Adsorptive Study for a Mixture of 4-chlorophenol, 4-aminophenol and phenol from Aqueous Solution onto Tire Char in Fixed-Bed Column

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Abstract
This study was carried out to study the capability of tire char and compare with modified char to get rid of phenolic compounds from waste water in fixed bed column. Phenol, p-chlorophenol and p-aminophenol were studied. The effect of operational parameters on the breakthrough time like bed height, flow rate, initial concentration and temperature was observed. Moreover, at breakthrough the capacity rose with fall off initial concentration and flow rate, temperature and increasing bed height. From results tire char is efficient and low-cost adsorbent and modified char was better than char in removal of phenolic compounds.

Keywords: Tire char, Fixed bed column, Modified char, Adsorption.

Introduction

Environmental contamination from waste effluents has seriously increased with the quick advancement of industries in Baghdad. Inappropriate discharge of industrial waste water contaminated with organics disposed a problem to the surroundings. Phenols usually locate in industrial wastewater and are popular aromatic compounds. Phenol is the fundamental structural unit of various synthetic organic compounds in wastewater from industrial operations such as petroleum refineries, the manufacture of pesticides, dyes and phenolic resins, textiles, plastics, rubber and pharmaceuticals. etc.[11,15] The removal of phenol from wastewater before discharge into water body is important because it is highly hazardous, carcinogenic and resistant to degradation[11,14].

The disposal of waste tires represents a main environmental problem. Different methods used waste tires to convert them to useful products in an environmentally friendly manner[1].

The process under vacuum at high temperatures (450°C–900°C) with thermal decomposition of waste tire is called pyrolysis. Pyrolysing waste tire materials could be alter-native because liquid, gas fractions and a solid residue will be produced[2,3].

Adsorption has been observed to be a very proficient method for the removal of organic/inorganic and toxic pollutants due to its_facility of running and its low cost.[13,18] Activated carbons are widely applied as successful adsorbents for treating of dye wastewaters as result of its altitude surface area and wide convenience and variety but, the comparatively high cost of activated carbons reduces their applicability in certain wastewater treatment applications[4,23].

Adsorption capacities from batch studies are helpful in giving data about the effectiveness of phenolic-adsorbent system and the form of isotherms [9]. However, the results from batch conditions are usually for the treatment of little volume of waste discharge, they are not useful in general for direct application on industrial-scale treatment. Therefore, continuous system experimental data can supply information for the design and operation of water treatment processes at the experimental and industrial level[12].

The main objectives of this study are (a) to calculate adsorption of phenolic compound by low cost adsorbent using fixed bed column (b) to study effect of bed height, flow rate, initial concentration and temperature on column adsorption and kinetic of breakthrough curve and (c) to improve char surface characteristic by modifying it.

Material and Methods

Adsorbate: Mixture of phenolic compounds (p-chlorophenol, p-aminophenol, phenol)
Adsorbate: Tire char

Synthesis of Char

(a) Preparation of Waste tire Char: The rubber tires were first washed with tap water to get red from dirtiness and dried in an oven at 110 ℃ for 24 h. The dried tire was sieved to a size of 1.5mm followed by pyrolysis in oxygen free atmosphere at 600℃ for 1h. This temperature was based on optimum results obtained. The substance has been subjected to the above process called char[16].

(b) Preparation of Modified Char: Char was synthesized by dissolving1.0 g char in 20 mL sodium hydroxide (5N), the solution was stirred for 24h at 120rpm.The filtration was used to separate liquid from solid by washing with distilled water until pH 7 was obtained and dried in an oven for 24 h at 110℃ [22]. Then, the char was sieved.

Column Experiments: The diagram of the column is shown in figure 1. Fixed bed experiments were employed using a 2cm i.d., 35cm length glass column near the column inlet, plastic beads and were put to deter channeling and guarantee even distribution of the solution. Flowing in the fixed bed was continuously in down mode as a down mode by a pump (Model W15G-15, TOTA) at temperature

(25,35,45°C). Outflow samples were collected from the column at specific time period. The experiments used initial concentration (75–225mg/L), flow rate (0.5–1.5 L/h) and bed height (5–15cm).

Result and Discussion

Effect of Volumetric Flow Rate: Figures 2 and 3 show the experimental breakthrough curves for mixture of phenol compounds concentration (75ppm) at different flow rates (0.5 and 1.5l/h) in terms of C/Co. When the volumetric flow rate is raised, the breakthrough time decreased, the breakthrough time at $C/C_o= 0.05$ is shown in table1. For char and modified char, it is clear modified char had longer tb than char. These results agree with Sotelo et al[19] and Sulaymon et al[18]. They used various flow rates to study the breakthrough curves of activated carbon adsorption.

Effect of bed height: Height of bed is the most important parameter in the design of fixed bed adsorption column. The breakthrough curves gained for various bed height of char (5, 10 and 15cm) at constant flow rate (1 L/h) and constant initial concentration(75mg/l) presented in figure 4,5 and 6. It is shown from these figures that at the Ce/Co smaller bed height increases more rapidly than at higher bed height. In addition to at smaller bed height, the bed is saturated in less time compared with the higher bed height. Also, rising bed height will rise the breakthrough time(tb) and the residence time of the phenol and its compound in the bed that will provide enough time for molecules to penetrate in to particles of adsorbent. At different length the breakthrough time $C/C_o=0.05$ was listed in table 1. Results are in agreement with several previous researchers[1,8,17].

Effect of Inlet Phenolic Compounds Concentration: The change in initial concentration phenolic compounds will have a considerable impact on the breakthrough curves. The experimental breakthrough curves are at different initial concentration (125 and 225 mg/l). Figures 7 and 8 show that the adsorption quantity at any period increases with increasing phenols influent concentration. The initial concentration is inversely related to the adsorption time. This may be explained by fact that in adsorption concentration gradient is the mean driving force, the driving force for mass transfer increases with increase of concentration of adsorption, it takes a longer contact time to extend adsorption equilibrium for case of low initial solute concentration values.

Effect of Solution Temperature: In the current study of concentration breakthrough curves, three distinct temperatures of 25, 30 and 45 ℃ are taken in account. All other conditions were kept constant (h=5cm, Q=1.5l/h). As it is shown from the plot, the breakthrough time of the sorption process starts decreasing with increase in the temperature. This means for higher temperatures the saturation of the char happens in less time. The decrease in time of saturation is proportional to the increase in the temperature, normally the adsorption reactions are exothermic, which means that the adsorption will increase with lowering temperature. The outcomes are shown in figures 9 and 10. The breakthrough time at $C/C_o=0.05$ is presented in table 1.

