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Research paper

Optimization of Zinc(II) Adsorption Using Agricultural Waste

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Abstract

With industrial growth, presence of pollutants is growing enormously. Removal of pollutant from waste water and effluents can be accomplished by various techniques, out of which adsorption was found to be an efficient method. Applications of adsorption limits itself due to high cost of adsorbent. In this regard, a low cost adsorbent produced from palm oil shell based agricultural waste is examined for its efficiency to remove Zn (II) from waste water and aqueous solution. The influence of independent process variables like pH, residence time, initial solution concentration, activated carbon dosage and process temperature on the removal of Zn(II) by palm shell based activated carbon from batch adsorption process are studied systematically. The results reveal that palm shell based activated carbon can be an effective adsorbent for removal of Zinc (II) and is efficient compared to other types of adsorbent produced from agricultural waste.

Keywords: *Activated Carbon, Zinc(II) removal, Adsorption, Kinetics, Isotherms, Optimization;*

I. Introduction

Rapid industrialization has led to increase disposal of heavy metals into the environment. Most of the heavy metals are toxic (Calace et al 2002) and they cannot be destroyed chemically as organic compounds. (Fonseca et al 2006). Zinc(II) is one of the most immediate concern heavy metals (Kadirvelu et al 2001) that naturally released into the environment which create potential problem to water and soil because of its high toxicity to plant, animal, and human life (Fonseca et al 2006). Since toxic zinc metal brings harmful for living organism, World Health Organization (WHO) has set a permissible limit of 5mg/L for Zinc (II) in drinking water (Mishra 2009); therefore, it is highly essential to remove Zinc (II) from aqueous environment.

Many technologies have been developed in order to remove metals ions from waste water included chemical precipitation, ion exchange, chemical coagulation, flotation, membrane filtration, electrochemical treatment and adsorption (Bashir et. al., 2017, Karri et al., 2017a). However, adsorption is founded as the most effective ways to remove metal ions (Rao et al., 2009, Karri et al., 2017b, Karri and Sahu, 2017,) from waste water and cheaper technology compared to the others. Besides that, adsorption has evolved as the front line of defense and especially for those which cannot be removed by other techniques (Mohan 2001, Madhavi et al., 2018, Karri 2011).

Adsorbent is needed for removal of metal ions from waste water by using adsorption technology. Many types of adsorbent such as silica gel, zeolites and activated alumina are used for adsorption process, however, as compared to those, activated carbon is still the most important and widely used adsorbent due to its large surface area (Wasey 1999), high porous structure and large adsorption capacity (Zabihi et al 2010). Since commercially available activated carbon is relatively high cost (Srivastava et al 2007), hence production of low cost activated carbon from cheaper and locally available agricultural waste materials has been greatly concerned by researchers (Imamoglu et al 2007).

Over the past 4 decades, palm industry has grown tremendously from year to year. With the huge mass generation of palm oil industry, a vast quantity of palm biomass is generated in the country. In spite of thrown the biomass into the surrounding milling ground and left to disintegrate, researchers have derived activated carbon from those waste and being use in many areas.

The objectives of present research is to study the equilibrium, kinetic and thermodynamic as well as to optimize the variables for removal of zinc from simulated zinc solution using palm shell based activated carbon.

2. Materials and Methods

2.1. Batch Adsorption Experiments and Sample Analysis

Batch adsorption experiments were carried out in a series of 100cm3 stoppered reagent bottles. For each reagent bottle containing 50mL of aqueous solution of known concentration and the reaction mixture was agitated at 120rpm in the shaker. The effect of solution pH (2-8), contact time (15-75min), initial concentration (10-100mg/L), activated carbon dose (2-20g/L) and temperature (30-70°C) were studied. Stock zinc solution (1000mg/L) was prepared by dissolving 4.40g of zinc sulphate ($ZnSO_4 \cdot 7H_2O$) using 1000mL deionized water. Desired test solutions of Zinc (II) ions which varies from 10 to 100mg/L were then prepared by using dilution method of the stock solution. The required pH value of each test solutions was adjusted with 0.1M NaOH or 0.1M HCl. The initial and final concentrations of Zinc (II) in the solution were determined by Inductively Coupled Plasma (ICP) mass spectrometry with Zinc (II) wavelength of 206.2µm. A pH meter was used for pH measurements. An incubator shaker was used for agitating the samples and temperature controlled.

