost agricultural or household waste which requires little processing to produce biosorbent is considered as a better choice. In the context of heavy metal removal, biosorbents derived from fruit waste materials such as orange, lemon, mandarin and pomelo peels were extensively investigated. Watermelon is one of the most abundant and cheap fruits available in the world. Being the largest and heaviest fruit with an estimated plantation of 3,413,750 ha worldwide in 2011 [15], watermelon flesh is edible, sweet and appears in red in colour. It is often used in juices and salads preparation but the outer rind is considered as waste which has no commercial value. The wastes create increasing disposal and potentially severe, environmental problems. Since watermelon rind waste is abundant and readily available, its conversion to adsorbent in wastewater treatment offers both economic feasibility and waste handling advantages. According to Quek et al. [16], watermelon rind consists of pectin, citrulline, cellulose, proteins and carotenoids. These are regarded as biopolymers with functional groups such as hydroxyl (cellulose) and carboxyl (pectin) that can easily bind with metal ions [5]. Hence, watermelon rind is well used as an adsorbent in water pollution control. Both untreated and chemically treated watermelon rind were reported to have successfully remove heavy metals such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+} and Cd^{2+} from wastewater [17–19]. This further evidenced the potential of watermelon rind to be exploited as adsorbent in the removal of heavy metals from wastewater.

Numerous reports in the literature had demonstrated the superiority of chemically modified adsorbents compared to the non-treated ones in their respective adsorption performances. To name a few, Yargıç et al. [20] investigated the performance of chemically treated tomato waste by using hydrochloric acid for the removal of Cu(II) while Demirbas et al. [21] studied the chemical modification of apricot stone, almond shell and cornelian cherry using concentrated sulfuric acid for the removal of Cr (VI) from aqueous solution. The results revealed that chemical treatment increased the efficiency of heavy metal adsorption following the removal of soluble organic compounds and elimination of colour pigment from the adsorbent [20–21]. This was also supported by Wan Ngah and Hanafia [22] who described that chemical modification improved the adsorption capacity of adsorbents mainly due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal uptake. Generally, chemical modification of native biosorbents involves washing or soaking of biosorbents in various chemical reagents such as mineral and organic acids, alkali, organic solvents and other chemicals [14, 23–24].

In view of that, chemically treated watermelon rind serves as an attractive approach in adopting these cheaply abundant natural resource wastes as adsorbents, besides providing an alternative solution for Zn^{2+} ions removal from wastewater streams. There are, however, multiple process variables that are possible in significantly affecting the removal efficiency, starting from the adsorbent pre-treatment step until the stage of adsorption process. Due to the large number of process factors studied, Fractional Factorial Design (FFD) was used in this study to screen the significant variables involving in the Zn^{2+} adsorption process using chemically treated watermelon rind as adsorbent. A number of common factors affecting the adsorption process such as solution pH, adsorption temperature, biosorbent dosage, initial metal ions concentration, contact time, concentration of pre-treatment solvent and stirring rate were studied. Insignificant variables can then be eliminated in order to obtain a smaller and more manageable set of process variables in controlling and manipulating the Zn^{2+} adsorption process. To the authors' best knowledge, report on the screening of adsorption process parameters prior to optimization study is limited in the literature. The outcome of the present study is expected to be beneficial in the subsequent optimization study of chemically treated watermelon rind to remove Zn (II) ions from aqueous solution.

2. Methodology and Experiment Setup

2.1 *Preparation of Chemically Treated Watermelon Rind Biosorbent*

Watermelon rind was collected from the local fruit stall and washed with tap water for several times to remove dust and soluble materials. It was cut into small pieces (1 cm × 1 cm) and dried at 80°C for 24 hours. The dried watermelon rind was then grounded into powder and sieved to uniform size of 150 µm. Subsequently, it was soaked into different chemical solvents which were inclusive of citric acid ($C_6H_8O_7$), sulfuric acid (H_2SO_4), calcium hydroxide ($CaOH_2$), and sodium hydroxide (NaOH) for 4 hours [19]. The treated watermelon rind was washed with distilled water repeatedly until constant pH was obtained. It was then dried at 60°C until constant weight was obtained. Lastly, the dried treated watermelon rind was stored in an airtight polyethylene container at room temperature prior to the characterization and adsorption studies.

2.2 *Preparation of Synthetic Zn (II) Solution*

The synthetic wastewater was prepared by dissolving zinc sulphate in distilled water to obtain 1000 mg/L of Zn^{2+} solution. The desired concentrations of Zn^{2+} solution were prepared by using appropriate dilutions from the stock solution.

2.3 *Characterization Study*

2.3.1 *Scanning Electron Microscopy (SEM)*

SEM analysis was performed to observe the surface structure of all biosorbents synthesized in Section 2.1, including the raw watermelon rind. The morphological modifications on the adsorbents' surface after different chemical treatments were observed and investigated. All samples were analyzed using JEOL model JSM-7800F Field Emission Scanning Electron Microscope (FESEM).