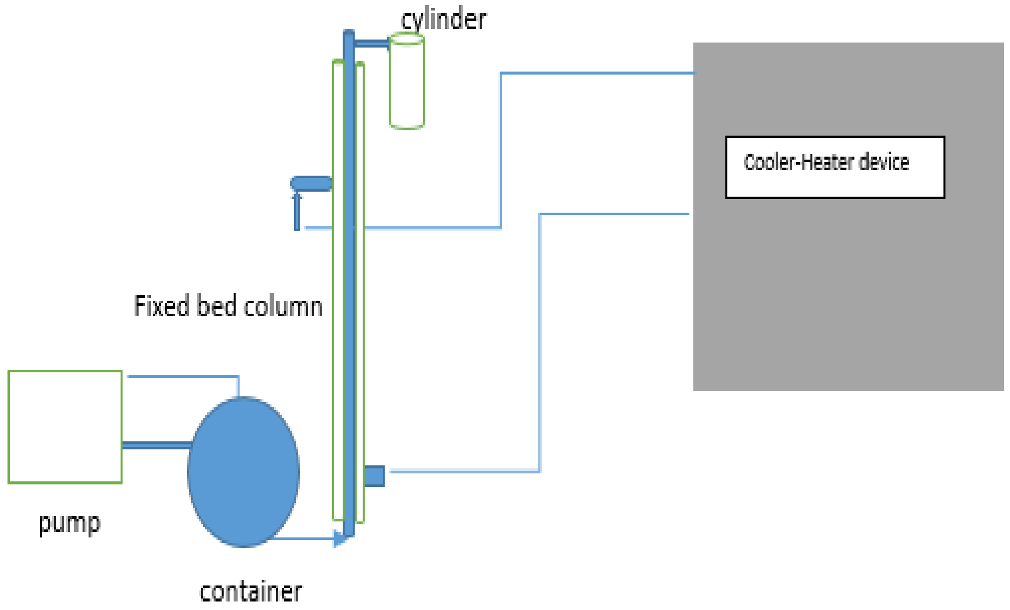
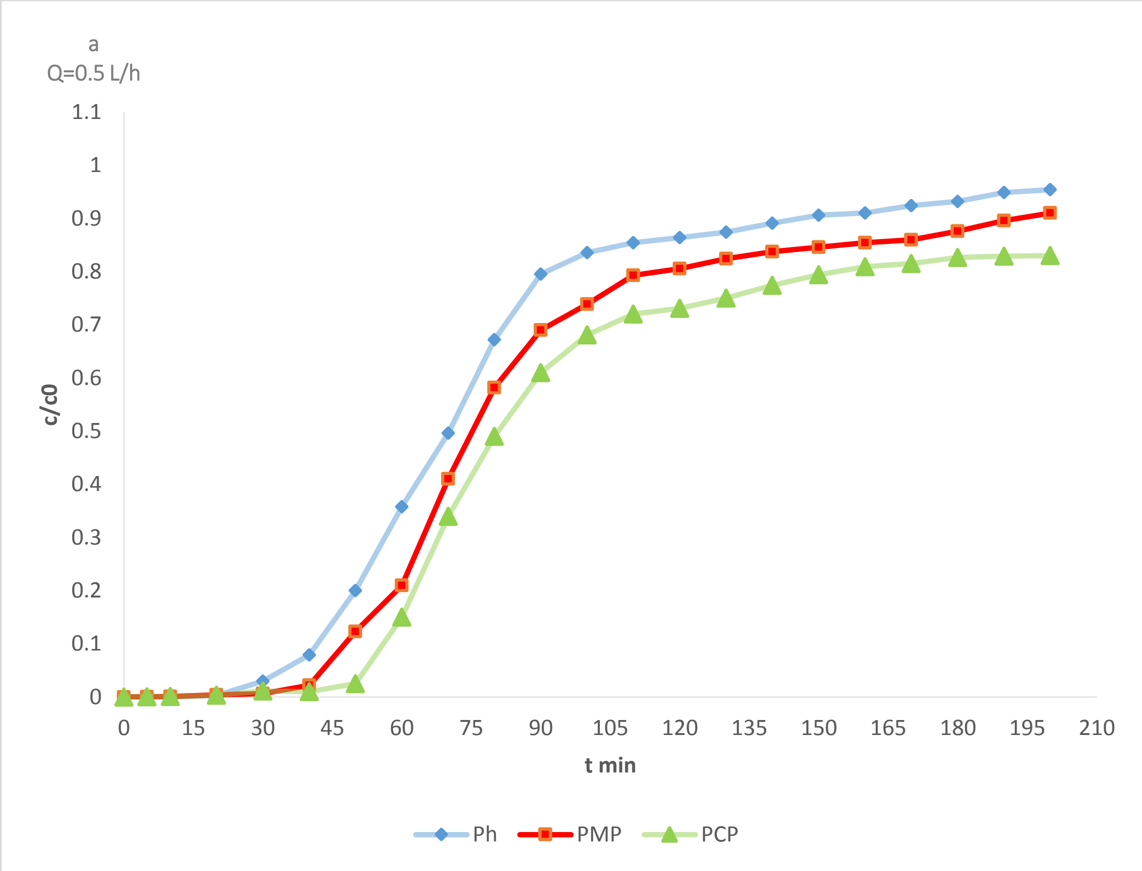


Figure 1: Schematic diagram of fixed bed adsorption apparatus



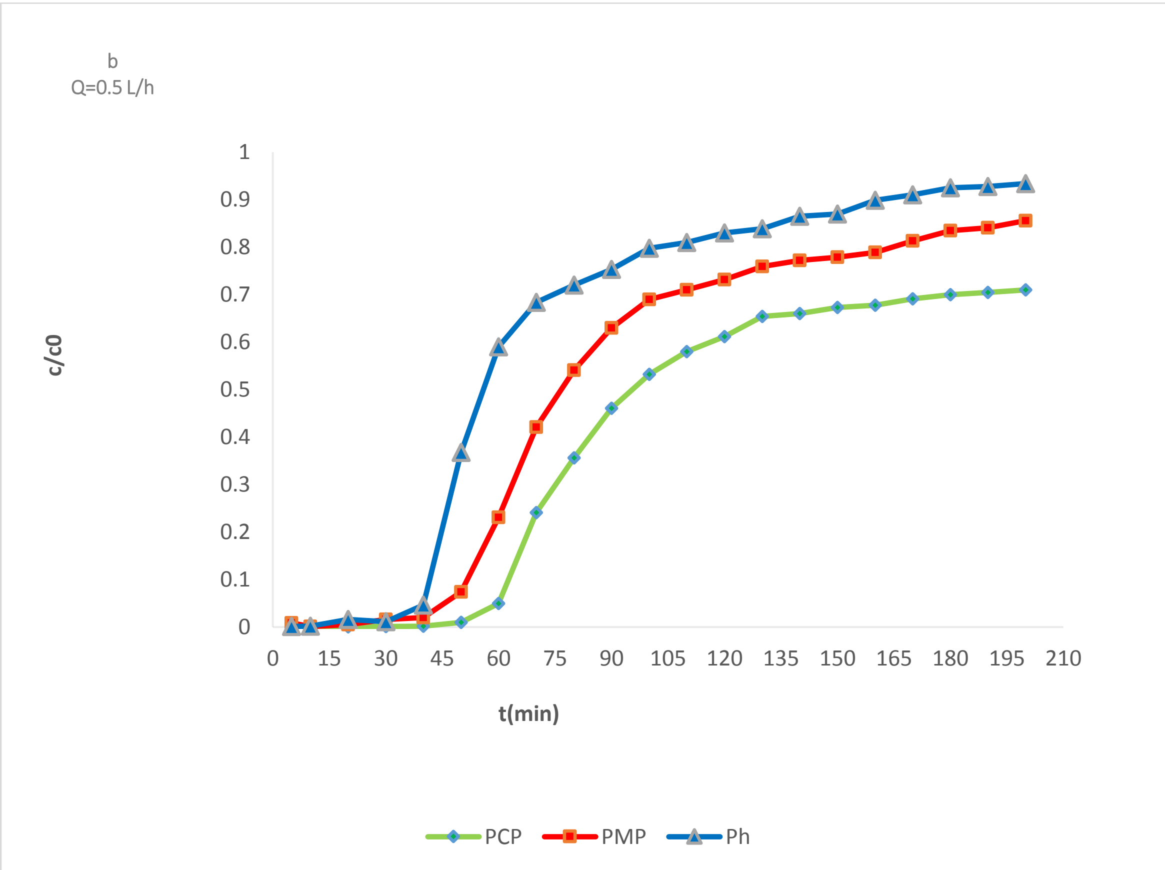


Figure 2: Breakthrough curves of multicomponent solution of (a) char (b) modified char (75mg/L; H=5cm, Q=0.5L/h)

