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ADSORPTION OF Cd(II) IN A SEMI-CONTINUOUS PROCESS BY RESIDUAL CHARCOAL FROM THE PYROLYZED OIL PALM SHELLS

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ABSTRACT
This study aims to evaluate the utilization of residual charcoal from the pyrolysis of oil palm shells as activated carbon for the adsorption of cadmium metal ions in a semi-continuous process. The charcoal was crushed with a ball mill to a size of 80-100 mesh and its activation was carried out chemically using 0.1 N NaOH. Cadmium metal ions were adsorbed in a semi-continuous operation using a cylindrical packed bed column, with variations in the inlet feed concentration, pH, column inside diameter, bed height, and flow rate. The initial concentration of cadmium before and after the adsorption was tested on an atomic absorption spectrophotometer. The adsorption isotherms were evaluated using the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models. The results showed that the best adsorption capacity was obtained at an initial concentration of 120 mg/L, pH 5, inside diameter of 26 mm, bed height of 50 cm, and flow rate of 10 ml/min. The isotherm model of cadmium metal ion adsorption followed the Langmuir isotherm with $R^2 = 0.99$.
Keywords: Oil Palm Shells, Adsorption, Cadmium, Langmuir, Packed Bed Column.

INTRODUCTION
The industrial world is one of the main sectors supporting the world economy. On the other hand, however, wastes from the industries can be a cause of environmental pollution that can reduce the quality of public health. One of the heavy metals from industrial waste found in water is cadmium (Cd). Among other heavy metal wastes, Cd waste is one of the most serious pollutants. If the concentration exceeds the threshold, it reduces the *biological* activity of microorganisms in the soil, thus reducing soil fertility. Moreover, Cd is difficult to degrade and remains in the soil for a long time. The negative impact of the presence of cadmium metal in waters is that it can cause poisoning in living things, especially humans. In the human body, heavy metals can accumulate and cause various health problems such as cancer and kidney damage.[1] Therefore, the maximum level of cadmium in drinking water should not exceed 3 μg/L.[2] There are several methods developed to treat Cd(II) waste including membrane technology, adsorption, ion exchange, extraction, and precipitation. Adsorption is one of the effective water treatments and is widely used to remove heavy metals.[3] In addition, this method has a low cost of operation while removing toxic metals properly.[4,5] At present, activated carbon as an adsorbent from renewable and inexpensive materials has become the main concern of most studies due to the high cost of conventional raw materials for activated carbon. One source of the cheaper adsorbent is oil palm shells. Oil palm shells contain cellulose, hemicellulose, and lignin which can be converted through the pyrolysis process into raw materials for activated carbon.[6] Thus, oil

palm shells can be utilized as a more economical source of activated carbon which could be a candidate for treating Cd waste.

There have been several batch studies conducted to examine the ability of activated carbon to remove heavy metals, including the use of activated carbon from oil palm shells to adsorb Cu[7], Pb, Ni[8], and Hg.[9] In addition, other biomass has also been widely used as an adsorbent, for example, the adsorption of Cu metal using activated carbon from grape seeds[10], adsorption of Cr(III) and Ni(II) using rice straw[11], adsorption of Hg using bagasse[12], and removal of methylene blue dye using rice husks.[13] Batch adsorption cannot be applied for industrial-scale with high flow rates, while adsorption in a packed bed column can be used continuously with high output flow rates and has been used in various pollution treatment processes, such as the removal of metal ions and toxic organic compounds.[14] Continuous studies for adsorption need to be developed to improve the process for the better. The success of adsorption in a column system is determined by several factors including flow rate, output fluid concentration, and the adsorbent bed height.[15,16]

The present study aims to investigate the effects of initial concentration, pH, bed height, column inside diameter, and flow rate on the adsorption capacity of activated carbon from oil palm shells in removing Cd(II) metal in a semi-continuous operation.

