CHAPTER IV
RESULTS AND DISCUSSION

4.1 Results

Base conditions were a pH of 12, a temperature of 30°C, 2 hours pre-soaking time, 2 hours shaking time, and absence of abrasive. Figures 1-10 show photographs of deinked samples and ink removal for the conditions studied. The critical micelle concentration (CMC) of CTAB in the absence of added electrolyte at 25°C is 0.92 mM.

4.1.1 Effect of CTAB Concentration and Abrasive

As shown in Figures 1 and 2, in the absence of ceramic pieces, there is no significant ink removal from the plastic surfaces below the CMC. There can be significant removal below CMC when abrasives are present. There is a CTAB concentration range in which deinking increases rapidly to 100 %; in the absence of abrasives, this concentration range is about 150 % higher than in the presence of abrasives. For example, 50% deinking occurs at 1.0 mM CTAB with abrasives and at 2.5 mM CTAB without abrasives. In either case, complete (100 %) deinking occurs at a CTAB concentration of 5 mM. So, abrasives speed up deinking, but are not necessary for complete deinking. The separation of abrasives from recovered plastic and from ink might make abrasives undesirable. On the other hand, if abrasives are discarded with detached ink, this results in an increase in solid waste disposal.

4.1.2 Effect of Pre-soaking Time

As shown in Figures 3 and 4, the shaking time required to attain a specified degree of deinking can be substantially reduced by pre-soaking. The effect is particularly pronounced at CTAB concentrations around the CMC. For example, at 2 x CMC, ink removal increases from 10 % to 80 % as pre-soaking time increases from 0 hr to 3 hr. Deinking efficiency can be dramatically affected at specific pre-soaking times in some cases. For example, for a pre-soaking time increase from 3 hr to 5 hr at the CMC, ink removal increased from 25 % to 90 %.

4.1.3 Effect of Shaking Time

Figures 5 and 6 show that shaking time can have a substantial effect on ink removal. Comparing Figures 3 and 5, there is sometimes an inhibition period of time for both pre-soaking and shaking during which little deinking occurs, followed by a narrow period of time (we will call this the detachment period) during which ink removal increases rapidly to near completeness. From a design viewpoint, it is important to choose residence times for pre-soaking and shaking which are at the end of the detachment periods for each. Longer pre-soaking times permit shorter shaking times and longer shaking times permit shorter pre-soaking times, so there is an economic optimization required to determine design conditions. For example, > 90 % ink removal can be attained at a CTAB concentration at the CMC with 5 hrs pre-soaking with the standard 2 hrs shaking time, while with 2 hrs pre-soaking, 4 hrs shaking time can yield > 90 % deinking. Since pre-soaking process units (holding tanks) generally require much less capital expense than agitated process units (agitated vessels), pre-soaking can improve process economics.

4.1.4 Effect of pH

The effect of pH on ink removal is shown in Figures 7 and 8, where a dramatic effect of pH is observed. At a pH of 11, almost no deinking is observed at any CTAB concentration. Yet, at a CTAB concentration of 5 x CMC and above, at a pH of 11.75 and above, almost complete deinking is observed. High pH (at least 11.5) is crucial for effective ink removal. Of course, under these extremely basic conditions, materials constraints increase process equipment costs substantially. As with temperature, pH effects on CMC were not accounted for and are assumed to be small at the added electrolyte levels (≤ 0.01 M) from added NaOH.

4.1.5 Effect of Temperature

Higher temperatures can substantially increase deinking efficiency as shown in Figures 9 and 10. At 45°C, > 90 % ink removal was observed even at a CTAB concentration of 25 % of the CMC. Higher temperatures can increase energy costs and robustness of process equipment materials (particularly at the high pH levels anticipated). Note that the CMC referred to here be that at 25°C. Since the CMC is only mildly dependent on temperature for ionic surfactants (Rosen, 1989), temperature corrections were not made. So, for example, when the CTAB concentration is referred to as at the CMC, this is not entirely accurate at 45°C. In terms of the fairly large concentration increments used here, this is not a significant consideration.

4.2 Mechamisms of Deinking

One problem with understanding physical mechanisms of ink removal is the ill-defined nature of the inks and binder due to their complexity and due

to the proprietary nature of their formulation. However, the results here can give some insight.