2.3.2 *Fourier-Transform Infrared Spectroscopy (FTIR)*

FTIR study was performed to identify the functional groups in the raw and chemically treated watermelon rind. The infrared spectra were measured using Perkin-Elmer (Spotlight 200i). Briefly, 1.0 mg of watermelon rind prepared in Section 2.1 was mixed with 99.0 mg of potassium bromide (KBr). The KBr die model was compressed by using a compressor by an applied pressure of 10 metric tons for about 3 mins to form pellets. The transmittance spectra were obtained in a wavelength ranged between 4000 – 400 cm^{-1}. The spectra of all samples were compared and discussed.

2.4 *Comparison of Adsorption Performance Using Different Chemically Treated Biosorbents*

The Zn^{2+} ions adsorption process was conducted based on the methods described by Othman et al. [25] with slight modifications. 250 mL of 100 ppm Zn^{2+} solution with pH 6 was heated up to 60°C. Then, chemically treated watermelon rind biosorbent was added into the solution at the ratio of 4 mg/ml. The mixture was stirred at 150 rpm for 1 hour. Following that, the mixture was filtered using filter paper and the filtrate was analyzed by AAS (Perkin-Elmer, AAnalyst 400). The removal efficiency of the biosorbent for Zn^{2+} ions was then calculated using Eq. (1).

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100\% \qquad (1)$$

where C_o was the initial Zn^{2+} ions concentration (ppm) and C_e was the final Zn^{2+} ions concentration (ppm). The procedures were repeated for all chemically treated watermelon rind biosorbent prepared in Section 2.1. The removal efficiencies obtained were compared to the raw watermelon rind used as biosorbent.

2.5 *Fractional Factorial Design (FFD)*

Screening of process parameters aims at reducing determinations as to which few parameters result in the greatest impacts on the Zn^{2+} adsorption efficiency. In this study, 7 independent factors (Table 1) were tested at both high (+1) and low (-1) level. The type of biosorbent used in this section was based on the one that demonstrated the best adsorption performance from Section 2.4. Zn^{2+} ions removal percentage was listed as the response variable. In order to evaluate the effect of adsorption parameters, 32 experiments were performed in random in order to cover all combinations of the factor levels in the FFD design. Statistical analysis of the FFD was performed in the form of analysis of variance (ANOVA) by using the software Design-Expert 10®. The analysis included the F-test associated with probability p(F) and determination of the coefficient, R^2. The t-value was also used to estimate the coefficients and associated probability p(t). All experiments were done in triplicate and data presented were mean values of the triplicates.

Table 1 Adsorption parameters and levels for the fractional factorial design (FFD)

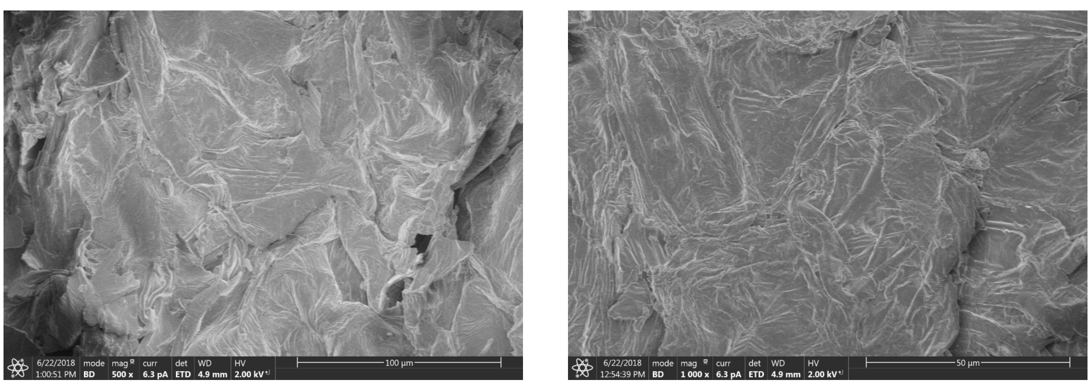
Factor	Parameter	Low (-1)	High (1)
A	pH	3	6
B	Temperature (℃)	30	70
C	Biosorbent dosage (mg/mL)	2	40
D	Initial metal ion concentration (ppm)	50	500
E	Stirring rate (rpm)	100	500
F	Concentration of pre-treatment solvent (M)	0.05	1.00
G	Contact time (hr)	1	3

3. Results and Discussion

3.1 *Characterization of Chemically Treated Watermelon Rind Biosorbents*

The adsorption capability of watermelon rind in the application of wastewater treatment had been proven in various researches such as the removal of nickel [26], lead and copper [18–19], and trivalent chromium [18]. In this study, different chemical pre-treatments were attempted on watermelon rind using different solvents, namely citric acid, sulfuric acid, calcium hydroxide and sodium hydroxide to investigate the possibility of enhancing the adsorption performance on the removal of Zn^{2+} ions. The pre-treated watermelon rinds were subjected to characterization studies in order to determine the significance alterations on the surface morphology and chemical properties of the watermelon rind adsorbents.

