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Equilibrium Process Optimisation For Adsorption Of Phenol From Aqueous Solution On Fly Ash During Batch Operation

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1. Introduction

Phenol and its higher homologues are the aromatic molecules that degrade aqueous environments in various ways. The origin is both anthropogenic as well as xenobiotic. Xenobiotic sources are industrial wastes derived from fossil fuel extraction, chemical process industries such as phenol manufacturing plants, pharmaceutical industries, wood processing industry, and pesticide manufacturing plants.

Continuous ingestion of phenol for a prolonged period of time may cause mouth sore, diarrhea, excretion of dark urineAnthropogenic sources are from forest fire, natural runoffs from urban area where asphalt is used as binding material and natural decay of lignocellulosic materials. and impaired vision at concentration levels ranging between 10 and 240 mg.dm^{-3} (1). Carbolic acid and cresols are used as anticeptic agents in surgery, which indicates that they are toxic to microbes. Lethal blood concentration for phenol is around 4.7 to 130 mg.dm^{-3}. Phenols are toxic to several biochemical functions (2) and to fish life (3). It acts as a substrate inhibitor in the biotransformation (4). Phenol at concentration as low as 5.0.10^{-3} mg.dm^{-3} imparts typical smell upon chlorination and that is why WHO has prescribed a concentration of 1.0.10^{-3} mg.dm^{-3} as the guideline concentration for drinking water (5). Elimination of phenol, thus, is a necessity to preserve the environmental quality.

Removal of phenol from wastewater by adsorption on activated carbon, synthetic resins have been reported (6-14). But the high cost and difficult procurement of activated carbon and synthetic resins prohibits their use for wastewater treatment. In an aim to search for an alternative, fly ash, the solid waste generated from thermal power plant is chosen as the adsorbent and its adsorption efficiency for phenol removal is highlighted in the present communication.

2. Materials and methods

All the reagents were of analytical reagent grade. Standard solution of phenol ($5.0.10^2$ $mg.dm^{-3}$) was prepared by dissolving it in minimum volume of acetone and diluting the solution with distilled water to prepare the test solutions. Fly ash was collected from Bandel Thermal Power Station, Triveni, West Bengal. It was dried, sieved for a definite size and used without pretreatment.

Procedure:

Batch study was performed by shaking 1.0 g of fly ash and 50 ml of aqueous phenol solution of appropriate concentration, temperature and pH in glass bottles placed in a shaking incubator. After attaining the equilibrium the adsorbent was removed and phenol concentration was measured spectrophotometrically at 270 nm.

3. Results and discussion

3.1. Physico-chemical characterisation of fly ash

The chemical analyses of fly ash include loss on ignition at 800°C, silica, aluminium oxide, calcium oxide and magnesium oxide. Physical properties such as specific gravity and surface area are also determined (Table 1).

Table 1. Physico – chemical characteristics of fly ash
Tabela 1. Fizyko – chemiczna charakterystyka popiołów lotnych

Constituent	Weight percentage
SiO_2	72.90
Fe_2O_3	03.70
Al_2O_3	14.51
CaO	02.00
MgO	00.80
Loss on ignition	08.99
Density	03.24 $g.\ cm^{-3}$
Surface area	12.97 cm^2

3.2. Optimisation of operational variables

Adsorption occurs due to the accumulation of solute from aqueous solution to the surface of adsorbent. The time at which equilibrium is attained is known as equilibrium time and the concentration at this time is the equilibrium concentration. The adsorption equilibrium and the adsorption time depend on several factors such as nature or speciation of phenol and surface property of fly ash, solution pH as well as the operational temperature.

In order to find out the time for equilibrium adsorption, the interaction period for phenol and fly ash was varied and the percent adsorption was plotted for different time intervals. It was found that at the initial stage, rate of adsorption of phenol is quite high and reaches a maximum after 240 minutes that does not change with further lapse of time (Fig. 1). The percent adsorption of phenol at this equilibrium time (240 minutes) is found 70.4% for a phenol concentration of 125 mg.dm^{-3}. Similar adsorption curves were obtained for phenol solution having different initial concentrations and percent adsorption vary from 70.4 to 41.9% for the initial phenol concentration between 125 to 500 mg.dm^{-3}.