2.2. Experimental Design

Usually multiple factors (parameters) affect the process and overall the removal percentage of any pollutant. The adsorption process can be very sensitive to few factors and may be less insensitive to another few factors. The sensitivity of the system can be studied by manually varying these factors one by one and analyze the outcomes. If the parameters are 2 or 3, its will be less troublesome to change each parameter (keeping other parameter constant) and analyze the sensitivity of that parameter on the outcome (Karri and Babovic, 2017). Whereas, if the parameters are more than 3, the exercise of change each parameter individually and analyzing its effect on the process can be very tedious and also this process has more permutations and combinations. In this scenario, manually varying each parameter (keeping other parameter constant) is not a good practice and hence a proper approach is needed to design the experiments. Generally, if we have multiple factors, by varying one parameter while keeping all other parameters as constant can result in optima for a given process. But this approach doesn't include the interactive effects among the different variables (parameters) and as a result the true optimal solution is not possible to achieve. Hence to overcome this, an optimization procedure is needed to design the number experiments and verify the interactive effects. So, this present study involves the optimization of different process parameters affecting the adsorption of zinc contaminated aqueous solution using palm shell based activated carbon. The optimum statistical design and analysis for Zinc (II) adsorption onto palm shell activated carbon were carried out by design of experimental matrix as shown in Table 1.

Table1: Factors and their corresponding levels.

Factors	Coded and Levels					
		-2	-1	0	1	2
pH	A	2	3.5±0.5	5	6.5±0.5	8
Carbon dose	B	2	6.5±0.5	11	15.5±0.5	20
Initial sol. conc	C	10	32.5±0.5	55	77.5±0.5	100
Time	D	15	30	45	60	75
Temperature	E	30	40	50	60	70

Optimized number of experiments required to investigate all of the factors were 47 runs as shown in Table 2. The design has five times repeated of center point in order to estimate the error and curvature.

Table 2: Design of experiments matrix

Run	pH	time	Co	AC dose	T
1	1	-2	-1	-2	1
2	0	0	0	0	0
3	-2	0	0	0	0
4	0	0	2	0	0
5	0	0	0	0	0
6	1	1	-1	1	-1
7	-1	-1	1	-1	-1
8	-1	1	-1	-1	1
9	2	0	0	0	0
10	0	0	0	-2	0
11	0	-2	0	0	0
12	1	-1	1	1	1
13	0	0	0	0	0
14	1	1	1	-1	-1
15	-1	-1	1	1	-1
16	1	1	-1	-1	-1
17	-1	1	1	1	1
18	-1	-1	1	1	1
19	0	0	0	0	0
20	1	-1	1	-1	1
21	1	-1	-1	-1	-1
22	1	1	-1	-1	1
23	0	0	0	0	0
24	1	-1	-1	1	1
25	-1	1	1	-1	1
26	-1	-1	-1	1	-1
27	1	-1	1	1	-1
28	-1	1	-1	-1	-1
29	-1	1	1	1	-1
30	0	0	0	2	0
31	0	0	-2	0	0
32	1	1	1	1	1
33	0	0	0	0	[illegible]
34	-1	1	1	-1	-1
35	0	1	0	0	0
36	-1	-1	1	-1	1
37	1	1	-1	1	1
38	0	0	0	0	-2
39	-1	1	-1	1	-1
40	-1	-1	-1	-1	1
41	1	-1	-1	1	-1
42	1	1	1	1	-1
43	1	1	1	-1	1
44	1	-1	1	-1	-1
45	-1	-1	-1	-1	-1
46	-1	1	-1	1	1
47	-1	-1	-1	1	1

3. Results and Discussion

3.1.Effect of Different Operating Conditions on Adsorption

3.1.1. Effect of Initial Solution pH

The solution pH is related to ability of H+ ions compete with Zinc (II) ions to palm shell activated carbon's active sites. From Figure 1, it is clearly showed that the adsorption capacity is low at low pH, however, by increasing of pH, the uptake of Zinc (II) ions onto activated carbon increased as well. The maximum adsorption efficiency was found at pH 4 and percentage of Zinc (II) removal is slightly decreased after pH 4. Less Zinc (II) ions are adsorbed at low pH because of repulsion between H+ ions that occupied the actives site. As the pH is increased, the surface of activated carbon become more negatively charged and result in increased of Zinc (II) ions removal. The decreased on adsorption capacity at higher pH mainly due to competition between Zinc (II) ions and hydroxylated complexes of zinc ions that formed at higher pH.