In this study, SEM was used to examine the surface modification changes in the untreated and pre-treated biosorbent. The SEM microscopic images of untreated watermelon rinds, and treated with organic acid (citric acid, $C_6H_8O_7$), inorganic acid (sulfuric acid, H_2SO_4) and different type of bases (calcium hydroxide, $Ca(OH)_2$ and sodium hydroxide, NaOH) at different magnifications are presented in Fig. 1 and 2, respectively.



(a) (b)

Fig. 1. SEM image of untreated watermelon rind at (a) 500x magnification; and (b) 1000x magnification

As evidenced in Fig. 1 (a) and (b), the surface of untreated watermelon rind observed under 500x and 1000x magnifications showed dense and rigid structure without any layer or irregular morphologies. The images showed a homogeneous surface without any porous structures.

Chemical pre-treatments with acids and bases could potentially modify the surface structure of the watermelon rind and it is depicted in Fig. 2 (a) – (d). For acid treatments, new pores were found to be developed on the surface structure due to the reaction between the watermelon rind and the acids (Fig. 2 (a) and (b)). These pores appeared in many different sizes and the shape was mainly round. Based on the results, treatment using inorganic acid (Fig. 2 (b)) created more pores as compared to the organic citric acid (Fig. 2 (a)). This could probably due to the strength of the latter that was weaker in nature. On the other hand, alkaline treated watermelon rinds demonstrated significant surface modifications as revealed in Fig. 2 (c) and (d). It was obvious that the surface was transformed into rough morphologies with diverse granule sizes compared to the untreated one (Fig. 1). Following alkaline treatments, formation of cavities and more porous surface structures with well-built pores suggested a high possibility for adsorbate diffusion onto the biosorbent. Hence, in this study, it is expected that enhancement on the access of Zn^{2+} ions onto the watermelon rind adsorbents' micro and mesopores can be achieved. Eventually, the adsorption of Zn^{2+} ions can then be improved following the interactions between these ions with the functional groups present on the surface of the treated watermelon rind adsorbents [27].