The surfactant can aid detachment by mechanisms such as adsorption on ink and plastic surfaces, decreasing ink/water and plastic/water interfacial tensions, making detachment more thermodynamically favorable. This is a common mechanism aiding detergency of both particulate and oily soils (Christian and Scamehorn, 1995; Rosen, 1989). Surfactant can sometimes "liquefy" soil, an ill-defined term implying that the soil either can flow and be removed by the roll-back mechanism (Borchardt, 1994; Christian and Scamehorn, 1995; Lange, 1994; Porter, 1994; Rosen, 1989) or can be shaken up into little pieces as surfactant diffuses or penetrates into the soil and loosens it up. The surfactant can also aid with wetting, aiding the formation of a water layer between ink particles and the polymer surface. The wetting enhancement is due to surfactant adsorption on ink and plastic - trapped air is displaced. The surfactant can aid in antiredeposition (preventing the ink from readsorbing) by dispersing solid ink particles by adsorbing in the ink surface, emulsifying liquid ink droplets, and solubilizing ink molecules in micelles (Christian and Scamehorn, 1995; Gecol, 1998a; Jakobi and Lohr, 1987; Lange, 1994).

The surface area of the polymer and ink are low enough that the final concentration of surfactant in solution is probably not significantly lower than the initial concentration. Above the CMC, the primary function of incremental surfactant is to solubilize ink molecules within micelles. A secondary advantage could be the micelles disassociating to provide surfactant monomer, speeding up rate-driven processes. However, over the time periods covered here (hours), this is generally not a significant factor, so solubilization can be deduced as an important mechanism of ink uptake by the solution. This implies that a significant amount of ink is molecularly dispersed in order to be

solubilized, instead of being present as particles or droplets. Another possibility is that the micelles are solubilizing the ink binder.

Both pre-soaking and shaking time are important. It is possible that either the rate of surfactant adsorption or rate of penetration or liquefaction can be the rate-determining step here. The beneficial effect of abrasives at short times imply that it is the rate of detachment of ink after surfactant adsorption has occurred which may be limiting, also consistent with no significant deinking with abrasive, but no surfactant. Solubilization is a very fast process (Rosen, 1989) and is probably not rate-determining.

Detergency generally is more effective at high pH as more negative charges are imposed on the contaminant and on the substrate, making them more repulsive from each other (Gecol, 1998a, b; Min, 1999). This would make ink detachment and antiredeposition easier in this case. The ink particles can be attached to the surface by binders. Attenuated total reflection (ATR) FTIR (Min, 1999) indicated that all of the ink binder contained ester groups for this system. The intense C=O stretching bond of saturated aliphatic ester groups is in the frequency range of $1750 - 1735$ cm^{-1} (Silverstein, 1991) in agreement with the spectrum observed for this ink. Sodium hydroxide, which was used for pH adjustment, is hypothesized to break up the ink binder by hydrolyzing the ester groups, especially at pH 12 (Gecol, 1998b; Min, 1999)

The improvement in deinking with increasing temperature is probably due to rate effects, since surfactant adsorption decreases with increasing temperature (Rosen, 1989) and solubilization is only mildly temperature dependent (Christian and Scamehorn, 1995).

CTAB concentration	Without abrasive	With abrasive
0	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
25% CMC	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
50% CMC	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
75% CMC	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
CMC	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
3 x CMC	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
5 x CMC		
7 x CMC		
10 x CMC		