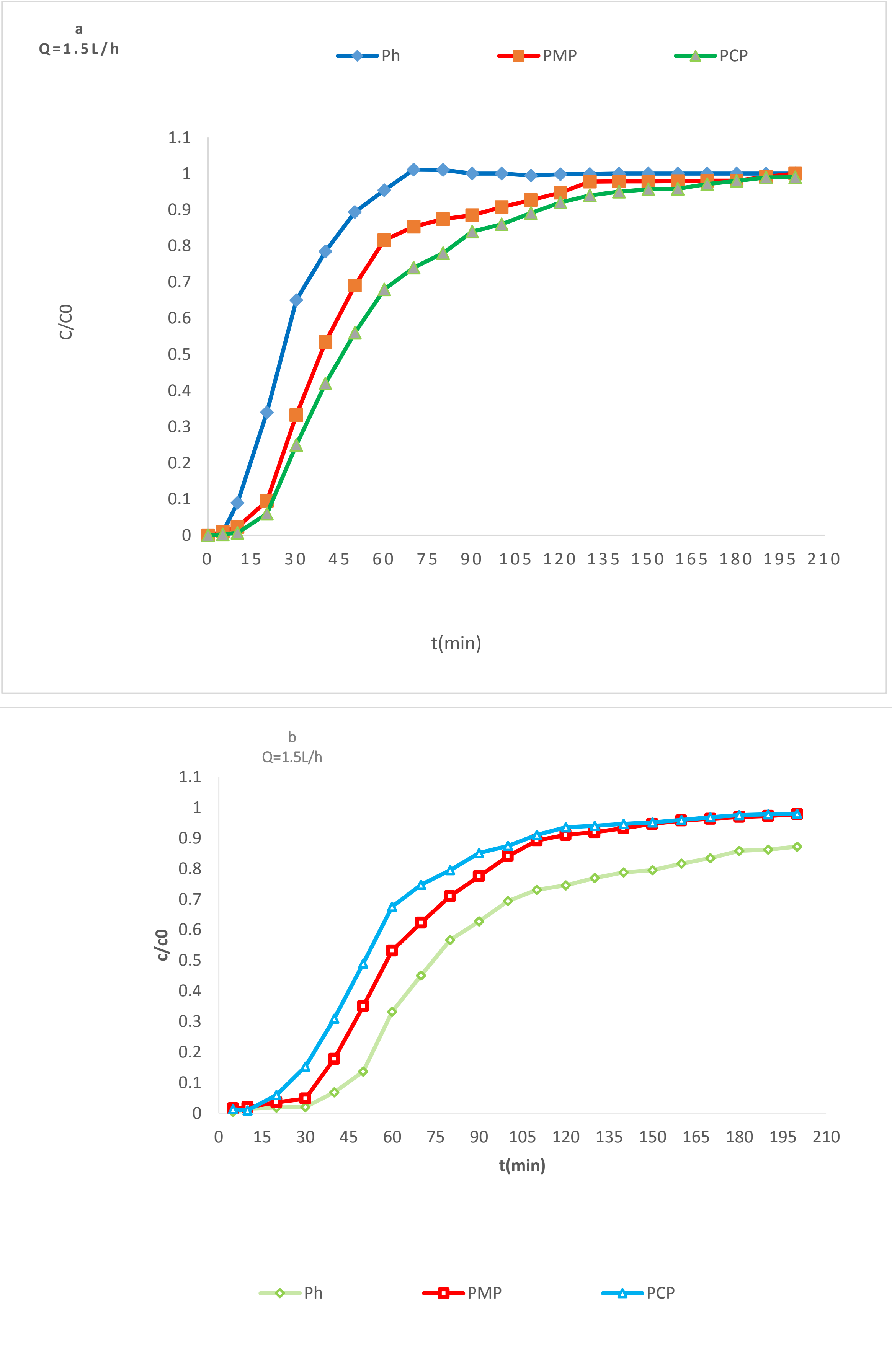
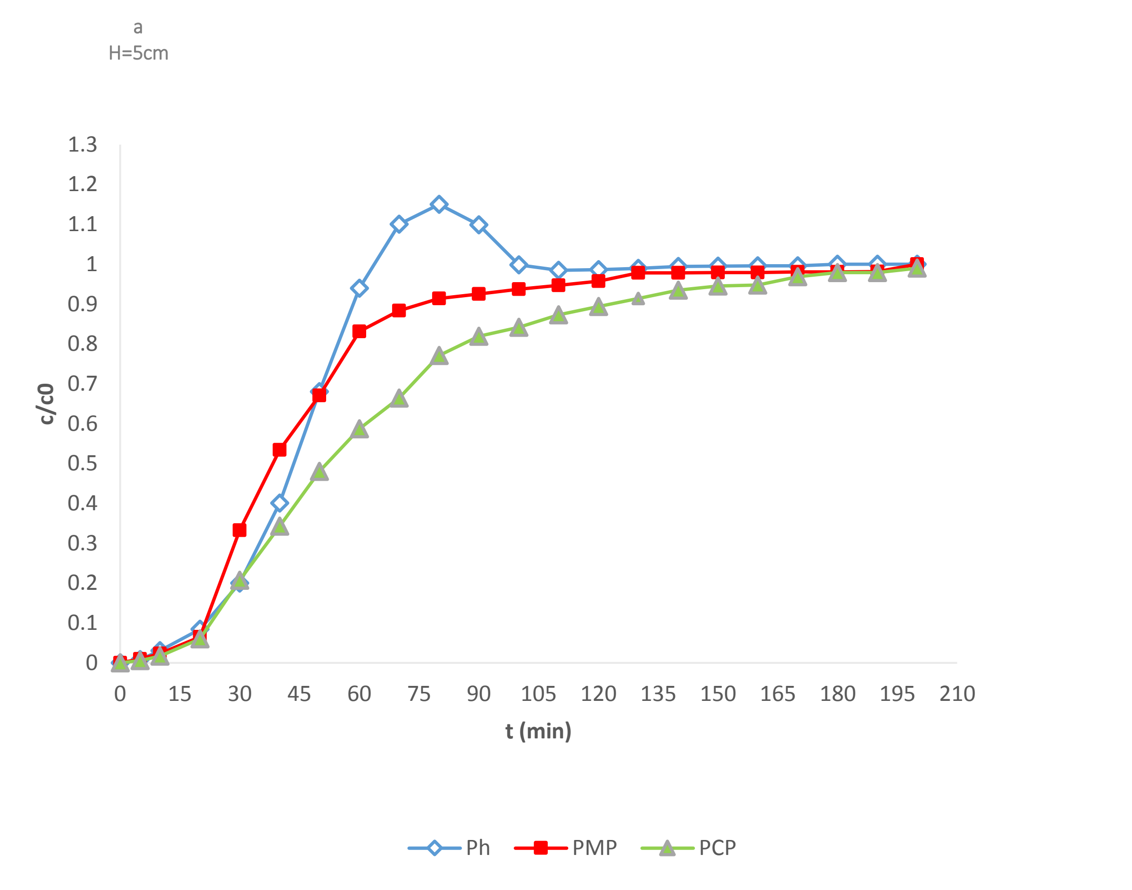


Figure 3: Breakthrough curves of multicomponent solution of (a) char, (b) modified char (75mg/L; H=5cm, Q=1.5L/h)