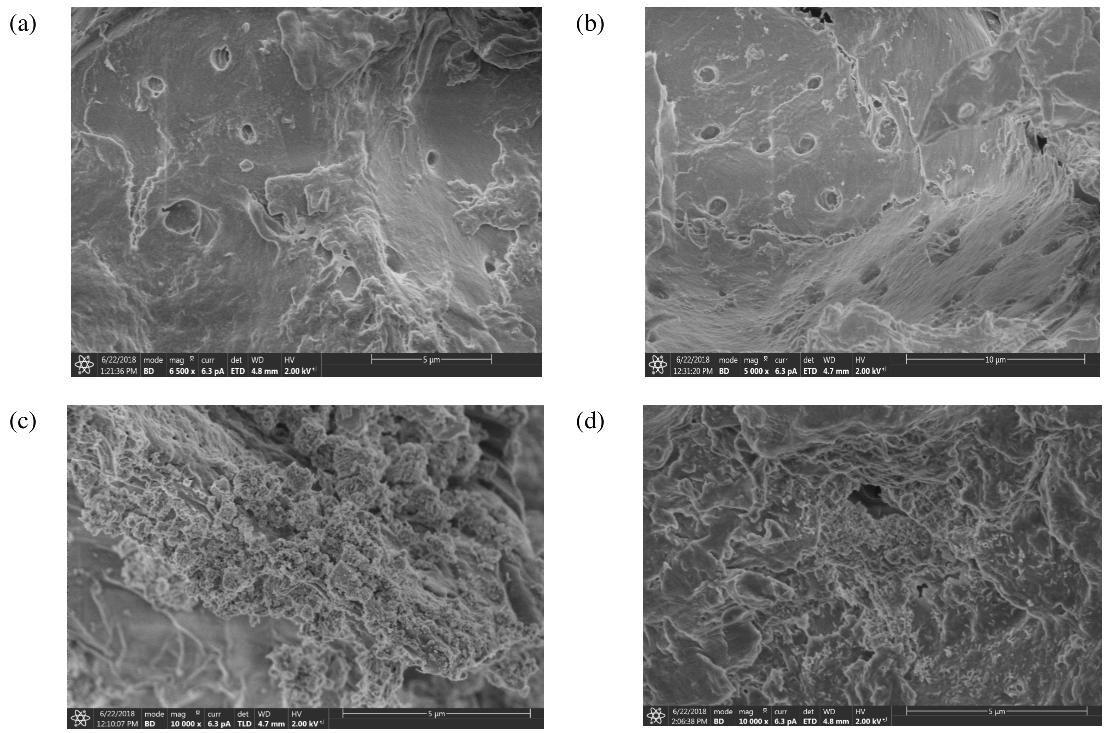
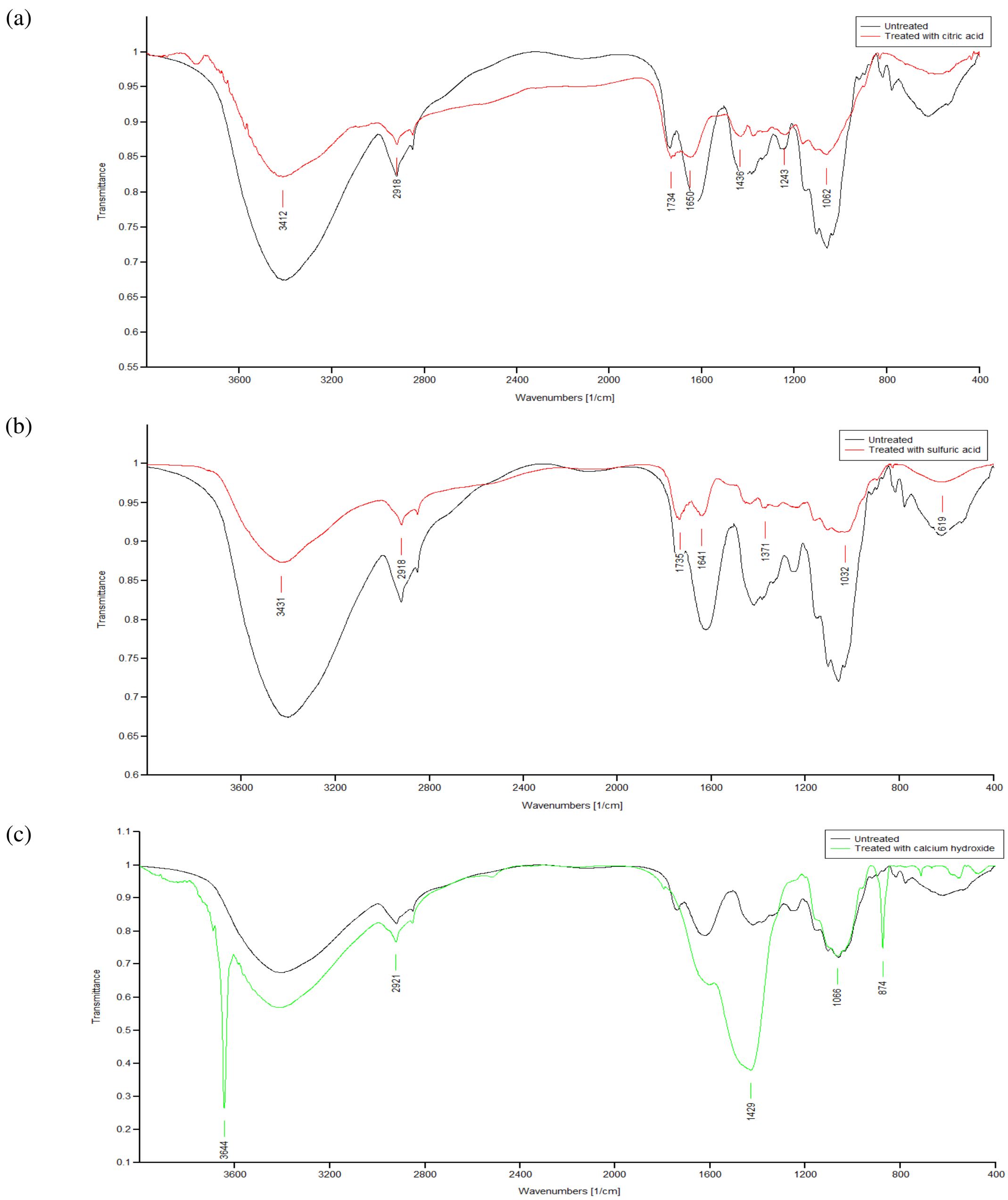


Fig. 2. SEM image of chemically treated watermelon rind with (a) citric acid; (b) sulfuric acid; (c) calcium hydroxide; and (d) sodium hydroxide at different magnifications (6500x – 10 000x)

By comparing Fig. 1 and 2, it clearly showed alterations in the watermelon rind surface morphologies after the chemical treatment processes. The surface features of the untreated watermelon rinds showed smooth and fine fibers structure with linear morphology. In contrast, the micrographs of chemically treated watermelon rind with both acids and bases revealed the existence of an accumulation of very fine particles, causing an irregular surface structures. To further elaborate on that, the surface of treated watermelon rind was rough, with no fixed shape and size, and was found to be more porous. The particles were of various dimensions, and contained a large number of steps and kinks on the external surface with broken edges. Therefore, it can be further confirmed that chemical treatments improved the surface structure of the biosorbent with improving porosity, thus, larger surface area is resulted as compared to untreated biosorbent. As described by Ibrahim et al. [28], chemical treatments promoted degradation of the hemicellulose and lignin components in watermelon rind that could be one of the plausible explanations for the improvement in porosity and surface area of the biosorbents. Following the enhancement in surface area, it is anticipated that the performance of chemically treated watermelon rind as biosorbent for metal biosorption will be improved.