EXPERIMENTAL

The material was obtained from the residue in the preparation of liquid smoke from oil palm shells pyrolyzed at 400°C. The detailed pyrolysis procedure can be found in previous studies.[17,18] The resulting oil palm shell carbon was crushed using a ball mill to a size of 80-100 mesh, then chemically activated by immersing it in a 0.1 N NaOH solution for 24 hours. The carbon was then filtered and distilled to a neutral pH, after which it was dried using an oven dryer (MEMMERT Drying Oven – OVEN, GE-171) at 105°C for 1 hour. The activated carbon was then used to adsorb Cd(II) metal from CdNO3 solution at various concentrations of 30, 60, 90, 120, 150 mg/liter and pH 1, 3, and 5. The adsorption process was carried out semi-continuously using packed bed columns with inside diameters of 16, 21, and 26mm. The height of the activated carbon bed was varied at 20, 35, and 50 cm. The packed bed columns were operated in downflow using a peristaltic pump at flow rates of 5, 10, and 20 mL/min. The concentration of Cd (II) before and after adsorption was analyzed with an atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan). The whole experiment was carried out at room temperature.

RESULTS AND DISCUSSION

Effects of Flow Rate on the Adsorption Capacity and Efficiency in the Removal of Cd(II)

The effect of the flow rate on the adsorption process is useful for conducting a scale-up of performance on a continuous column.[19] The effects of flow rate on adsorption capacity can be seen in Fig.-1. Figure-1 shows that at a flow rate of 5 mL/min, the adsorption capacity was 0.004772 mg/gr and it increased to 0.007942 mg/gr at a flow rate of 10 mL/min.
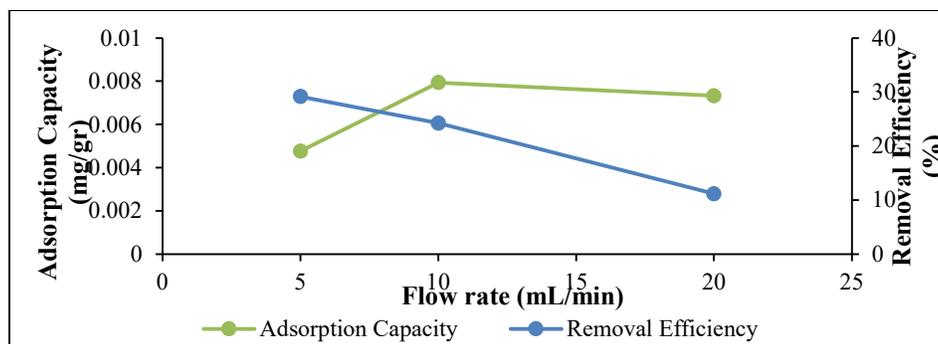

Fig.-1. Effects of Flow Rate on the Adsorption Capacity and Efficiency in the Removal of Cd(II) (Initial Concentration 120 mg/L, pH 5, Column Inside Diameter 21 mm, and Bed Height 35 cm)

However, the adsorption capacity decreased at a flow rate of 20 mL/min. This was because when the flow rate increased to 10 mL/min, the volume of the adsorbed metal solution also increased. The same trend was also identified in a previous study[20] for the removal of chromium ion using an adsorbent from cashew kernel shells. The volume of the efficiently treated effluent also decreased as the flow rate increased. This was due

to the reduced contact time between Cd(II) and the adsorbent, which did not allow saturation of the active site by metal ions and ultimately caused a decrease in the adsorbed metal ions.[21]

The results of this study are also in line with a study by Lim and Aris[22] on the use of a calcareous sponge for the removal of Cd(II) metal, in which the unadsorbed Cd metal was high and increased with flow rate. The influent velocity highly affected the contact time between the adsorbate and the adsorbent and became relatively short as the flow rate increased. Therefore, the adsorption process could not run properly, and the column filled up quickly. The removal efficiency of Cd metal decreased from flow rates of 5, 10, and 20 mL/min to 29.17%, 24.27%, and 11.2% respectively. The increase in the solution flow rate decreased the contact time, thereby limiting metal ions to diffuse into the pores of the adsorbent.[15]

Effects of Column Inside Diameter on the Adsorption Capacity and Efficiency in the Removal of Cd(II)