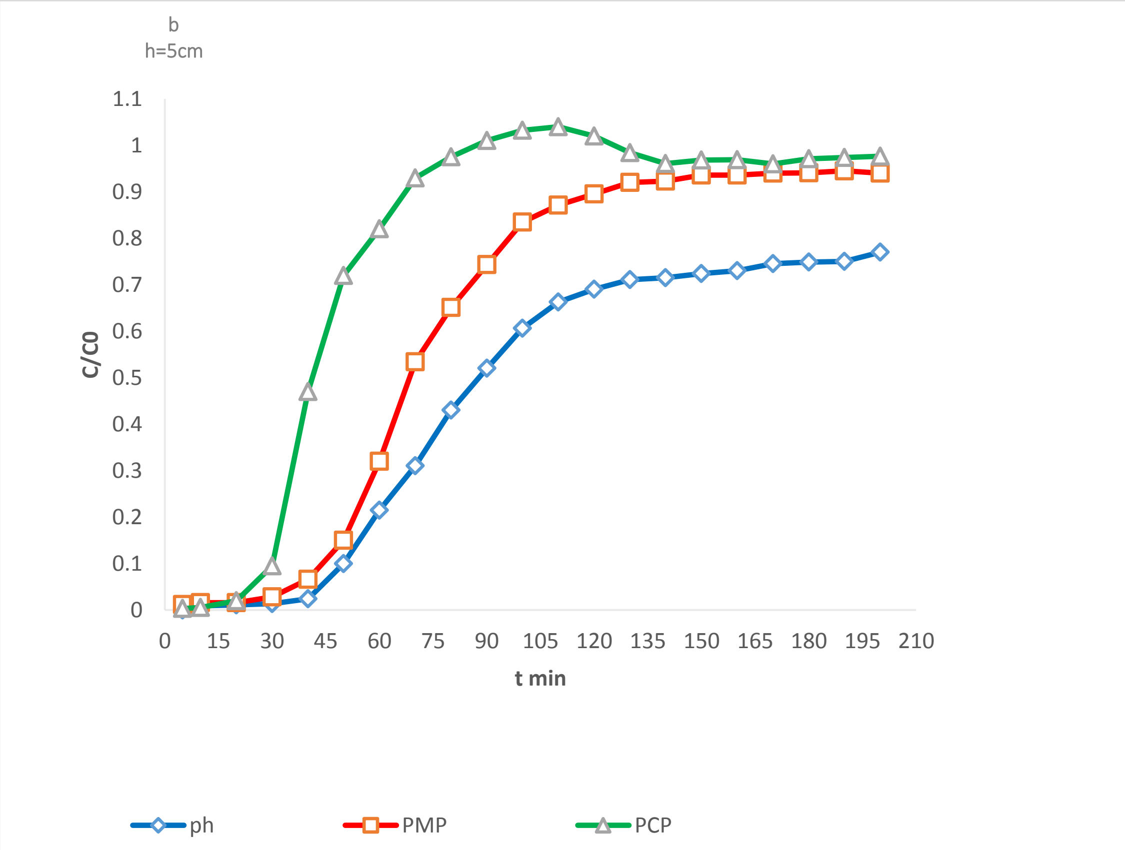


Figure 4: Breakthrough curves of multicomponent solution (a) char, (b) modified char 75mg/L; Q = 1L/h, H=5cm

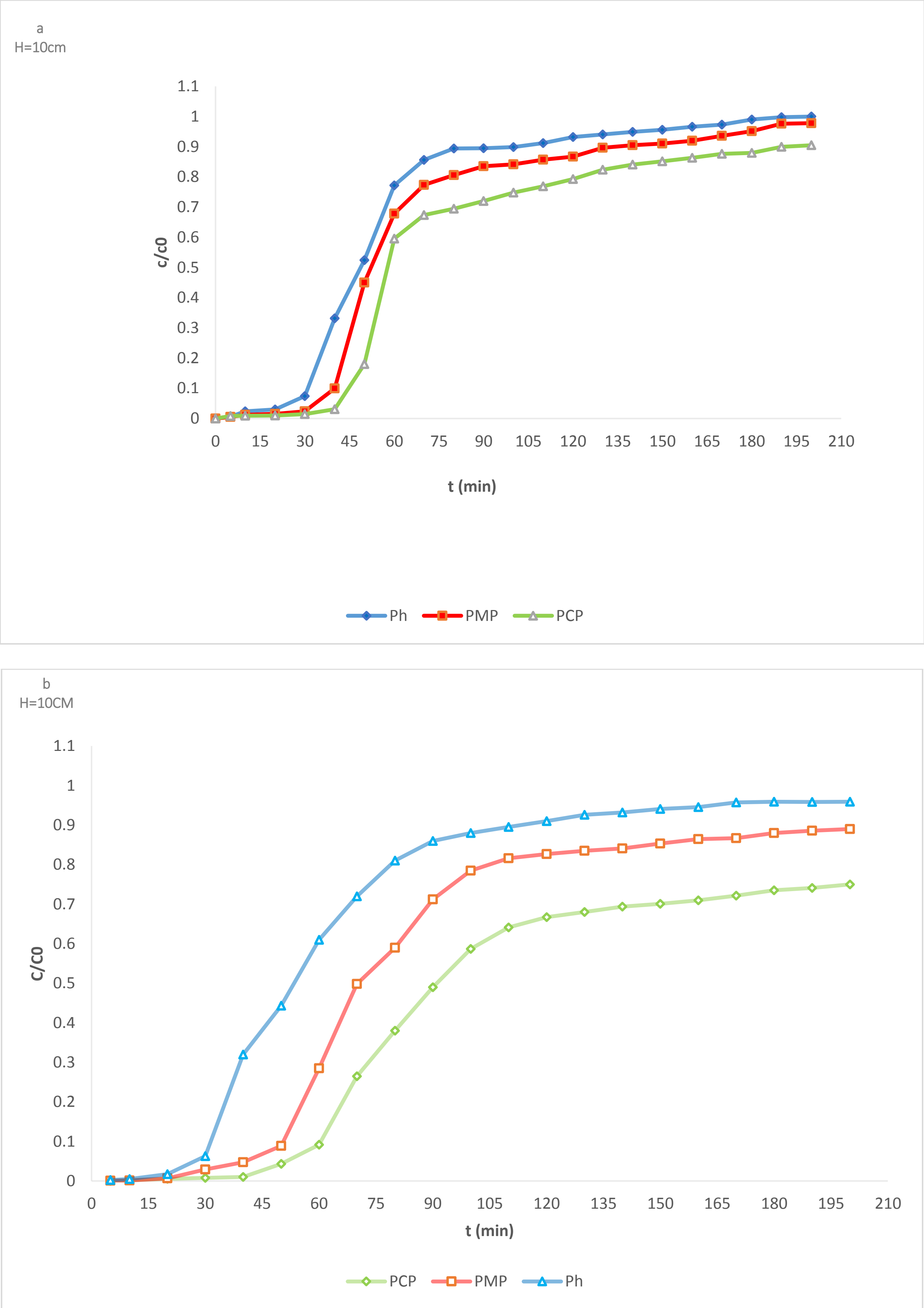


Figure 5: Breakthrough curves of multicomponent solution (a) char, (b) modified char 75mg/L; Q = 1L/h,H=10cm)