On the other hand, Fourier-Transform Infrared Spectroscopy (FTIR) spectra was used for the determination of potential changes in vibration frequency in the functional groups of the untreated and chemically treated watermelon rinds. The FTIR spectra obtained are presented in Fig. 3 (a) – (d).



(d)

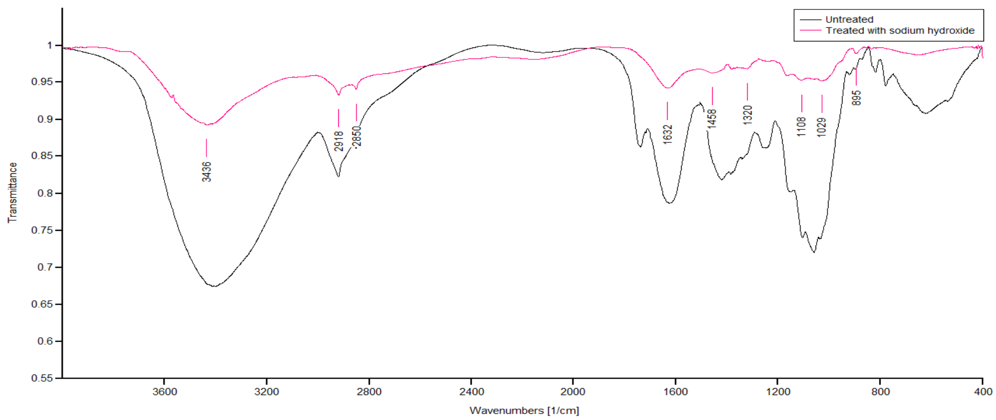


Fig. 3. FTIR spectra of untreated watermelon rind and chemically treated with (a) citric acid; (b) sulfuric acid; (c) calcium hydroxide; and (d) sodium hydroxide

FTIR analysis reveals the characteristic bonds of watermelon rinds. Based on the spectra obtained for all samples, there was a broad band at the wavenumber 3401 cm^{-1}, probably due to the OH stretching of polymeric compounds. The characteristic peak at 2919 cm^{-1} was the symmetric stretch of aliphatic chains (-CH). Furthermore, the peak at wavenumber 1739 cm^{-1} was identified as the stretching vibration of C=O and COO groups, and the peak at 1419 cm^{-1} could be either phenolic O-H and C=O stretching of carboxylates [29]. Also, according to Cardoso et al [30], the wavenumber at 1247 cm^{-1} was due to vibration of carboxylic acids. Finally, Calero et al [31] mentioned that any peak that was less than 900 cm^{-1} could be regarded as C-Hn aliphatic or aromatics. As observed in Fig. 3 (a) and (b), acid treatments resulted in decreased peak intensity at 1624 and 1247 cm^{-1}. This changes indicated possible disruptions of aliphatic and aromatic links, which were presented originally in untreated watermelon rind. In regards to basic treatments, chemical modification on the cell wall components due to removal of impurities from the surface of watermelon rind was evidenced. This observation was attributed by the disappearance of peak at 1739 cm^{-1} in Fig. 3 (c) and (d) [31]. A sharp peak recorded at wavenumber 3644 cm^{-1} in Fig. 3 (c) however might be caused by undissolved calcium hydroxide [32]. Nevertheless, it was worth to highlight that the formation of additional functional groups, such as carboxyl (-COOH), carboxylate (-COO-), and alcoholic (-OH) were spotted in spectra of alkaline treated watermelon rinds. All these functional groups are important for an efficient biosorption process. In view of this, better adsorption performance is expected from calcium hydroxide and sodium hydroxide treated watermelon rinds compared to those of citric acid and sulfuric acid treatments.

3.2 *Comparison of Adsorption Performance Using Different Chemically Treated Biosorbents*

The adsorption performances of watermelon rind treated using different solvents were compared on the removal of Zn^{2+} ions from aqueous solution. The results are presented in Fig. 4.