When conducting small-scale studies on adsorption columns, it is often desirable to minimize the column diameter so that the volume of waste to be tested can be minimized.[23] In the adsorption process, the average diameter of the adsorbent is 0.5-4 cm, and the minimum diameter of the column is 10 times the diameter of the adsorbent to avoid wall effects.[24] The effects of the column inside diameter on the adsorption capacity can be seen in Fig.-2. As shown in Fig.-2, in the columns with inside diameters of 16 mm, 21 mm, and 26 mm, the adsorption capacity was 0.004383 mg/gr, 0.007942 mg/gr, and 0.008104 mg/gr respectively. There is an increase in the adsorption capacity as the inside diameter of the column increases. The increase in the inside diameter is identical to the increase in the amount of adsorbent in the column.[21] The removal efficiency of Cd(II) also increased with the increase in the column inside diameter. At a diameter of 26 cm, the adsorption efficiency of 33.77% was obtained. The result is similar to that in the study by Rangabhashiyam *et al.*[25] on the removal of chromium metal by Swietenia mahagoni shells, where the increase in the column inside diameter was in line with the increase in chromium removal from 62.84% to 69.04%.
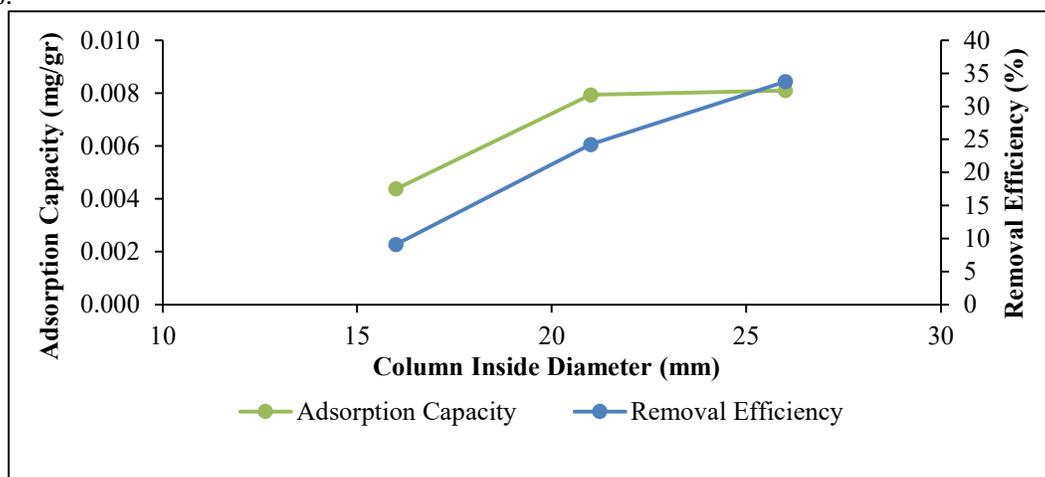

Fig.-2. Effects of Column Inside Diameter on the Adsorption Capacity and Efficiency in the Removal Of Cd(II) (Initial Concentration 120 Mg/L, Ph 5, Flow Rate 10 Ml/Min, and Bed Height 35 Cm)

Effects of Bed Height on the Adsorption Capacity and Efficiency in the Removal of Cd(II)

The effects of bed height on the adsorption capacity are presented in Fig.-3. The results showed that the volume of the incoming solution increased along with the increase in bed height in the column due to the availability of more adsorption sites. The adsorption capacity at equilibrium increased with increasing bed height as shown in Fig.-3, where the adsorption capacity increased along with the higher bed height of the column. At a bed height of 20 cm, the adsorption capacity was 0.004598 mg/gr and it increased up to 100% at a bed height of 50 cm. This indicates that at lower bed height, the concentration ratio of the adsorbate output increased faster than that in the highest bed height so that the lowest bed height was associated with a smaller amount of adsorbent and shorter saturation time. At a higher bed height, more contact time with the adsorbent will be available, resulting in a bigger amount of heavy metal removal.[26] At the highest bed height, the amount of adsorbent in the column increased and the surface for adsorption was wider so that a