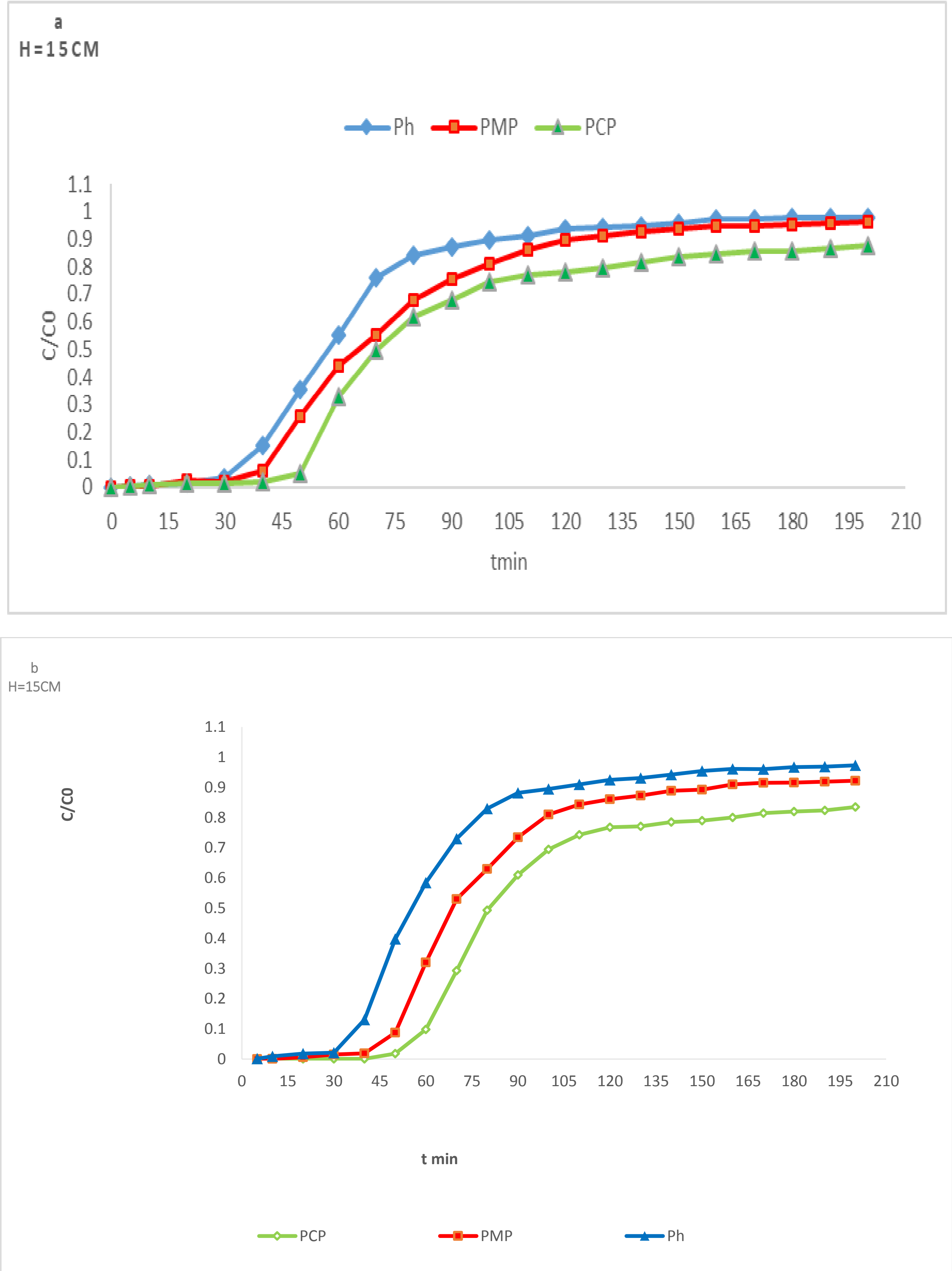


Figure 6: Breakthrough curves of multicomponent solution (a) char, (b) modified char 75mg/L; Q = 1L/h, H=15cm)

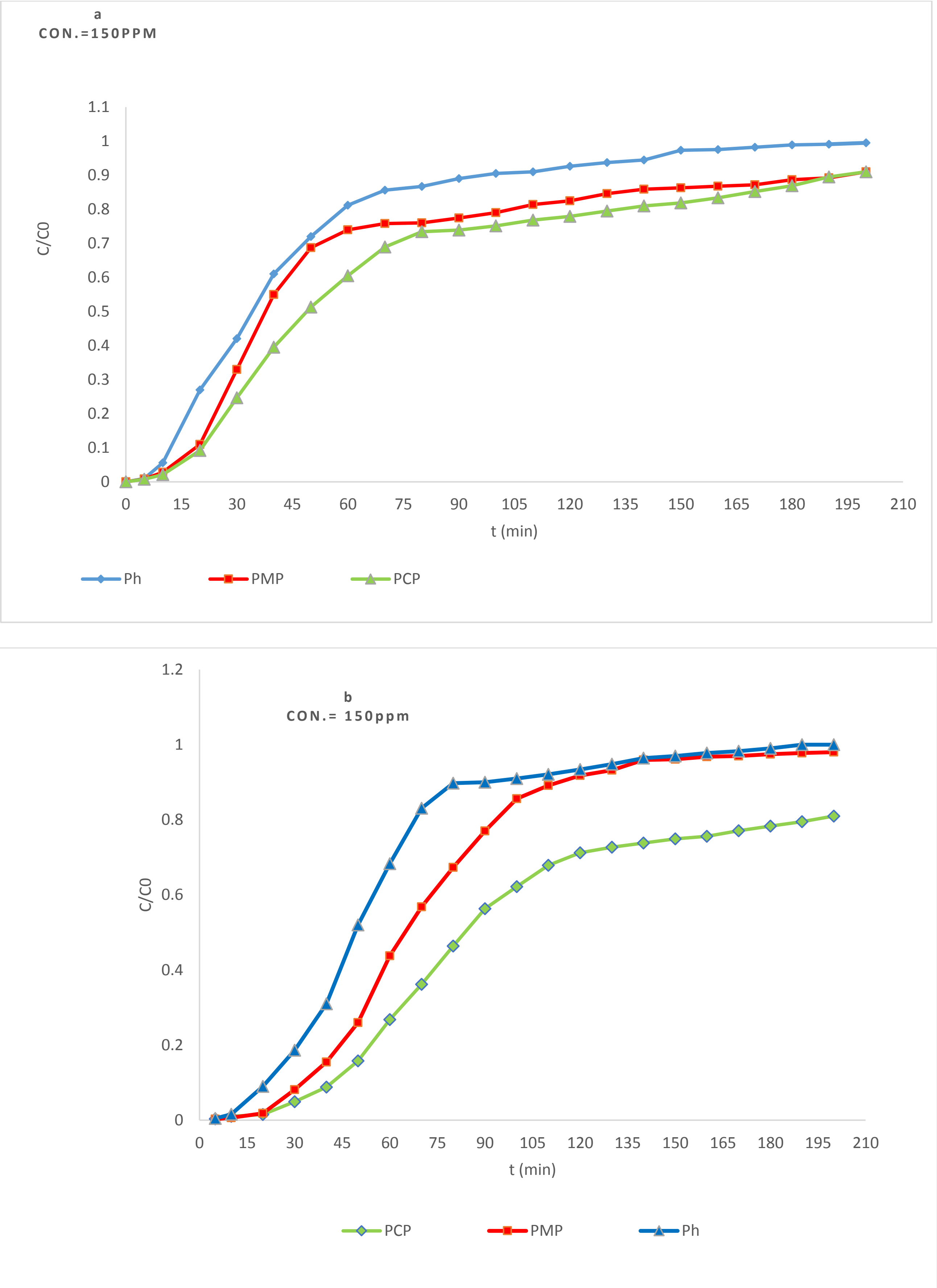
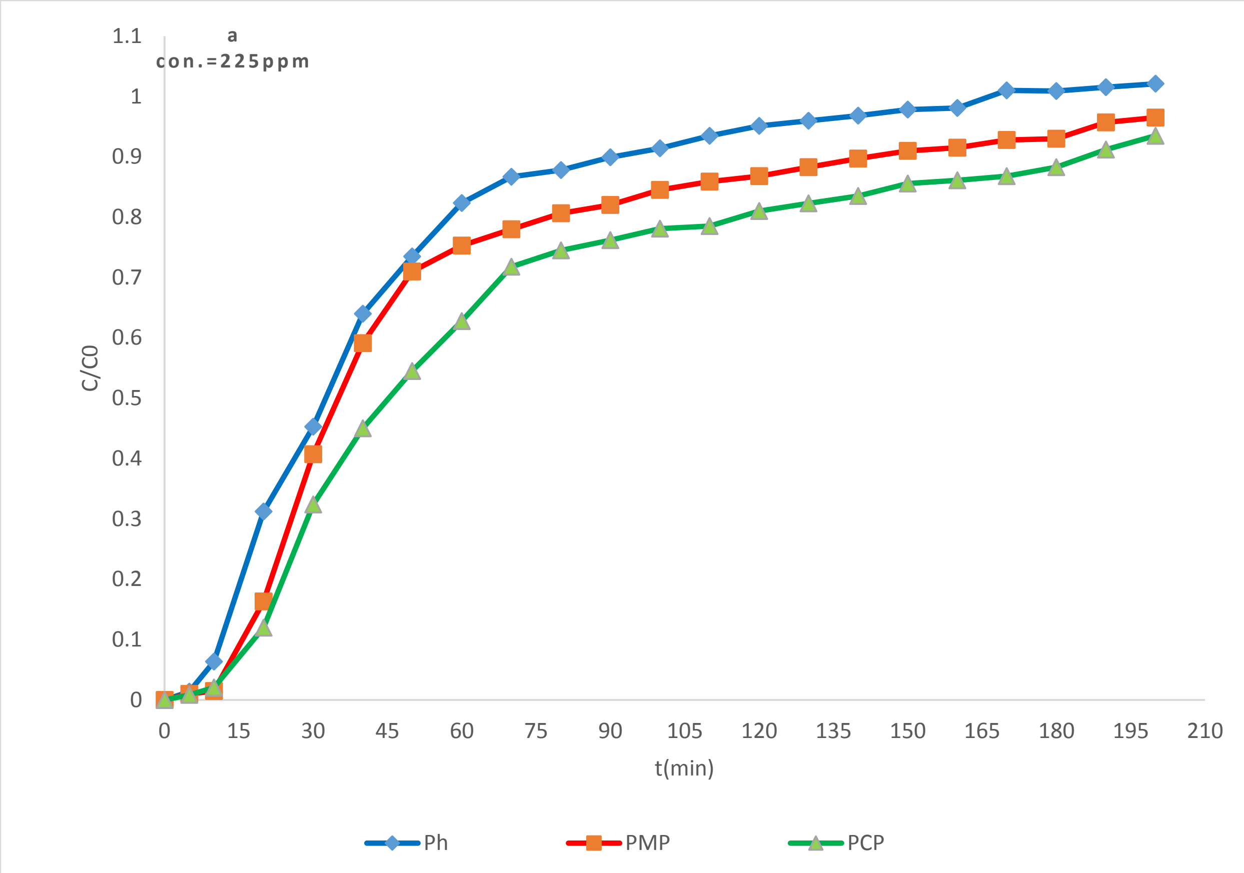