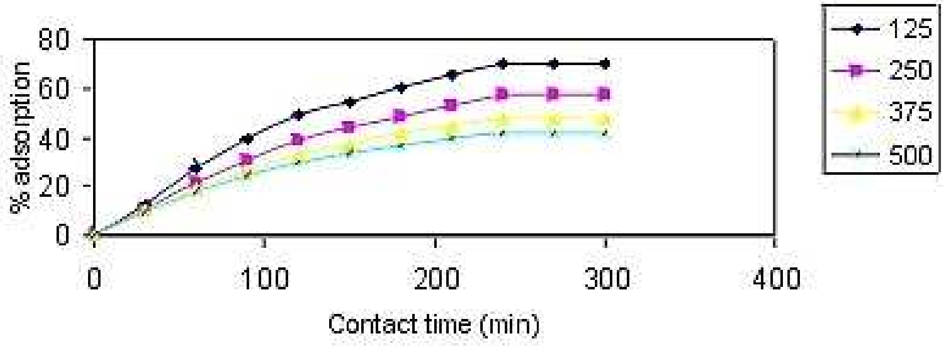

Fig. 1. Effect of contact time on the percent adsorption at different initial phenol concentrations

Rys. 1. Wpływ czasu kontaktu na procentową adsorpcję przy różnych początkowych stężeniach fenolu

The determination of optimum dose and selection of effective particle size of fly ash are essential for optimisation of the removal process. It is observed that with an increase of dose of fly ash for a fixed initial phenol concentration the percent adsorption increases (Fig. 2). The optimum dose corresponding to that maximum adsorption is found to be 1.0 gm per 50 ml for an initial phenol concentration of 125 mg.dm^{-3}.

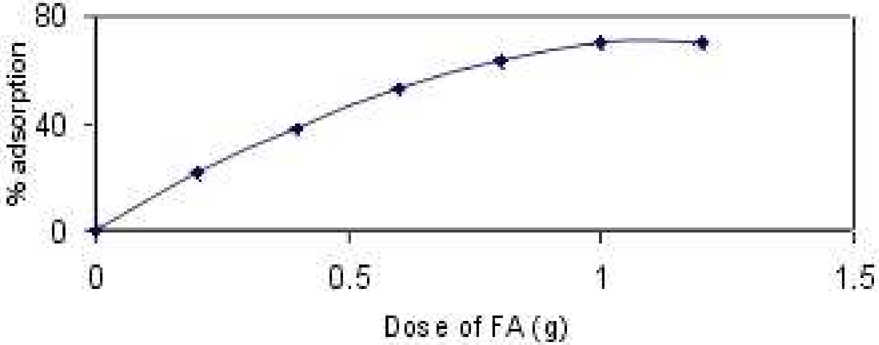

Fig. 2. Effect of dose of FA on the percent adsorption of phenol
Rys. 2. Wpływ dawki FA na procentową adsorpcję fenolu

The batch adsorption experiment was similarly carried out with fly ash of varying particle sizes ranging from 125 to 53 μm. It was found that finer particles adsorbed phenol to a large extent compared to the coarse particles (Fig. 3). It is quite justified because the smaller particles provide larger surface area and sites for favorable adsorption to a larger extent. For a phenol concentration of 125 $mg.dm^{-3}$ at pH 6.8 and temperature 293K the percent adsorption of phenol is found to be 76.2% using fly ash of particle size 53 μm compared to 66.1% adsorption with fly ash of particle size 125 μm.

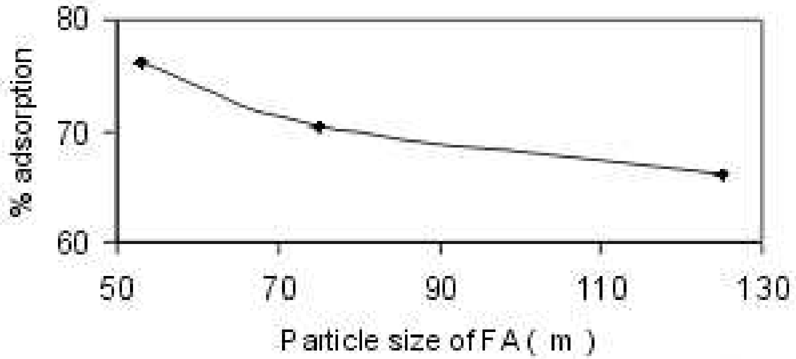

Fig. 3. Effect of particle size of FA on the percent adsorption of phenol
Rys. 3. Wpływ wielkości ziaren FA na procentową adsorpcję fenolu