Figure 4.1 Deinked plastic surfaces which have been treated with and without abrasive material as a function of CTAB concentration
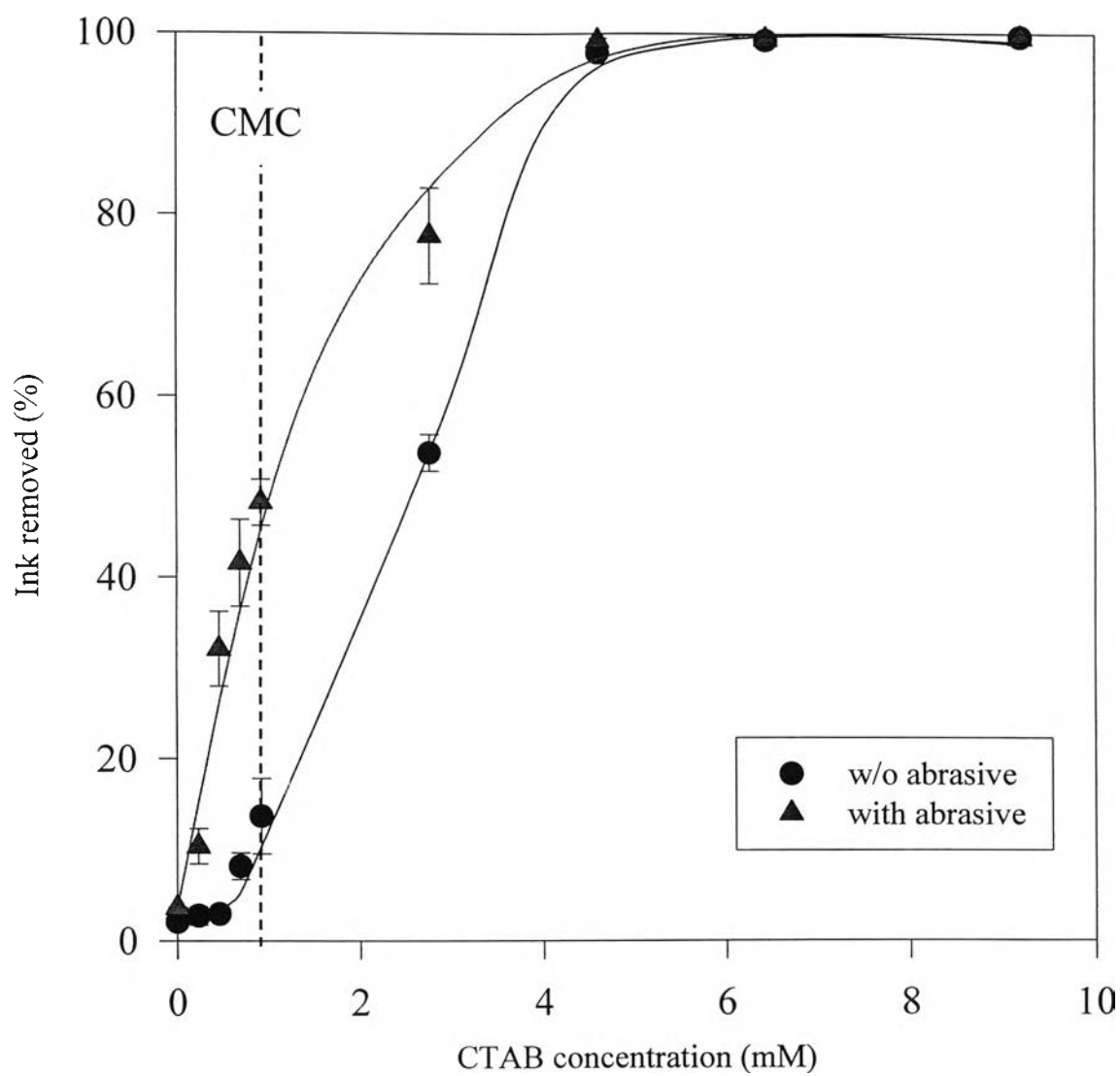
Figure 4.2 Amount of ink removed from printed plastic surfaces with and without abrasive material as a function of CTAB concentration

Pre-soaking Time (hr)	25% CMC	CMC	2 x CMC	5 x CMC	10 x CMC
0	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	
1	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์		
2	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์		
3	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพ มพันธ์ทิพย์			
4	มพันธ์ทิพย์ มพันธ์ทิพย์	มพ พย์			
5	มพันธ์ทิพย์ มพันธ์ทิพย์				
6	มพันธ์ทิพย์ มพนธ์ทิพย์				ๆ
7	มเธพย มพนธทพย์				