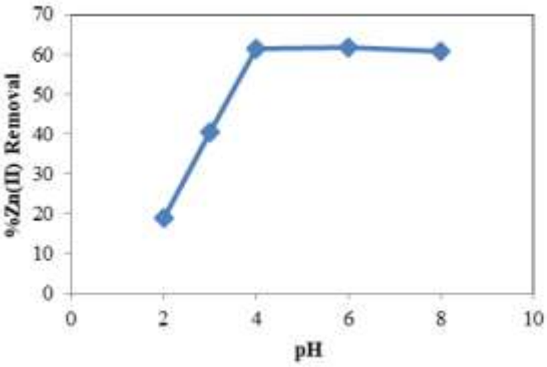

Figure1: Effect of pH on adsorption.

3.1.2. Effect of Palm Shell Activated Carbon Dose

The number of available sites and exchangeable ions for the adsorption process depends on the amount of activated carbon in the adsorption process. Figure 2 showed the adsorption capacity of Zinc (II) with different dose of activated carbon and the maximum was found at 8 g/L. The percentage of Zinc (II) removal is increased sharply with increase of activated carbon dose initially and almost constant after 8 g/L. Increasing of removal percentage with increased activated carbon dose is due to increase number of actives sites that available for adsorption process and become constant due to reduction in concentration gradient. The maximum removal efficiency of Zinc (II) ion onto activated carbon was found to be 62% at 8 g/L of activated carbon.

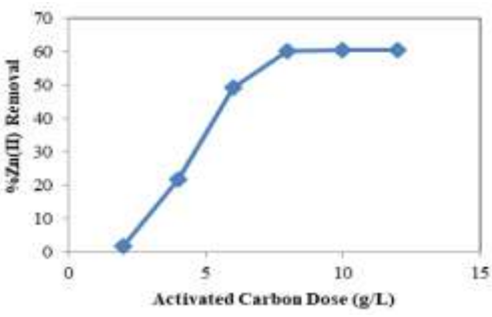

Figure 2: Effect of activated carbon on adsorption.

3.1.2. Effect of Initial Solution Concentration

The percentage of Zinc (II) removal is decreased as the initial concentration of solution increased for a fixed amount of activated carbon dose as shown in Figure 3. At low concentration, the adsorption is higher due to the available of more actives sites. As the concentration increased, the actives sites that available are not enough for Zinc (II) ions that are increasing, therefore, the percentage of removal is decreasing. On the other hand, the adsorption capacity is increased which may due to the higher adsorption rate and all the active sites for adsorption is utilized at higher Zinc (II) concentration.

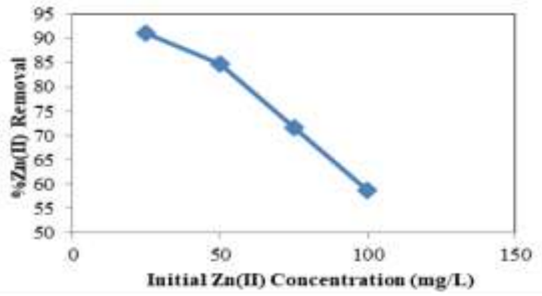

Figure 3: Effect of solution initial concentration on adsorption.

3.1.3. Effect of Contact Time

Adsorption of Zinc (II) ions onto palm shell activated carbon was studied at different interval of time for different of initial solution concentration as shown in Figure 4. The percentage of removal is increasing sharply at the beginning due to more actives sites available for Zinc (II) ions. The uptake rate is decreasing and towards constant after 35 minutes. Since the actives sites available is a fixed number, therefore the adsorption slow down after 35 minutes because of the decreasing in vacant actives sites for remaining Zinc (II) ions in the solution.

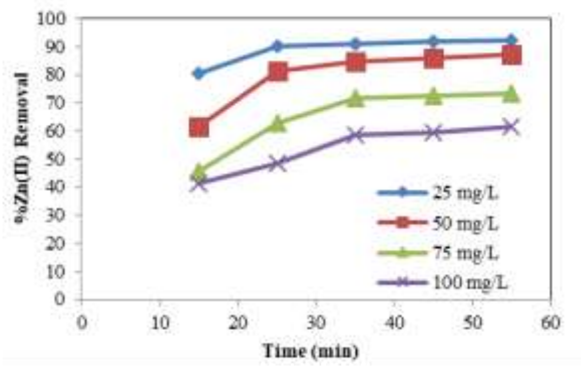

Figure 4: Effect of time on adsorption.

3.2. Effect of Temperature

It is observed that as temperature increased, the percentage removal of Zinc (II) ions is increased from Figure 5. This is because the actives sites on activated carbon are increased as the temperature, this indicates the adsorption process between Zinc (II) and activated carbon is an endothermic process. Besides that, it also indicated that the surface activity of palm shell activated carbon has increased with increased of temperature.