The effect of pH on the adsorption of phenol was studied varying the pH from 2 to 11. The percent adsorption is found less for pH between 2 to 3, increases within the pH range 3.78 to 7.91 and again decreases from pH 7.91 to 11. Within the pH range 3.78 to 7.91 an appreciable amount of adsorption occurs being maximum at pH 7.8 (Fig. 4). This can better be explained considering both the speciation of phenol and the net effective surface charge of fly ash with varying pH of the solution. At low pH (less than 3.78) a positive charge develops on the surface of the oxides of fly ash and the possibility of formation of the phenolate ion is also low at this pH. Thus the solute experiences lesser attraction for the fly ash. On the other hand, at higher pH (>7.91) the positively charged surfaces of fly ash are expected to be neutralised, at least partially, by the OH^- ion, thereby inhibiting the phenolate ion (expected to be present largely in this pH), from adsorption on the surface of fly ash. It seems that within the pH range 3.78 to 7.91 the extent of formation of phenolate ion to that the positively charged surface of fly ash finds a suitable condition for increased adsorption.

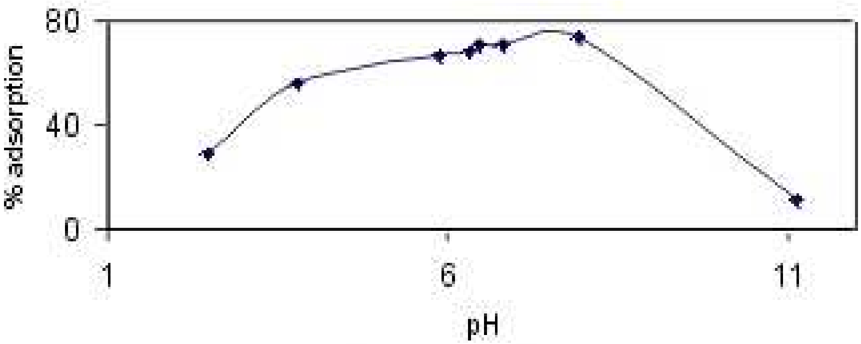

Fig. 4. Effect of pH of the solution on the percent adsorption of phenol
Rys. 4. Wpływ pH roztworu na procentową adsorpcję fenolu

It is generally expected that temperature influence the rate process of adsorption as well as surface characteristics of fly ash. With an increase of solution temperature by 20 degrees (from 293 to 313K) the percent adsorption increases only by 9.6% (70.4 to 80.0%) keeping initial phenol concentration at 125 $mg.dm^{-3}$ (Fig. 5). The process is thus endothermic in nature. The increased adsorption with increase in temperature is thought to be due to increased kinetic energy and enhanced rate of intraparticle diffusion.

It seems interesting to correlate the influencing parameters (initial phenol concentration, dose and particle size of fly ash, pH and temperature) and the extent of adsorption for ready reference and modeling purpose. In the present case a correlation model is developed as follows,

$$\%\ \text{adsorption} = 0.00672 C_0^{-0.3720}\ P_s^{-0.1627}\ pH^{0.3833}\ T^{1.9402} \quad (1)$$

where, C_0 = initial phenol concentration,
P_s = particle size,
T = absolute temperature.

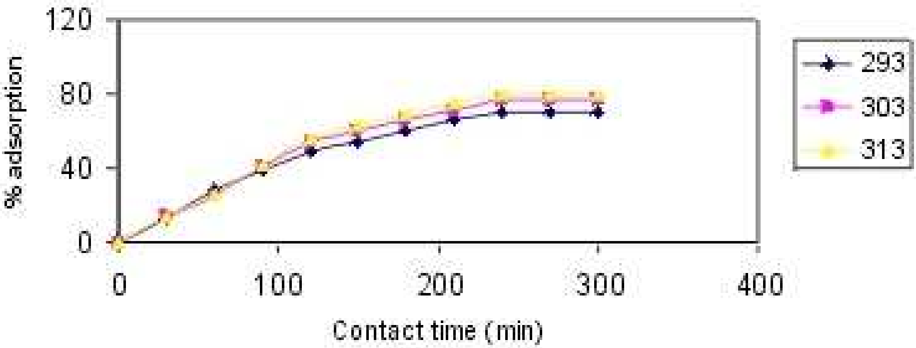

Fig. 5. Effect of contact time on the percent adsorption of phenol at different temperatures