Figure 4.3 Deinked plastic surfaces which have been treated with selected CTAB concentrations at various pre-soaking times
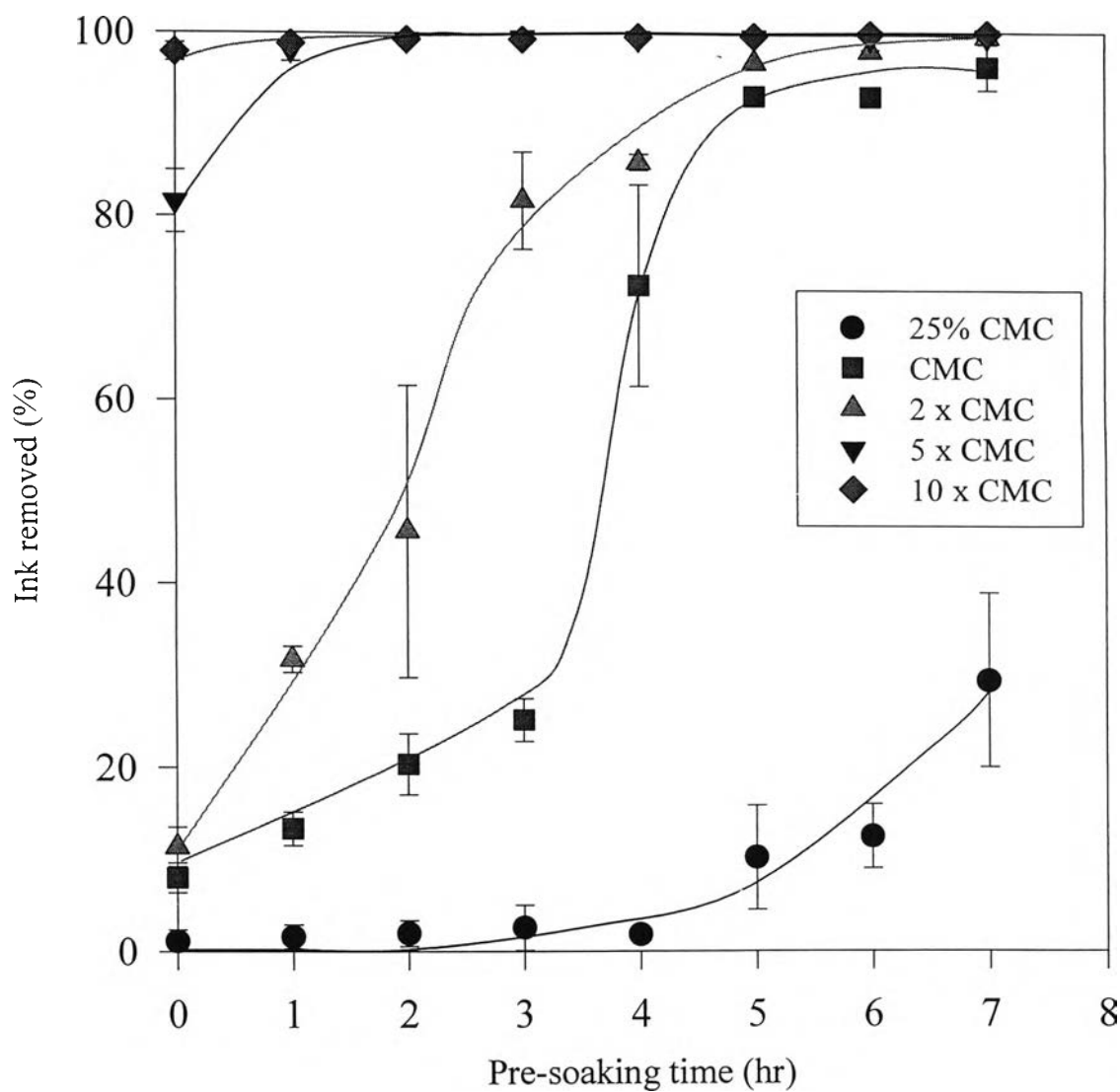
Figure 4.4 Amount of ink removed from printed plastic surfaces at selected CTAB concentrations as a function of pre-soaking time

Shaking Time (hr)	25% CMC	CMC	5 x CMC	10 x CMC
0	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
1	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	
2	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ บพันธ์ทิพย		
3	มพันธ์ทิพย์ มพันธ์ทิพย			
4	มพันธ์ทิพย มพันธ์ทิ			
5	มพันธ์ทิพย์ มพัน ทิ ย์			
6	พ ธทพ			
7	ม ย มา พย			