The adsorption results showed that chemical treatment with alkali solutions improved the adsorption capacity of watermelon rind significantly. However, acid treatment was found to retard the removal efficiency. This observation could be associated with protonation of watermelon rind cell wall following the acidic treatment. Consequently, Zn^{2+} ions could not attach to the surface of biosorbent due to the presence of repulsive forces. The best adsorption result was obtained when alkaline modified watermelon rind was used as biosorbent, achieving the removal percentage within the range of 70 – 90%. Enhancement in the Zn^{2+} ions removal percentage as compared to control sample (untreated watermelon rind) could be explained by the significant improvement obtained in both physical and chemical properties such as surface area, total volume of porous surface, and alkaline functional groups, following the chemical treatments with sodium hydroxide and calcium hydroxide (Section 3.1). Comparing with untreated watermelon rind, sodium hydroxide chemical treatment enhanced the zinc removal amount drastically, up to almost 40%. Table 2 tabulates the comparison of adsorption capacity using different types of watermelon rind. Consistent with the results of Zn^{2+} ions removal percentage, NaOH treated watermelon rind exhibited the highest adsorption capacity at 22.55 mg/g, while sulfuric acid treated watermelon rind demonstrated the poorest adsorption capacity among all.

Table 2 Adsorption parameters and levels for the fractional factorial design (FFD)

Type of Watermelon Rind	Adsorption Capacity (mg/g)
Untreated	13.10
Citric Acid	5.08
Sulfuric Acid	3.78
Sodium Hydroxide	22.55
Calcium Hydroxide	17.55

The findings obtained in the present study were consistent with various reports in literature that the metal uptake of chemically treated biosorbent was higher than the untreated one in all cases. For instance, Tarley et al. [33] found that the removal efficiency of Cd was almost increased by double when rice husk was treated with NaOH. Also, another finding reported by Šćiban et al. [34] related to the efficiency of sawdust in the removal of Cu^{2+} and Zn^{2+} ions found a noticeable increase in the adsorption efficiency after treatment of the sawdust with NaOH, prior to the removal process. In fact, the authors reported that adsorption capacities of alkali modified adsorbents were higher than unmodified one from 2.5 to 5 times for copper ions, and about 15 times for zinc ions. With the results obtained from current work, NaOH treated watermelon rind showed the best performance in terms of improvement of adsorbent's physical and chemical properties, as well as the subsequent Zn^{2+} ions removal percentage. Therefore, this adsorbent was used as the sample for the following parameters screening experiments.

3.3 *Screening of Process Variables by Fractional Factorial Design*

In order to identify the significant parameters affecting the removal efficiency of chemically treated watermelon rind, FFD with the level of 2^{7-2} was selected considering the large number of variables. It was used to reduce the number of experiments, resources, and time without jeopardizing the accuracy of results. The experimental and predicted removal efficiencies of Zn^{2+} ions with different experimental combinations are presented in Table 3.

Analysis of variance (ANOVA) was performed on the main effects and the results are summarized in Table 3. Results of the F-value and the probabilities of Prob > F are also shown. The result indicated the adsorption parameters that significantly affected removal of Zn^{2+} ions using NaOH treated watermelon rind. The value of Prob > F was found to be <0.0001, indicated that the model was significant (Table 4) and hence, was adequate to represent the adsorption process in this study. The generated model correlating the percentage of Zn^{2+} ions removal to the significant parameters is presented in Eq. (2).

$$\text{Removal efficiency } (\%) = +48.15 - 6.68A - 5.44B + 5.47C + 26.73CD \quad (2)$$

Out of the 7 parameters investigated in this study, only 4 of them were identified as significant, which were inclusive of solution pH (A), adsorption temperature (B), biosorbent dosage (C), and initial metal ions concentration (D). Based on the ANOVA analysis, interaction effect between C and D, however, posed the most significant effect to the removal percentage compared to other parameters, as evidenced by the smallest Prob > F value among all (that were less than 0.05). The deduced multiple regressions as presented in Eq. (2) results in the linear correlation coefficient (R^2) values at 0.88 and Adj. R^2 at 0.85. This indicates that the predicted data are well fitted by the model which variations caused by the variables accounted up to 88% of the variation in the Zn^{2+} ions removal percentage in this study. In addition, according to Chang et al. [35], the value of adequate precision revealed the reliability of the model, where the value of higher than 4 was desirable. In this study, the result obtained was approximately 14, which further verified the reliability of the proposed model.