Rys. 5. Wpływ czasu kontaktu na procentową adsorpcę fenolu przy różnych temperaturach

However, as a particular operation is performed at a fixed solution temperature the contribution due to temperature effect can be ignored in the above equation. Therefore, for evaluating the role of other parameters significantly the correlation equation may be written as,

$$\% \text{ adsorption} = 410.77C_0^{-0.3720}.P_s^{-0.1627}.pH^{0.3833} \qquad (2)$$

3.3. Adsorption isotherm study

Adsorption equilibrium data are conveniently expressed by adsorption isotherm that may be helpful in determining the adsorption capacity of fly ash, the adsorbent in the present study. The equilibrium adsorption data were tested with Linear Langmuir adsorption isotherm equation generally represented as,

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \qquad (3)$$

where, C_e is equilibrium concentration of solute in solution (mg.dm^{-3}),
q_e is amount of solute adsorbed at equilibrium (mg.g^{-1}),
Q_0 (mg.g^{-1}) and b (dm^3.mg^{-1}) are the Langmuir constants; Q_0 signifies the adsorption capacity of the adsorbent and b is related to energy of adsorption process.

Plot of C_e/q_e against C_e (Fig. 6) yields a straight line and Q_0 and b are obtained from the slope and intercept.

Langmuir isotherm curves were drawn with three different temperatures and the constants were evaluated. The higher regression coefficient value (>0.99) and lower value of variance (<0.27) in each temperature indicates the applicability of Langmuir adsorption isotherm in the present case. Moreover, it reveals that adsorption capacity of fly ash increases with rise in solution temperature suggesting that higher the temperature more favorable is the removal of phenol using fly ash as the adsorbent.

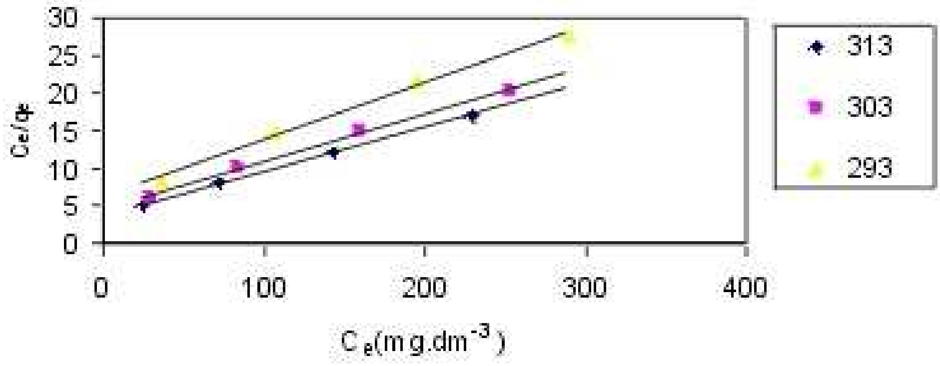

Fig. 6. Langmuir of adsorption at different temperatures
Rys. 6. Wykres adsorpcji Langmuira przy różnych temperaturach

Table 2. Langmuir adsorption isotherm parameters at different temperatures
Tabela 2. Parametry izotermy adsorpcji Langmuira przy różnych temperaturach

	293K		303K		313K	
Langmuir parameters	Q_0	b	Q_0	b	Q_0	b
	13.1585	0.0129	15.8722	0.0138	17.0897	0.0156
	R^2 = 0.9943 Variance = 0.2704		R^2 = 0.9977 Variance = 0.1753		R^2 = 0.9987 Variance = 0.1223	

3.4. Thermodynamic parameters of adsorption

Feasibility of any process as well as its nature may be examined by thermodynamic parameters like free energy change, (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS). The governing relations are as follows,

$$\Delta G = -RT\ln K^{/} \qquad (5)$$

and

$$\Delta H = \Delta G + T\Delta S \qquad (6)$$

Therefore,

$$\ln K^{/} = -\Delta H/RT + \Delta S/R \tag{7}$$

where, $K^{/}$ the equilibrium constant is defined as,

$$K^{/} = C_{Ac} / C_{e}, \tag{8}$$

C_e is equilibrium concentration in solution ($mg.dm^{-3}$),
C_{Ac} is the equilibrium concentration on the adsorbent ($mg.kg^{-1}$),
R is the universal gas constant and
T is the absolute temperature.