Figure 7: Breakthrough curves of multicomponent solution of (a) char (b) modified char (L = 5cm; Q = 1L/h, Con.=150ppm)



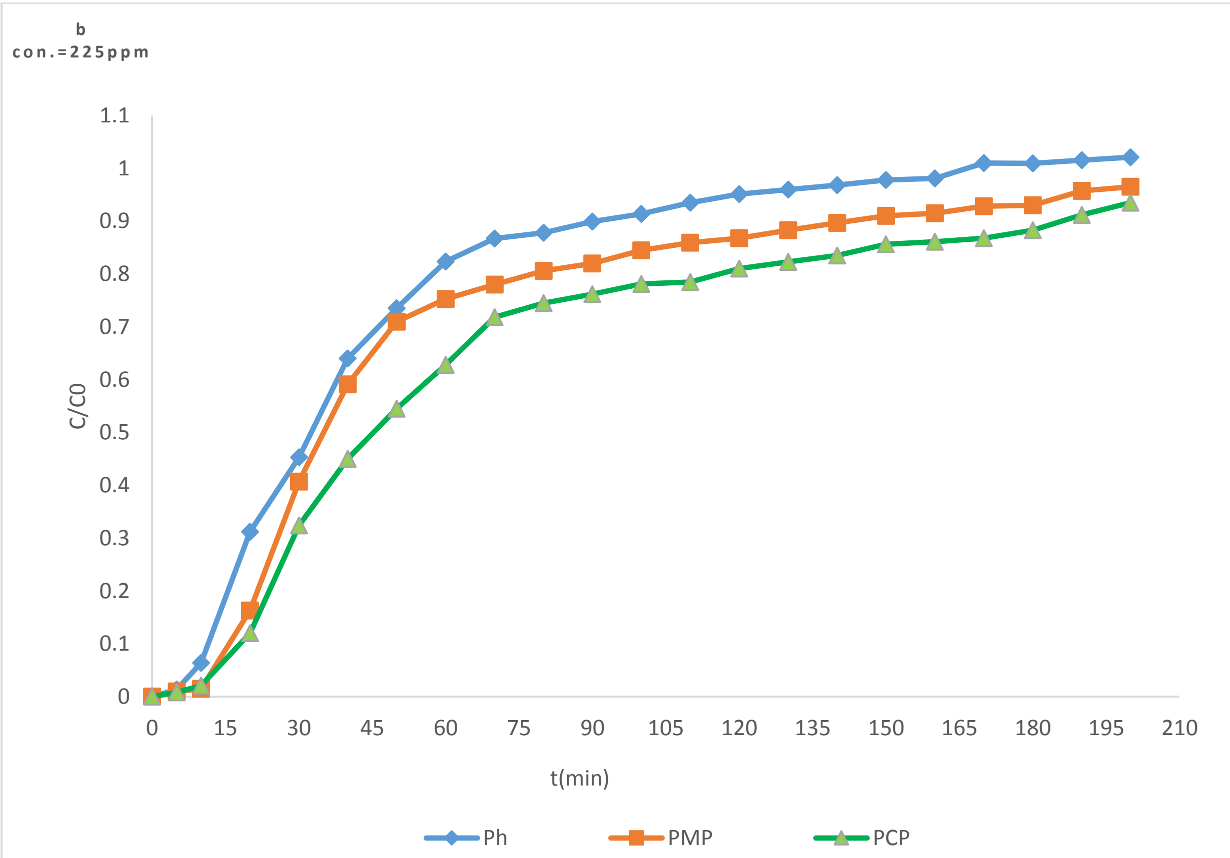
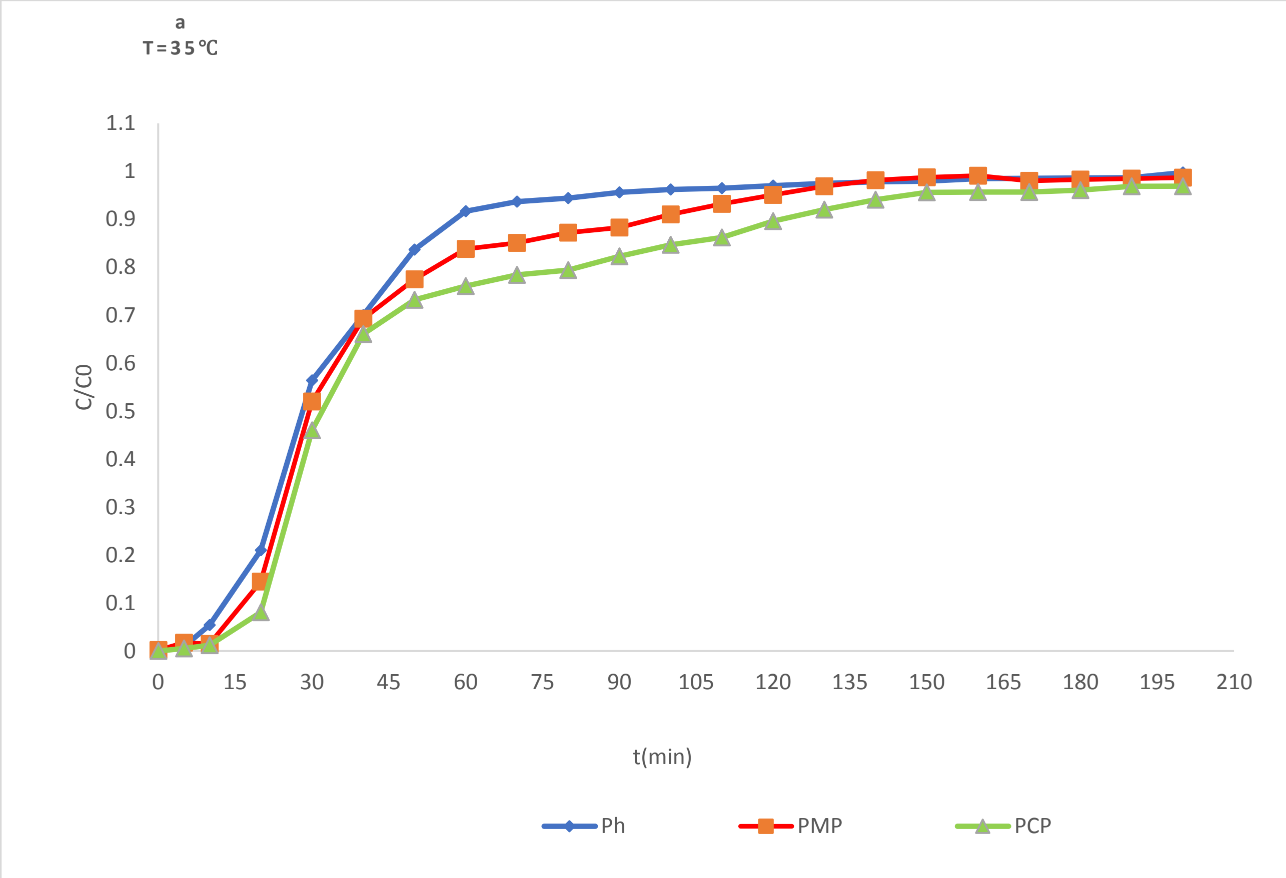


