Removal of Cu^{++} from industrial wastewater by cementation on Zn impeller of batch-agitated vessels

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Rates of Cu^{++} removal from synthetic waste solution by cementation on Zn impeller in batch agitated vessels were studied under different conditions of impeller type, impeller rotation speed, initial Cu^{++} concentration, and time of cementation. It was found that the rate of Cu^{++} removal increases with increasing rotational speed, initial Cu^{++} concentration, and residence time. The four blades 45° pitched turbine was more effective for removal of Cu^{++} than the four blades flat turbine. The presence of baffles in agitated vessels was found to increase the rate of cementation of Cu^{++} on Zn impeller by an amount ranging from 32 to 94% depending on the impeller type and rotational speed. Addition of drag reducing polymers (polyox WSR-301) in the form of suspension to Cu^{++} bearing solution was found to decrease the cementation rate of Cu^{++} on Zn impeller by an amount ranging from 2% to 40% depending on impeller type, rotational speed, and polymer concentration. Mathematical treatment of mass transfer data using the method of dimensionless analysis resulted in the following overall correlations:
(i) For the four blades flat turbine under the conditions:
$1461 < Re < 54466$ and $1428 < Sc < 1536$ $\quad Sh = 4.75\ Sc^{0.33}\ Re^{0.607}$
(ii) For the four blades 45° pitched turbine under the conditions:
$1461 < Re < 54466$ and $1428 < Sc < 1536$ $\quad Sh = 5.17\ Sc^{0.33}\ Re^{0.605}$.

تمت دراسة معدلات أزالة أيونات النحاس من مياه الصرف الصناعيه بأستخدام السمنته على قلاب من الزنك في مفاعل دفعي مقلب تحت ظروف مختلفه و هي نوع القلاب، سرعة القلاب، التركيز الأبتدائى لأيونات النحاس، و زمن تفاعل السمنته. و قد بينت النتائج أن معدلات أزالة أيونات النحاس تتزايد مع زيادة سرعه القلاب و زيادة التركيز الأبتدائى لأيونات النحاس و زمن تفاعل السمنته. بينت النتائج أيضا أن القلاب ذو الأربع ريش بزاويه ٤٥ درجه كفاءته أعلى من القلاب ذو الأربع ريش المستويه. و قد زادت معدلات أزالة أيونات النحاس في وجود حواجز للسريان و ذلك بمعدلات تتراوح من٣٢ الى ٩٤% تبعا لنوع القلاب و معدل التقليب. ، عند اضافة بوليمر مقلل للأحتكاك و جد أن معدلات أزالة أيونات النحاس تناقصت بنسب تتراوح من ٢% الى ٤٠% تبعا لنوع القلاب و معدل التقليب و تركيز البوليمر. و بأجراء معامله رياضيه لمعاملات انتقال الماده أمكن التوصل للعلاقات التاليه:
$Sh = 4.75\ Sc^{0.33}\ Re^{0.607}$ في حالة القلاب ذو الأربع ريش المستويه و $Sh = 5.17\ Sc^{0.33}\ Re^{0.605}$ في حالة القلاب ذو الأربع ريش بزاويه ٤٥°.

Keywords: Wastewater, Cementation, Copper removal, Agitated vessels, Drag reducing polymers

1. Introduction

The presence of toxic heavy metals over the permissible levels in wastewater discharges may pose a potential threat to the environment and the ecosystems of receiving water bodies as they are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders. Besides, heavy metals are considered toxic for biological treatment plants. Copper is one of the most toxic metal ions that must be removed to a certain level to meet the discharge requirements. The primary sources of copper in industrial wastewater are metal-process pickling baths, electroplating baths, metal finishing plants, and circuit board manufacturing. Copper may also be present in wastewater from variety of chemical manufacturing processes which use Copper salts or a copper catalyst.

The removal of toxic heavy metal ions from wastewater is an important and widely studied research area. A number of technologies have been developed over the years to remove toxic metal ions from wastewater. Cementation is one of the most effective and economic techniques used for recovering toxic and/or valuable metals from industrial wastewater. Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salt by another electropositive metal.