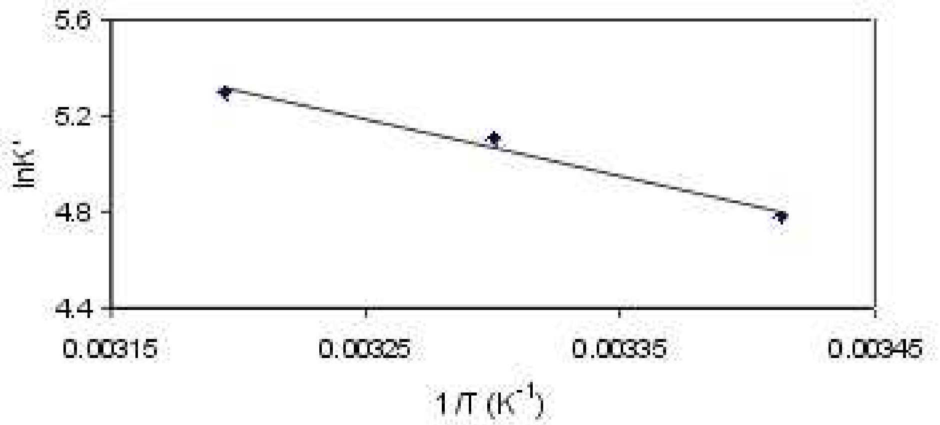

Fig. 7. van't Hoff plot of adsorption
Rys. 7. Wykres adsorpcji van't Hoffa

ΔG values were calculated following Equation (5) which were found to be –2.81, –3.07 and –3.33 kCal mol $^{-1}$ respectively at 293, 303 and 313K. The negative value of ΔG at each temperature indicates that the process of adsorption is favorable as well as spontaneous. Plot of $\ln K^{/}$ vs. 1/T (Eq. 7) was made. The values of ΔH (4.75kcal mol $^{-1}$) and ΔS (25.83 cal mol $^{-1}$) were obtained from the slope and intercept respectively from the vant Hoff plot through linear regression (Fig. 7). Here both ΔH and ΔS are found to be positive. The process may therefore be denoted as endothermic and associated with increased randomness (15).

References

1. **Barkar, E. I., Peter, E. B., Grant, S. K.:** Phenol poisoning due to contaminated drinking water. Arch. Env. Health 33, 89 – 94. (1978)
2. **Kumaran, P.:** Development of biotechnology of toxic waste treatment. Proc. Symp. Env. Biology of Coastal Ecosystem, p.11 – 19. (1986).
3. **Sufit, D. J.:** Some effects of exposing rainbow trout in phenol solution, J. Fish. Biology, 13, 7 – 17. (1978).
4. **Hill, G. A., Robinson, C. W.:** Substrate inhibition kinetics, phenol biodegradation by P. putida, Biotechnology Bioengg., 17, 199 – 207. (1975).
5. **WHO**, Guidelines for Drinking Water Quality, Vol. 1, p. 85. World Health Organisation, Geneva. (1984).
6. **Van Stone, G. R.:** Treatment of coke plant effluent, Ind. Waters, (1972), 18, 23 – 35. (1972).
7. **Wheeler, O. H., Levy, E. M.:** Adsorption of sterically hindered phenols on carbon, Canadian J. Chem., 37, 1235 – 1240. (1959).
8. **Chand, S., Majumder, C. B., Kumar, V.:** Removal / Recovery of acetic acid from waste water by adsorption on bagasse and coconut jute carbon, Indian J. Environ. Hlth., 41(3), 170 – 175. (1999).
9. **Devarajulu, T., Vanusree, G., Krishnaiah, A.:** Competitive adsorption of phenol and p-chlorophenol from aqueous solution on Amberlite XAD-7 resin, Indian J. Environ. Hlth., 41(2), 98 – 106. (1999).
10. **Poots, V. J. P., McKay, G., Healy, J. J.:** The removal of acid dye from effluent using natural occurring adsorbents – I, Peat, Water Res., 10, 1061 – 1066. (1976).
11. **De, A. K.:** Removal of phenolic compounds from wastewater by adsorption, Chem. Environ. Res., 2(374), 161 – 166. (1993).
12. **Madhukumar, A., Anirudhan, T. S.:** Phenol exchange characteristics of sediment samples from coconut husk retting zones, Indian J. Environ. Prot.,14(10), 772-782. (1994).
13. **Mahadeva Swamy, M., Mall, I. D., Prasad, B. and Mishra, I. M.:** Sorption characteristic of o-cresol on bagasse fly ash and activated carbon, Indian J. Environ. Hlth., 40(1), 67 – 78. (1998).
14. **Caturla, F., Martin – Martinez, J. M., Molina – Sabio, M., Rodriguez – Reinoso, F., Torregrosa, R.:** Adsorption of substituted phenols on activated carbon, J. Colloid. Interface Sci., 124(2), 528 – 534. (1988).
15. **Barrow, G. M.:** Physical Chemistry, 4th edn., McGraw Hill, Kogakusha, Ltd. (1979).