Figure 8: Breakthrough curves of multicomponent solution of (a) char (b) modified char (L = 5cm; Q = 1L/h,Con.=225ppm)



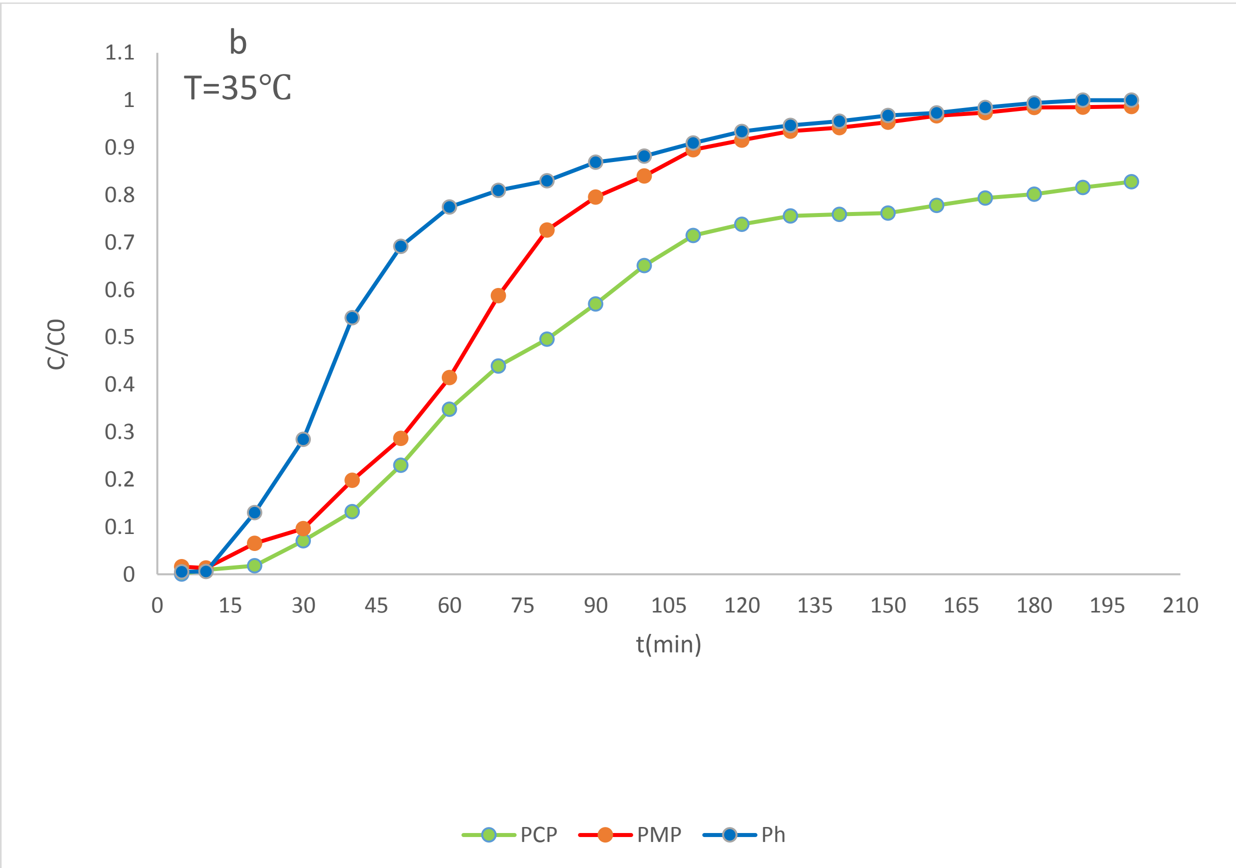
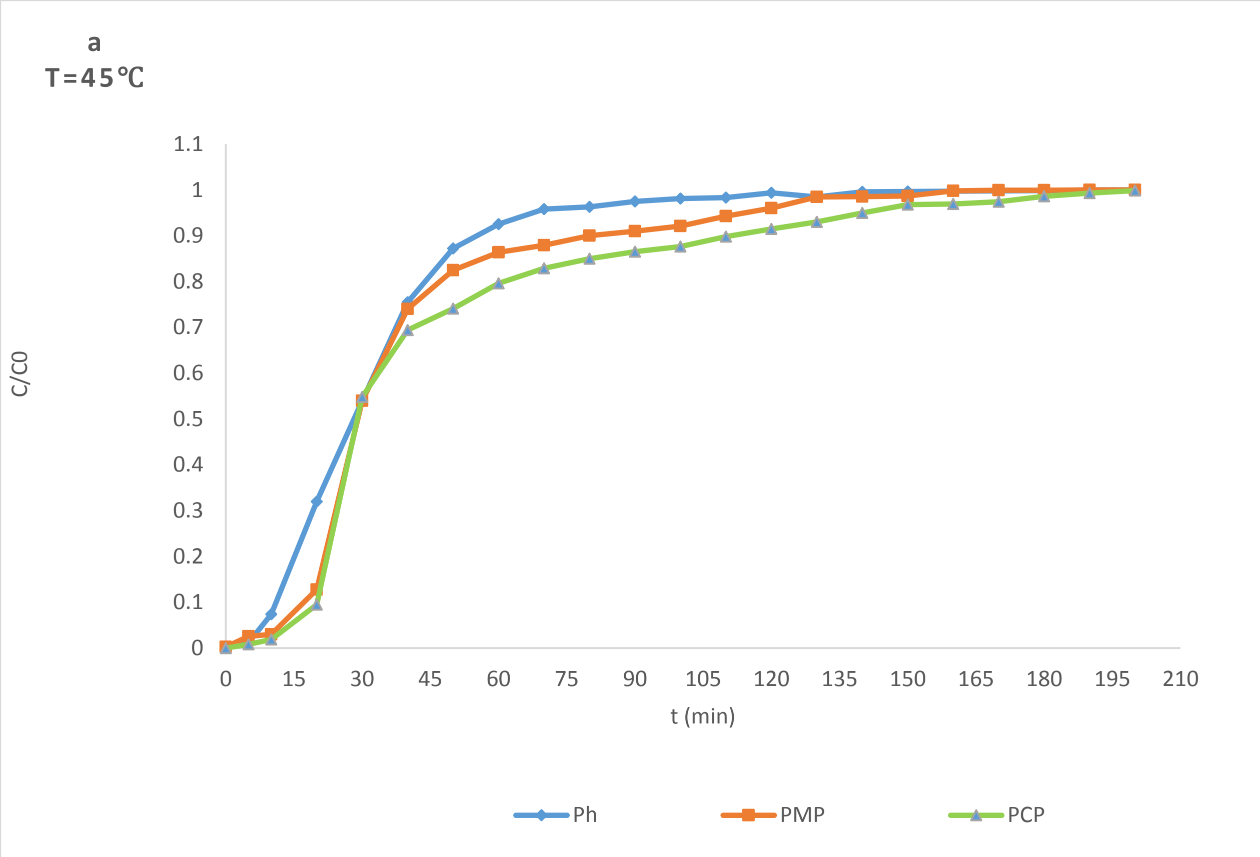