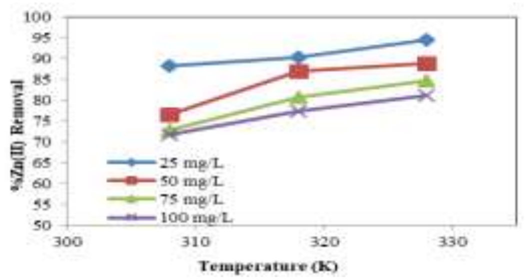

Figure 5: Effect of temperature on adsorption.

3.3. Response Analysis and Interpretation

The ANOVA for response surface reduced cubic model (Table 3) which was used to check the fitness and significant of the model applied. F-value of the model was 38.22 which implied that the model is significant and less than 0.01% chance for the model could occur because of noise. On the other hand, the lack of fit for F-value was 0.52 which indicated that the lack of fit is not significant to pure error. Besides that, lack of fit F-value has 78.72% of chance that occur due to noise. Adequate precision of 26.175 indicated that it is an adequate signal. Not all the effects of parameters on percentage of zinc (II) removal were significant, only the values of Prob>F less than 0.05 indicate that the model terms were significant. As in this case, B, E and interaction terms A^2, B^2, C^2, D^2, E^2, AB, AC, AE, BC, BE, CE, B3, E3, ABC, ABE, ACE, and BCE were significant model terms. Therefore, in order to enhance the effect of significant parameters, the insignificant parameters were eliminated. The final equation in terms of coded factors was expressed as:

Y = 93.42 - 5.21B + 9.36E + 1.73A2 - 9.70B2 + 1.77C2 + 1.70D2 + 1.88E2 - 7.16AB + 7.82AC - 1.58AE + 7.94BC - 1.49BE + 1.98CE + 7.08B3 - 2.33E3 - 2.23ABC + 8.53ABE - 7.74ACE - 7.75BCE

Table 3: ANOVA for Response Surface Reduced Cubic Model.

Source	Sum of squares	DF	F-value	Prob>F
Model	21760.09	35	38.22	<0.0001*
A	63.16	1	3.88	0.0745
B	390.35	1	24	0.0005*
C	29.68	1	1.82	0.2039
D	0.76	1	0.047	0.8332
E	1261.12	1	77.52	<0.0001*
A2	87.13	1	5.36	0.041
B2	2750.34	1	169.07	<0.0001*
C2	92.05	1	5.66	0.0366
D2	84.74	1	5.21	0.0434
E2	103.75	1	6.38	0.0282
AB	1639.39	1	100.78	<0.0001*
AC	1958.35	1	120.38	<0.0001*
AD	6.15	1	0.38	0.551
AE	79.95	1	4.91	0.0486
BC	2017.54	1	124.02	<0.0001*
BD	2.23	1	0.14	0.7182
BE	70.76	1	4.32	0.0611
CD	32.6	1	2	0.1846
CE	125.5	1	7.71	0.018
DE	21.83	1	1.34	0.2713
A3	12.61	1	0.78	0.3975
B3	2886.6	1	177.44	<0.0001*
C3	5.8	1	0.36	0.5626
D3	1.07	1	0.066	0.8026
E3	313.6	1	19.28	0.0011
ABC	158.91	1	9.77	0.0097
ABD	37.35	1	2.3	0.1579
ABE	2331.75	1	143.34	<0.0001*
ACD	8.94	1	0.55	0.4741
ACE	1915.45	1	117.75	<0.0001*
ADE	0.49	1	0.03	0.8649
BCD	19.22	1	1.18	0.3003
BCE	1835.58	1	112.84	<0.0001*
BDE	0.84	1	0.051	0.8248
CDE	10.45	1	0.64	0.4398
Residual	178.94	11		

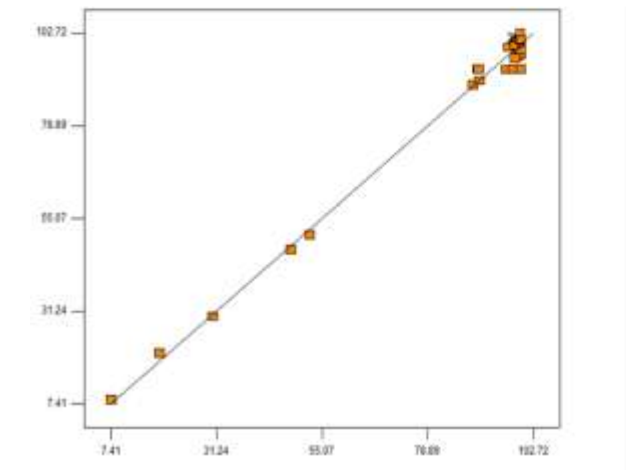

Figure 6: Predicted against experimental values.