Optymalizacja równowagowa procesu adsorpcji fenolu z wodnego rotworu na popiołach lotnych w czasie operacji okresowych

Streszczenie

Praca dotyczy optymalizacji procesu równowagowego adsorpcji fenolu z wodnych roztworów przy wykorzystaniu lotnych popiołów. Fenole i ich wyższe homologiczne są związkami aromatycznymi, które powodują degradację środowiska wodnego. Stężenia fenoli w granicach od 10 do 240 mg/dm^3 są groźne dla organizmów żywych, nie tylko człowieka ale również świata zwierzęcego. Człowiek odczuwa zapach fenolu już przy stężeniach $5\cdot10^{-3}$ mg/dm^3, podczas gdy Światowa Organizacja Zdrowia dopuszcza spożywanie wody pitnej przy stężeniu fenolu poniżej $1\cdot10^{-3}$ mg/dm^3. Jest to zatem temat istotny problem badawczy. Autorzy przeprowadzili badania adsorpcji i oczyszczania roztworów z fenolu.

Do badań doświadczalnych autorzy przyjęli standardowy roztwór fenolu $5\cdot10^{-2}$ mg/dm^3 przez rozpuszczenie go w minimalnej ilości acetonu i wykonanie roztworu do testowania z wodą destylowaną. Lotne popioły do badań pobrano z Ciepłowni Triveni w Zachodnim Bengalu, Indie. Wykonano charakterystykę fizykochemiczną pobranych popiołów a następnie przeprowadzono optymalizację zmiennych operacyjnych. Wiadomo, że szybkość procesu adsorpcji wzrasta wraz z temperaturą, co przedstawiono w postaci modelu. Przy stałej temperaturze, proces adsorpcji zależy jedynie od trzech parametrów: Co - początkowego stężenia fenolu, PS - wielkości cząstki adsorbentu, oraz pH - kwasowości/zasadowości środowiska.

Do zbadania danych adsorpcji równowagowej wykorzystano równanie izotermy adsorpcji Langmuir'a. Krzywe izotermy Langmuir'a wykreślono dla trzech różnych temperatur, na podstawie których wyznaczono stałe Langmuir'a Qo (mg/g) i b (dm^3/mg). Wysokie współczynniki regresji, wynoszące ponad 0,99 i niskie wartości wariancji (0,27 i mniej) świadczą o prawidłowym wyborze izotermy adsorpcji Langmuir'a.

Dla zbadania natury jak i możliwości przeprowadzenia procesu wyznaczono termodynamiczne parametry adsorpcji. Ujemne wartości zmiany energii swobodnej Gibbs'a OG dla trzech badanych temperatur świadczą, że proces adsorpcji fenoli przebiega spontanicznie, natomiast pozytywna wartość entalpii OH poparta rosnącą losowością (dodatnia wartość entropii AS) mówi, że jest to proces endotermiczny.