Figure 4.5 Deinked plastic surfaces which have been treated with selected CTAB concentrations at various shaking times
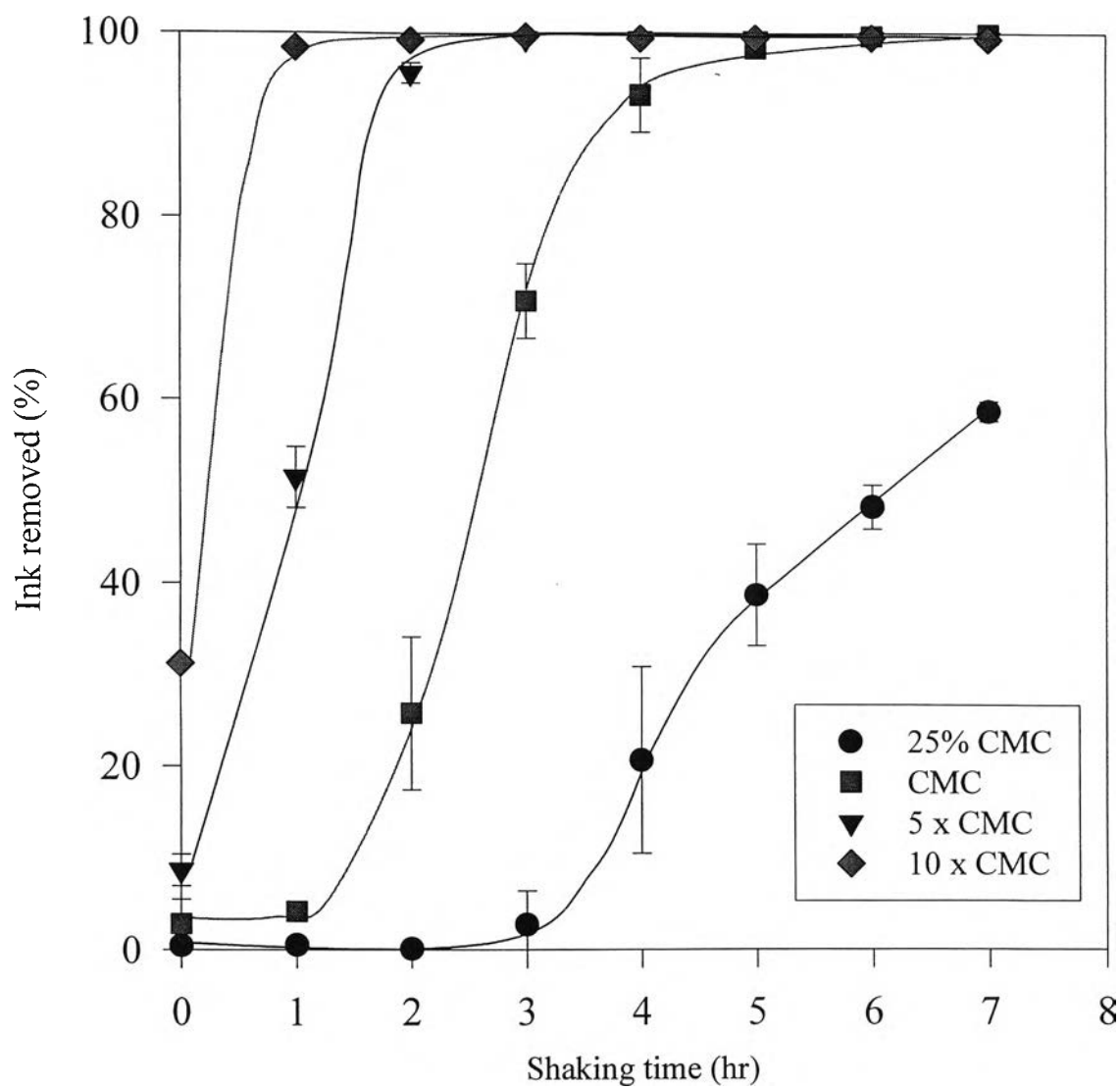
Figure 4.6 Amount of ink removed from printed plastic surfaces at selected CTAB concentrations as a function of shaking time

pH	25% CMC	CMC	2 x CMC	5 x CMC	10 x CMC
11.00	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
11.25	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
11.50	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์
11.75	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์		
12.00	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์		