The adjusted R^2 is 0.9659 and predicted R^2 is 0.9761, this near to unity signifies that the model is good in predicts a response value, this also can be seen well in Figure 6 which showed the experimental values were almost fitted to predicted values.

3.4. Process Optimization

The effects of two factors on the percentage of Zinc (II) removal are given in Figure 7(a-f). As in Figure 7(a), it is observed that as the percentage of Zinc (II) removal was increased sharply at the beginning with increased contact time and pH but remain constant after time 35minutes. This is due to the active sites on activated carbon have saturated with Zinc (II) ions. The optimum pH was found at 3.5. Figure 7(b) explained that the adsorption capacity is depends on both initial concentration and pH of the solution. If the pH of low initial concentration is small, the adsorption capacity is low. Referred to Figure 7(c), it is very obvious to show that the percentage of Zinc (II) removal is decreased with decreased of temperature. This means that the activity of available sites on activated carbon is bigger with higher temperature. It is also supported that the adsorption process is endothermic. Effect of initial concentration and contact time onto Zinc (II) removal is shown in Figure 7(d). At a fixed contact time, the percentage of removal is decreased win increased of concentration. This is due to at lower concentration, the competition to occupy the active sites of activated carbon is lesser, and hence the adsorption capacity increased.

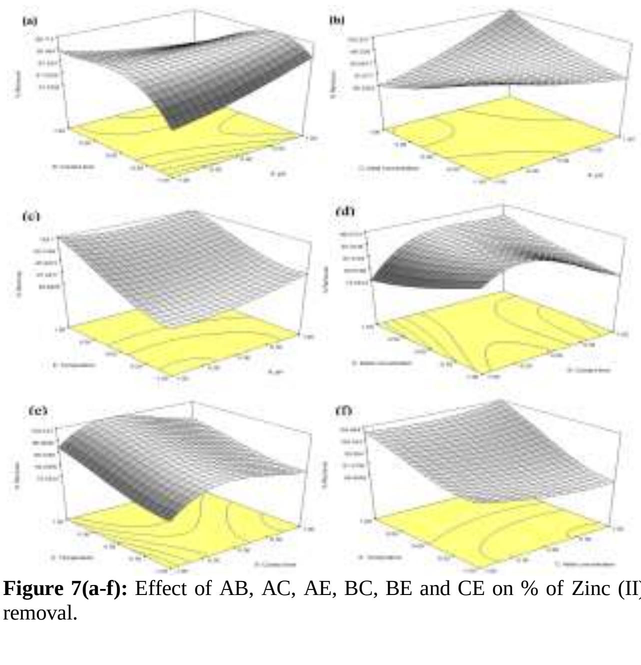

Figure 7(a-f): Effect of AB, AC, AE, BC, BE and CE on % of Zinc (II) removal.

In Figure 7(e), it is observed that regardless whatever the temperature of the solution for the adsorption process, the percentage of Zinc (II) removal is depends on the contact time as well. The adsorption will become constant after certain time as the available sites on activated carbon are already saturated with the Zinc (II) ions. Last but not least, as in Figure 7(f), it showed that the temperature of the different initial concentration of Zinc (II) solutions is affecting the adsorption capacity.
At last, few optimum operating conditions were suggested by the Design Expert. The best one were suggested at pH 3.5, activated carbon dose of 8.5 g/L, initial solution concentration of 75 mg/L, contact time of 35 minutes, and temperature at 318 K. The optimized result from response surface methodology is similar to the optimum operating conditions obtained from batch adsorption experiments for characteristics of Zinc (II) removal on activated carbon at pH 4, 8 g/L of activated carbon and 35 minutes of contact time. The temperature and initial solution concentration of batch adsorption experiments for characteristics of Zinc (II) removal on activated carbon are same as the optimized values from response surface methodology.

4. Conclusions

From the results obtained, percentage of zinc (II) ions removal was increased with increased of pH, activated carbon dose, time, and temperature, but decrease with initial concentration of zinc (II) ions solution. The predicted R^2 is 0.9761 (~=1), signifies that the model is good in predicts a response value, The optimized result from response surface methodology is similar to the optimum operating conditions obtained from batch adsorption experiments for characteristics of Zinc (II) removal on activated carbon at pH 4, 8 g/L of activated carbon and 35 minutes of contact time.

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