Table 3 Fractional design matrix with experimental and predicted responses

Run	Coded Values of Independent Variables							Removal Efficiency, %	
	A[a]	B[b]	C[c]	D[d]	E[e]	F[f]	G[g]	Experimental	Predicted
1	1	1	1	1	-1	1	-1	62.68	68.23
2	-1	-1	-1	-1	1	1	-1	94.40	81.53
3	1	1	1	-1	1	-1	1	27.60	68.23
4	-1	-1	-1	1	-1	-1	1	36.10	81.53
5	1	1	-1	-1	-1	1	1	84.60	57.29
6	-1	-1	1	1	1	1	1	92.76	92.47
7	1	1	-1	1	1	-1	-1	21.92	57.29
8	-1	-1	1	-1	-1	-1	-1	64.20	92.47
9	1	-1	1	1	1	-1	-1	87.98	25.65
10	1	-1	1	-1	-1	1	1	35.20	25.65
11	-1	1	-1	-1	-1	-1	-1	84.00	17.19
12	-1	1	-1	1	1	1	1	9.80	17.19
13	1	-1	-1	-1	1	-1	1	52.20	14.71
14	-1	1	1	-1	1	1	-1	6.20	28.13
15	-1	1	1	1	-1	-1	1	86.46	28.13
16	1	-1	-1	1	-1	1	-1	2.40	14.71
17	-1	1	1	-1	-1	1	1	4.00	28.13
18	1	-1	-1	-1	-1	-1	-1	61.40	14.71
19	-1	1	1	1	1	-1	-1	82.54	28.13
20	1	-1	-1	1	1	1	1	20.48	14.71
21	-1	1	-1	-1	1	-1	1	66.60	17.19
22	1	-1	1	-1	1	1	-1	9.92	25.65
23	1	-1	1	1	-1	-1	1	84.24	25.65
24	-1	1	-1	1	-1	1	-1	34.08	17.19
25	1	1	-1	-1	1	1	-1	13.40	57.29
26	1	1	-1	1	-1	-1	1	1.40	57.29
27	-1	-1	1	1	-1	1	-1	86.28	92.47
28	-1	-1	1	-1	1	-1	1	29.80	92.47
29	1	1	1	-1	-1	-1	-1	19.00	68.23
30	-1	-1	-1	1	1	-1	-1	20.72	81.53
31	1	1	1	1	1	1	1	79.10	68.23
32	-1	-1	-1	-1	-1	1	1	79.40	81.53

[a] pH; [b] Temperature (°C); [c] Biosorbent dosage (mg/mL); [d] Initial metal ions concentration (ppm); [e] Stirring rate (rpm); [f] Concentration of pre-treatment solvent (M); and [g] Contact time (hour).

Table 4 Analysis of variance (ANOVA) for selected factorial model

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Status
Model	26189.91	4	6547.48	35.29	<0.0001	Significant
A	1428.72	1	1428.72	7.70	0.0117	
B	947.21	1	947.21	5.11	0.0352	
C	957.69	1	957.69	5.16	0.0343	
CD	22856.29	1	22856.29	123.21	<0.0001	
Residual	3710.16	20	185.51			
Cor. total	33124.77	31				
R^2	0.8759					
Adj. R^2	0.8511					
Adeq. precision	14.602					
Std. Dev.	13.62					

3.4 *Effect of Solution pH*

Based on the ANOVA analysis, pH was one of the significant adsorption parameters affecting the adsorption of Zn^{2+} ions. Generally, at very low pH value (pH < 2), the removal efficiency is reduced due to the positive metal ions are in competition with the hydrogen protons for the binding sites on the adsorbents' surface. Thus, reducing the removal efficiency of the adsorption process. Also, attachment of metal ions onto the surface of adsorbents will be restricted due to repulsive force of same charges. When the pH is in between 3 – 6, the optimum efficiency is obtained in most of the adsorption processes, mainly due to the presence of more ligands with negative charges in the solution with the subsequent increase in attraction sites to positively charged heavy metal ions. However, when the pH is higher than 6, the removal efficiency increases drastically due to the formation of metal hydroxides with their respective metal ions. In other word, the removal of metal ions from the wastewater is due to metal precipitation as the formation of hydroxides is induced in this pH range. Hence, it is not adsorption mechanism but the formation of precipitates.

The result from this study was in agreement with the study by Reddy et al [18] on the removal of trivalent chromium from aqueous solution using watermelon rind. It was found that pH ranged from 2 – 3 resulted in the best removal efficiency, however, when it was increased beyond 6, metal ions started to precipitate and form metal hydroxides. Also, if the pH was below 2, the authors reported that there was a slight decrease in removal efficiency of the adsorption process. They explained these phenomena with the exchange or release of H^+ ions from several functional groups such as carboxyl and hydroxyl groups of watermelon rind, which was in agreement to the results in the present study.

3.5 *Effect of Adsorption Temperature*

Adsorption is an exothermic process. Hence, temperature plays an important role in the process. However, high temperature does not guarantee high removal efficiency. Temperature leads to two major effects on the adsorption process. Firstly, when temperature is increased, the rate of adsorbate diffuses into the pores increases. This is due to the fact that viscosity of the solution reduces at higher temperature and therefore metal ions have higher kinetic to diffuse onto the active sites of the adsorbents. However, in all adsorption processes, it is crucial to maintain a balance between the rate of adsorption and desorption. Bhaumik et al. [36] mentioned that the rise in temperature also escalated the escaping tendency of molecules from adsorbent interface and therefore diminished the extent of adsorption (i.e. decrease in adsorption capacity). In view of that, the temperature can neither be too low nor too high in order to ensure effective and efficient adsorption process.