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better result in heavy metal removal would be obtained.[27] At the lowest bed height, metal ions do not have sufficient time to be adsorbed on the adsorbent.[28] The metal adsorption efficiency increased with increasing bed height in the column. At a bed height of 20 cm, the metal removal obtained was 15.33%, which then increased to 24.27% for a bed height of 35 cm. Higher Cd metal removal was obtained at a bed height of 50 cm, which was 41.66%, because an increase in bed height would provide more sites for the adsorption process to take place.[26]
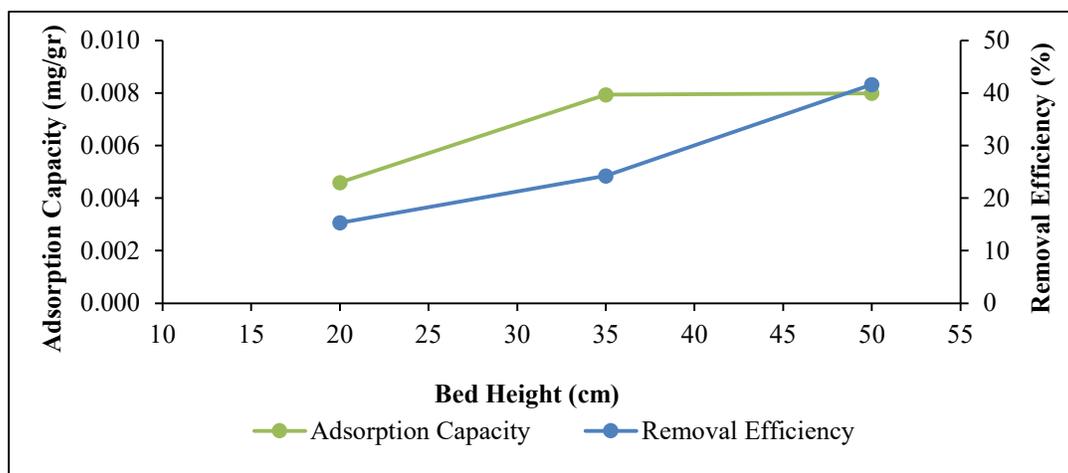

Fig.-3. Effects of Bed Height on the Adsorption Capacity and Efficiency in the Removal of Cd(II) (Initial Concentration 120 mg/L, pH 5, Flow Rate 10 mL/min, and Column Inside Diameter 21 mm)

Adsorption Isotherm

An adsorption isotherm model can be used to determine the mechanism of Cd metal adsorption by activated carbon from oil palm shells. Three adsorption isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich were evaluated in order to describe the process. In the adsorption of Cd metal, the Langmuir isotherm model can be obtained by plotting a curve of the relationship between C_e/Q_e and C_e. Meanwhile, the Freundlich isotherm model can be obtained by plotting a curve of the relationship between log Q_e and log C_e (C_e = the equilibrium concentration in the liquid phase (mg/L); Q_e = the amount of adsorbate in the adsorbent at equilibrium (mg/gr)). Finally, the Dubinin-Radushkevich adsorption isotherm of Cd metal can be obtained by plotting a curve of the relationship between ln Q_e and ε^2, where ε is the Polanyi Potential Constant, obtained from the equation $\varepsilon = RT \cdot \ln(1 + \frac{1}{C_e})$.

The calculation results of the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherms at various initial concentrations of $CdNO_3$ solution are presented in Fig.-4. Figure-4 shows that the isotherm data for Cd(II) adsorption by activated carbon from oil palm shells is closer to the Langmuir equation than the Freundlich and Dubinin-Radushkevich equations. The correlation coefficient value is $R^2 = 0.99$, which is higher than that for the Freundlich adsorption isotherm ($R^2 = 0.71$) and the Dubinin-Radushkevich isotherm ($R^2 = 0.41$). Based on the comparison of the three models, the linearity of the adsorption isotherm of the Langmuir model is closer to 1 compared to that of the Freundlich and Dubinin-Radushkevich isotherms. Thus, the number of active sites on the carbon surface was limited and the adsorption of Cd (II) formed a single layer on the surface. A previous study by Wang *et al.*[29] on the adsorption of Cd (II) by high-density polyethylene adsorbent also showed that the Langmuir isotherm was more suitable for isotherm equilibrium data. The Langmuir, Freundlich, and Dubinin-Radushkevich constants and their correlation coefficient (R^2) can be seen in Fig.-4. The Langmuir adsorption isotherm assumes that adsorption is chemical adsorption, due to the presence of a single layer of adsorbate on the surface of the adsorbent.[30] An important feature of the Langmuir adsorption isotherm is an equilibrium parameter or separation factor (R_L) which can be represented in the following Eq (1).[31]