Figure 9: breakthrough curves of multicomponent solution of (a) char (b) modified char (L =5.0cm; Q = 1 L/h, T=35℃, Con.=75ppm)



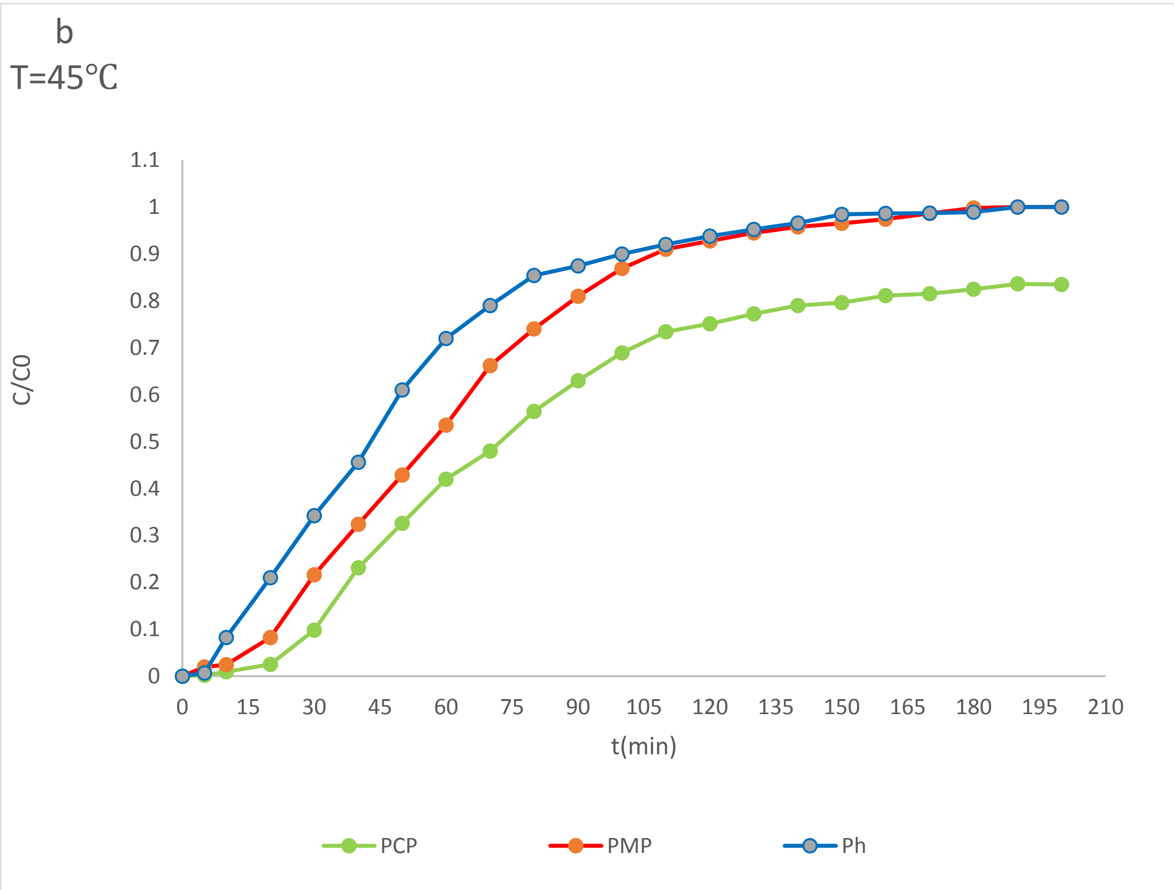


Figure 10: Breakthrough curves of multicomponent solution of (a) char (b) modified char (L =5.0cm; Q = 1 L/h, T=45℃, Con.=75ppm

Table 1
Data and parameters of fixed bed adsorption and of multicomponent solution

parameters		Char (tb min)			Modified char (tb min)		
		cp	mp	ph	cp	mp	ph
Volumetric flow rate, cm^3/min	0.5	52	42	31	58	45	40
	1	35	29	20	43	35	23
	1.5	18	15.5	8	34	24	18
Length of bed, cm	5	35	29	20	43	35	23
	10	41	32	22	50	38	28
	15	50	37	30	55	45	33
Inlet concentration, mg/l	75	35	29	20	43	35	23
	150	14	12	9	30.5	25	15
	225	12	11	7	21	18	15
Temperature, ◦C	20	35	29	20	43	35	23
	35	14.5	11.2	9	25	18	15
	45	12	10.2	7	20	12	8

Conclusion

The performance of char and modified of tire char for multicomponent solution in continuous system was investigated. Breakthrough curve was created under changing flow rate, initial concentration column height and temperature. Data mark with lowering flow rate and initial concentration, temperature and increasing column height led to increase of breakthrough time. The break through curve could be arranged in order of PCP >PMP > P, tb was 35>29>20 for PCP, PMP and Ph respectively at $Q=1cm^3/min$, con. = 75ppm, l=5cm. Modified char gave also the best result in phenolic removal with increasing breakthrough time 43>35>23 for PCP, PMP and Ph respectively at $Q=1cm^3/min$, con. = 75ppm, l=5cm.

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