Uslu and Tanyol [37] utilized *Pseudomonas putida* for the biosorption of lead (II) and copper (II) ions with varied pH and temperatures. They reported that when the temperature increased from 20 to

25°C, the rate of adsorption increased to the maximum and the rate of removal efficiency was improved from 18 to 22 mg g^{-1} min^{-1}. However, when the temperature was further increased from 25 to 35°C, the adsorption rate started to decline. Besides, temperature was also reported to impose significant effect on the removal of Cd (II), Zn (II) and Mn (II) by using maize stalks [38]. The biosorption capacities were found to decrease from 34 to 16 % for Cd (II) ions, 52 to 28 % for Zn (II) ions and 39 to 13 % for Mn (II) ions as the temperature increased from 25 to 55°C. The authors explained that this behavior was due to the damage of active adsorption sites of biosorbent or increasing number of metal ions escaped from the biosorbent surface to the solution due to higher kinetic energy of metal ions at higher temperature. These proved that temperature could improve the rate of adsorption process but high temperature could also retard the adsorption and promote desorption process.

3.6 *Effect of Biosorbent Dosage*

Generally, when more biosorbent is added into the biosorption process, the removal efficiency increases accordingly. This is due to the correlation between biosorbent dosage with the availability of binding sites. Therefore, increase in the amount of biosorbent leads to a substantial availability of active sites. However, at a point of saturation, the removal efficiency will become steady and even start to decrease when the dosage is further increased beyond that. This phenomenon is contributed by the presence of biosorbent in excess that will in turn block the active sites, thus, reducing the total surface area of binding [26].

For instance, in the study of utilizing honey dew rind as one of the potential biosorbents for zinc removal [25], the optimum biosorbent amount for the adsorption was found to be 1.5 g. With further increase in the dosage, a decreasing trend in the metal uptakes was observed. The authors highlighted that at lower biosorbent dosage, higher metal uptake was accomplished and this was due to the increased ratio of biosorbent to metal ions. On the other hand, in the exploitation of lignocellulosic fiber derived from *Citrus reticulata* (Kinnow) waste biomass as biosorbent, the authors found that reduction in maximum adsorption capacities were observed with increasing biosorbent dosage [39]. They revealed that there was significant decrease in adsorption capacities of Cu (II) and Zn (II) as *C. reticulata* dosage increased. They further explained that the behavior was attributed to overlapping of active sites on biosorbent, leading to a decrease in the total surface area. Consequently, the adsorption performance declined.

3.7 *Effect of Interaction Between Biosorbent Dosage and Initial Heavy Metal Ions Concentration*

According to the ANOVA analysis (Table 3), the interaction effect between biosorbent dosage and initial heavy metal ions concentration demonstrated the highest F-value. This indicated that the interaction effect was affecting the Zn^{2+} ions removal by NaOH treated watermelon rind biosorbents to the greatest extent among all parameters studied. Based on the work reported by Moyo et al [40], marula seed husk was used for the removal of Pb (II) and Cu (II) from aqueous solution. The authors revealed a significant decrease in the removal of Cu (II) ions from 84.9 to 64.2 % with increasing initial metal ions solutions. At low concentrations, most of the metal ions were able to interact with the active sites on biosorbent resulting in a higher removal rate. In contrast, at higher concentrations, all the actives sites became saturated. Thus, adverse effect on the removal efficiency was observed. At this point, if the biosorbent dosage was increased, more actives sites would be available, which would in turn enhance the removal efficiency. Hence, interaction between these process parameters was identified as the major factor affecting the Zn^{2+} ions removal percentage in this study.

4. Conclusion

The results of this study suggested that watermelon rind, with its low cost and abundant availability has a potential to be used as an adsorbent for contaminant such as zinc in wastewater. Chemical treatment using different chemical solutions on the watermelon rind revealed that alkaline treatment resulted in the best surface morphological modification, enhancement of functional groups and subsequently improvement in the Zn^{2+} ions removal efficiency. By adopting fractional factorial design and analysis of variance, the effective main parameters which significantly influenced the adsorption efficiency of NaOH treated watermelon rind towards Zn^{2+} ions were obtained by conducting the least number of experimental runs. Out of 7 process parameters, only 4 of them which were inclusive of pH, temperature, biosorbent dosage, and the interaction effect between biosorbent dosage and initial metal ions concentration demonstrated significant effects to the removal percentages. Findings in this work were helpful in further optimization studies of the adsorption conditions, particularly to take into consideration of the interactions between the significant process parameters and their corresponding effects on Zn^{2+} ions removal efficiency. Subsequently, it is also possible to determine the best adsorption conditions in order to maximize the removal of zinc pollutants, with the minimization of the energy and cost of the process.

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