Figure 4.7 Deinked plastic surfaces which have been treated with selected CTAB concentrations at various pHs
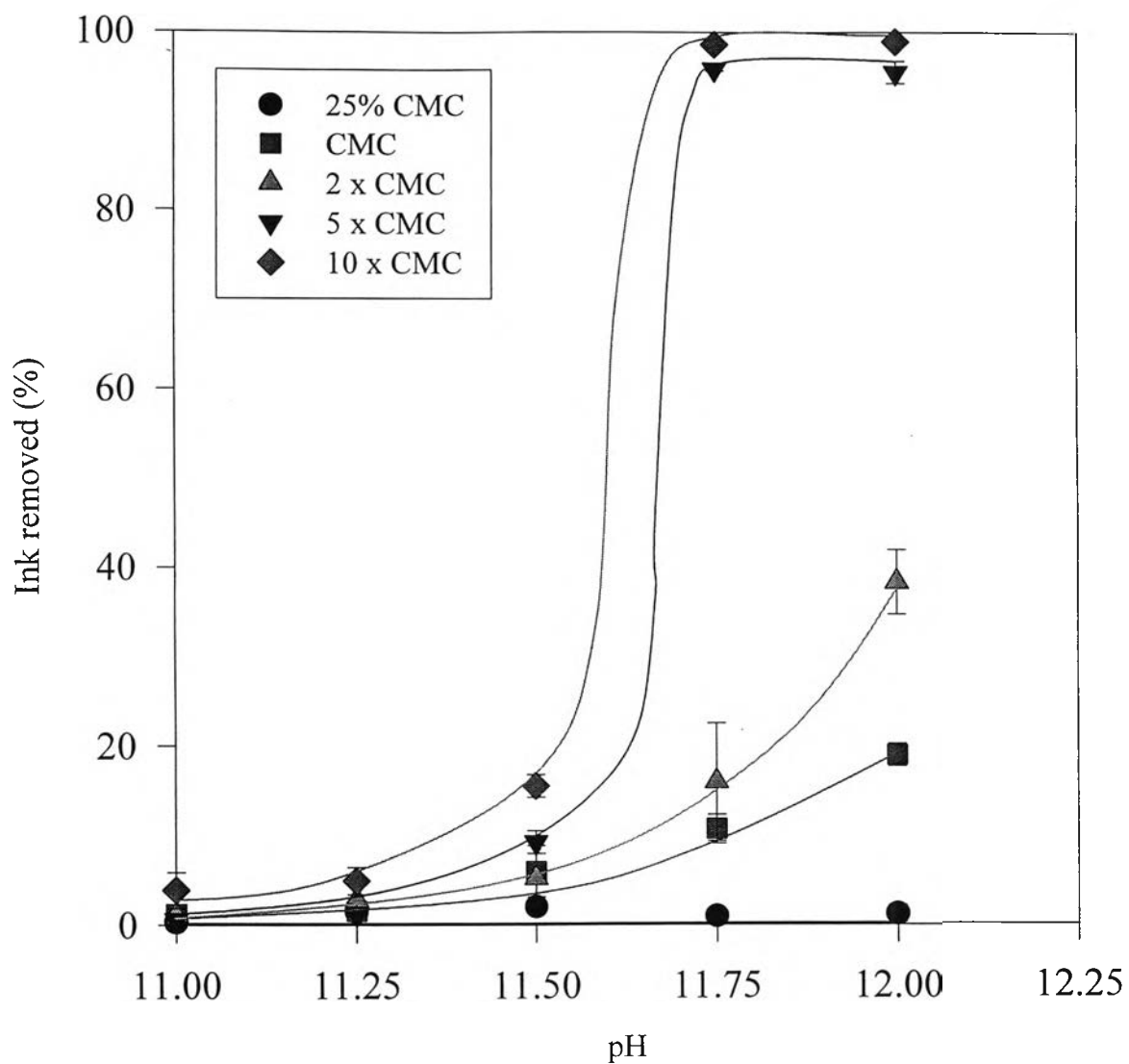
Figure 4.8 Amount of ink removed from printed plastic surfaces at selected CTAB concentrations as a function of pH

T (C)	25% CMC	CMC	2 x CMC	5 x CMC	10 x CMC
30	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิ ม พันธ์ทิพย์		
35	มพันธ์ทิพย์ มพันธ์ทิพย์	มพันธ์ทิพย์ มพันธ์ทิพย์			
40	นธ์ทิพ มพันธ์				
45					