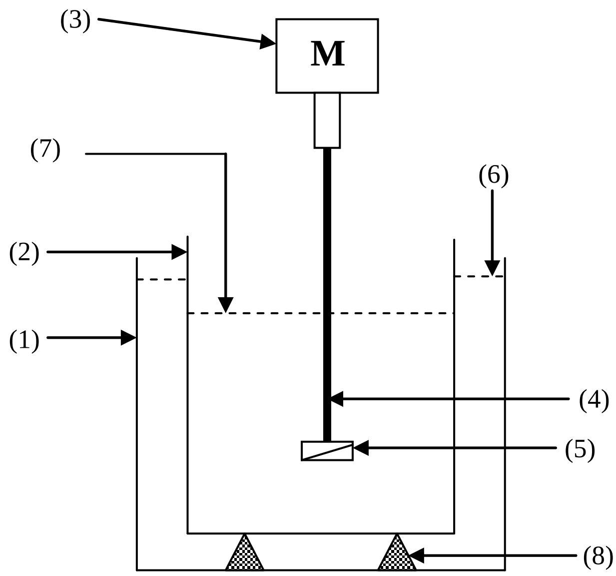
The cementation technique has been used in industry for a long time for recovery of copper from dilute leach solutions and purification of process streams. Previous studies on cementation of copper on less noble metals have shown that the reaction is controlled by boundary layer diffusion. [1, 2] Accordingly, to increase the rate of cementation stirring is essential. Previous studies have used different means of stirring such as rotating disc [2], rotating cylinder [3], gas sparging, [4] fixed and fluidized bed, [5, 6] and surface vibration (oscillation) [7] to enhance the rate of cementation. Recently, Mubarak [8] used mechanical stirring for removing Cu^{++} from waste solutions by cementation on Zn cylindrical sheets lining the walls of baffled-agitated vessel. The present work is to explore the possibility of cementing Cu^{++} on the impeller of the agitated vessel, the idea stems from the fact that previous mass transfer studies in agitated vessels have shown that the rate of mass transfer at the impeller is higher than elsewhere in the agitated vessel [9].

To this end Cu^{++} removal from synthetic waste solutions, by cementation on four blades Zn turbine of either flat or 45° pitched blades in baffled and unbaffled agitated vessel was carried out. Previous fluid mechanic studies on the effect of drag reducing polymers on the performance of agitated vessels have shown that drag reducing polymers save considerable power consumption by an amount ranging from 10% to 30% depending on impeller geometry, polymer concentration, and Re. As drag reducing polymers have the potential of being used in agitated vessels to cut down mechanical energy required to rotate the impeller by virtue of the ability of polymer molecules to damp the small scale high frequency eddies responsible for energy dissipation, the present work aims also at testing the effect of drag reducing polymers on the rate of cementation of Cu^{++} on Zn impellers.

2. Experimental technique

Fig. 1 shows the experimental setup used in the present work, it consisted of 2 liters unbaffled cylindrical glass container. An impeller made of 99.9% pure zinc of 4 cm diameter was mounted centrally on an epoxy-isolated shaft connected to variable speed motor. The rotational speed was adjusted by a variac and measured by an optical tachometer. The cylindrical glass container and its contents were immersed in a rectangular thermostated water bath to control its temperature.

A similar vessel with four baffles of 1 cm width and 0.2 cm thickness was made to study the effect of baffles. Baffles were made of Plexiglass strips and were fixed perpendicular to the wall of the cylindrical glass container by epoxy adhesive. Two types of zinc impeller were used, namely four blades 45° pitched turbine and four blades flat turbine.



1- Thermostatically controlled water bath.
2- Cylinderical glass container.
3- Variable speed motor. 4- Agitator.
5- Zn turbine. 6- Water level.
7- $CuSO_4$ solution level. 8- Plastic support.

Fig.1. Experimental apparatus.

Before each run a fresh Zn impeller was used, 1500 milliliters of fresh copper sulfate solution were introduced into the cylindrical vessel; the rate of cementation was followed by withdrawing 5 milliliters samples at 2-5 minutes intervals for Cu^{++} analysis by atomic absorption method. The temperature was fixed at 25°C for all experiments. The copper-bearing solution was prepared using A.R. grade copper sulfate and distilled water. The initial copper concentrations used in this study were 0.005, 0.010, and 0.025 M $CuSO_4.5H_2O$. In order to test the effect of drag reducing polymers on the rate of Cu^{++} cementation on Zn impeller, polyethylene oxide (Polyox WSR-301) was used in the form of suspended solids at concentrations of 100, 200, 300 ppm.