$$R_L = \frac{1}{1 + K_L C_o} \tag{1}$$

Where K_L = The Langmuir constant ; Co = The initial concentration of the solution. The R_L value indicates the type of Langmuir isotherm, be it irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or favorable ($0 < R_L < 1$). An R_L value between 0 and 1 indicates the preferred adsorption.

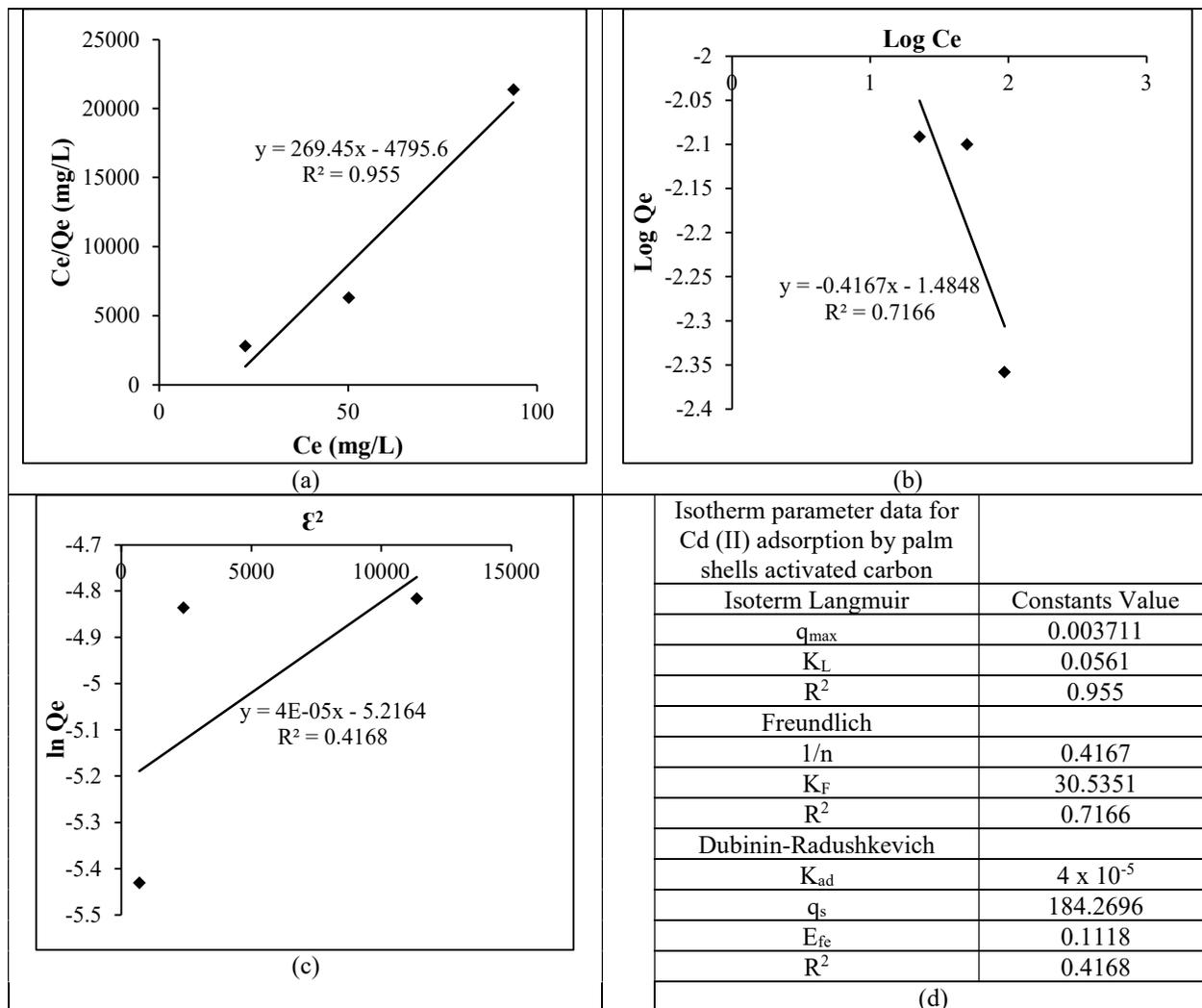| Isotherm parameter data for Cd (II) adsorption by palm shells activated carbon	
Isoterm Langmuir	Constants Value
q_{max}	0.003711
K_L	0.0561
R^2	0.955
Freundlich	
1/n	0.4167
K_F	30.5351
R^2	0.7166
Dubinin-Radushkevich	
K_{ad}	4×10^{-5}
q_s	184.2696
E_{fe}	0.1118
R^2	0.4168