Figure 4.9 Deinked plastic surfaces which have been treated with selected CTAB concentrations at various temperatures
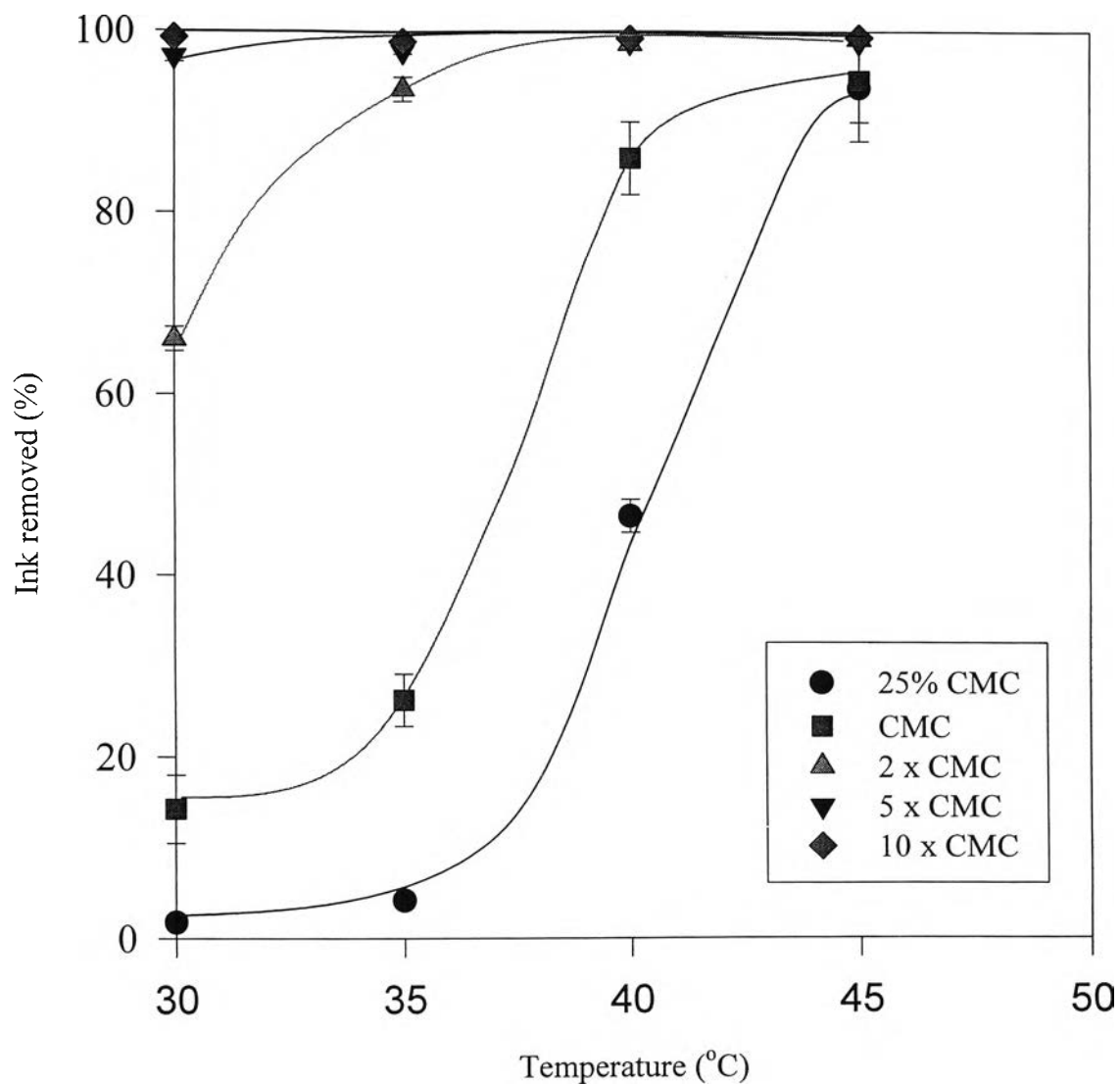
Figure 4.10 Amount of ink removed from printed plastic surfaces at selected CTAB concentrations as a function of temperature