Fig.-4. Isotherm Models of Cd(II) Adsorption by Activated Carbon from Oil Palm Shells (a) Langmuir; (b) Freundlich; (c) Dubinin-Radushkevich; and (d) Isotherm Parameter

In Fig.-5 it can be seen that all R_L values are in the range of 0 and 1 which indicates the adsorption process was going well.
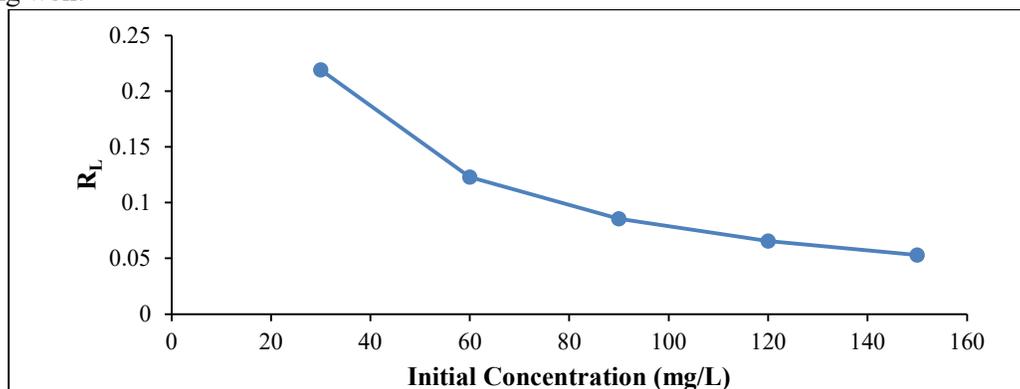
Fig.-5: Relationship Between R_L And Cd(II) Initial Concentrations

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The obtained RL values decreased for the initial concentrations of 30, 60, 90, 120 and 150 mg/L, that is, 0.21901; 0.12297; 0.08549; 0.06551 and 0.05311 respectively. This indicates that the adsorption process took place better or advantageously at higher initial concentrations, similar to that obtained by Tan *et al.*[32] for the adsorption of Cd metal by activated carbon from oil palm shells. In the Langmuir isotherm model, adsorption takes place when free adsorbate molecules collide with vacant adsorption sites and each adsorbate molecule has the same percentage of desorption.[33]

CONCLUSION

The solution's initial concentration and pH, flow rate, column height and diameter affected the capacity and efficiency of Cd metal removal. The best adsorption capacity of Cd(II) of 0.008 mg/gr was obtained at an initial concentration of 120 mg/L, pH 5, flow rate 10 ml/min, column inside diameter 26 mm and bed height 50 cm. The adsorption efficiency under these conditions was 41%. The results of isotherm evaluation showed that the isotherm model for Cd(II) metal adsorption by oil palm shell activated carbon followed the Langmuir isotherm model with $R^2 = 0.9673$. Langmuir's constant obtained was qmax = 0.003711 and K_L = 0.0561, with R_L in the range between 0 and 1.

ACKNOWLEDGEMENT

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