3. Results and discussion

The rate of cementation of Cu^{++} on rotating Zn impeller in batch agitated vessel containing copper sulfate solution is given by the equation

$$-V_s\, dC/dt = kA\,(C-C_o), \tag{1}$$

which upon integration gives:

$$\ln C_o/C = kAt\, /\, V_s. \tag{2}$$

Where C_o is the initial Cu^{++} concentration, C is the concentration at anytime t, V_s is the volume of the solution in the agitated vessel, k is the mass transfer coefficient of the cementation of Cu^{++} on the rotating Zn impeller.

Fig. 2 shows a typical $\ln C_o/C$ versus t plots at different speeds of rotation, different initial Cu^{++} concentrations, and two types of turbines (four blades 45° pitched turbine and four blades flat turbine). The mass transfer coefficient was calculated from the slope kA/V_s. In view of the hydrodynamic complexity of the present system arising from the turbulent nature of the flow at the rotating impeller, it is difficult to correlate the present data using a model based on the established mass transfer theories such as the hydrodynamic boundary layer theory. Accordingly, the method of dimensionless analysis was used to correlate the present data. The mass transfer coefficient can be correlated to different variables by the functional equation:

$$k = f\,(\mu, \rho, D, n, d). \tag{3}$$

Where k is the mass transfer coefficient ($cm.s^{-1}$), μ is the solution viscosity ($g.cm^{-1}.s^{-1}$), ρ is the solution density ($g.cm^{-3}$), D is the diffusivity of copper sulfate solution ($cm^2.s^{-1}$), d is the impeller diameter (cm), and n is the rotational speed of the impeller (s^{-1}). Dimensionless analysis leads to the dimensionless equation:

$$kd\, /\, D = a\,(\mu\, /\, \rho D)^{\alpha}\,(\rho n d^2\, /\, \mu)^{\beta}. \tag{4}$$

i.e

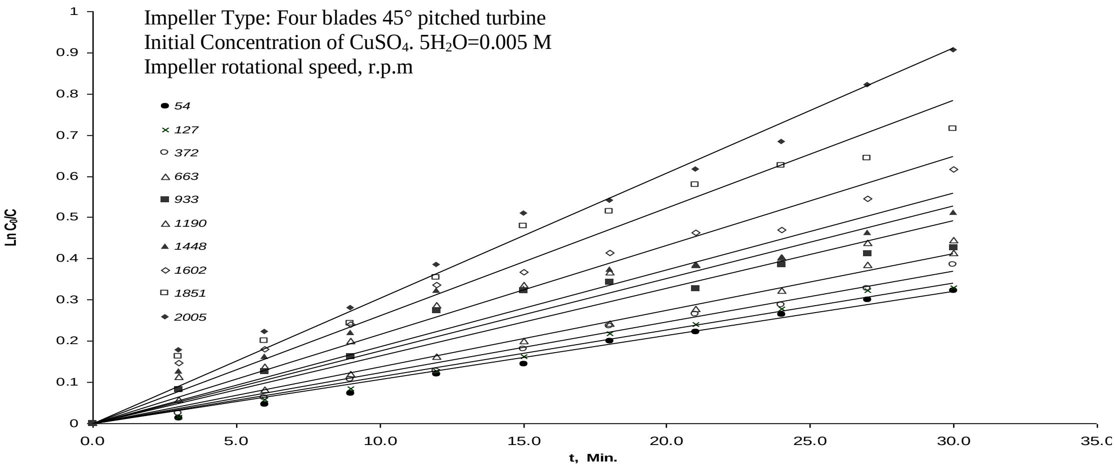


Fig. 2. Typical $\ln C_o/C$ V_s t for the cementation of copper on four blades 45° pitched Zn turbine.

$$Sh = a\, Sc^{\alpha}\ Re^{\beta}. \quad (5)$$

Where a, α, and β are constants.

Following previous theoretical and experimental mass transfer studies, the value of α was taken as 0.33 [10]. To obtain β, log *Sh* for the cementation of Cu^{++} on Zn impeller was plotted against log *Re* as follows:

(i) For 4 blades flat turbine, the data of fig. 3 fit the equation

$$Sh = a_1\ Re^{0.607}. \quad (6)$$

(ii) For 4 blades 45° pitched turbine, the data of fig. 4 fit the equation

$$Sh = a_2\ Re^{0.605}. \quad (7)$$

Figs. 3 and 4 show that the rate of mass transfer (represented by *Sh*) increases with increasing *Re*, confirming the diffusion controlled nature of the cementation reaction [12, 13]. The increase in the rate of mass transfer with increasing *Re* may be attributed to the increase in the intensity of turbulence which decreases the thickness of laminar sub layer and the diffusion layer at the impeller surface with a consequent increase in the mass transfer coefficient, which is related to the diffusion layer thickness (δ) by the eq. (10, 11)

$$k = D / \delta. \quad (8)$$

The high increase in the rate of mass transfer and the rate of cementation with increasing impeller rotation speed may suggest that the liquid phase mass transfer resistance is more important than the solid porous layer resistance surrounding the Zn impeller. The low resistance of the porous solid layer of copper surrounding the Zn impeller to the rate of mass transfer may be ascribed in part to the high porosity of the deposited copper layer. Besides, it is also possible that the high sheer stress, which prevails in the agitated vessel, limits the thickness of the porous layer by removing the loosely adherent copper from the thin copper layer deposited on the Zn blades.

Hydrodynamic studies of the agitated vessels [12] have revealed the fact that the

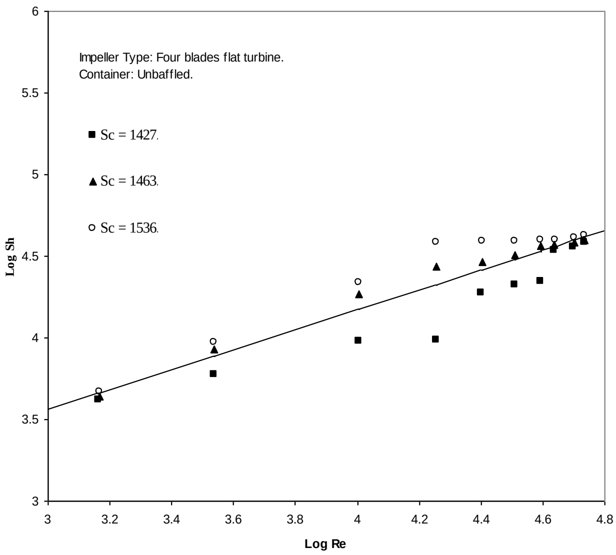


Fig. 3. Log *Sh* versus log *Re* for the cementation of Cu^{++} on four blades Zn turbine at different concentrations.

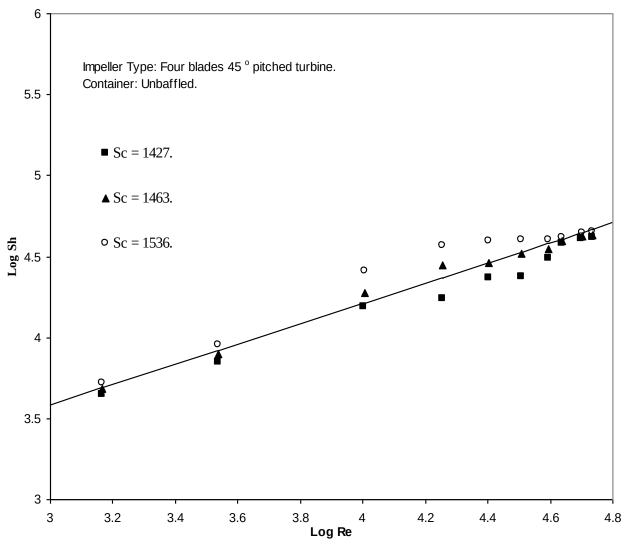


Fig. 4. Log *Sh* versus log *Re* for cementation of Cu^{++} on 45° pitched Zn turbine at different concentrations.

flow is laminar in the tank for *Re* < 10, turbulent for *Re* > 10000, and for the range between 10 and 10000 the flow is transitional, being turbulent at the impeller and laminar in remote parts of the vessel. Accordingly, the range of *Re* used in this study lies mostly in the turbulent region.

The insensitivity of the data shown in fig. 3 and 4 to *Sc* may be attributed to the relatively narrow range of *Sc* used in the present study (1428 < *Sc* < 1536).

Figs. 5 and 6 show that, for the same *Re*, the 4 blade 45° pitched turbine gives higher rate of mass transfer than that obtained in case of four blades flat turbine and this may be explained by the different flow pattern in both cases, as the turbine with flat blades gives radial flow, while in case of pitched turbines with 45° angle, some axial flow is imparted and the axial flow is more effective for creating a zone of rapid currents, high turbulence and intense shear near the impeller. Besides, in absence of baffles, tangential (swirl) flow, which is considered ineffective for mass transfer, predominates in agitated vessels provided with flat turbine to an extent higher than that prevailing in case of 45° pitched turbine [13, 14].

Figs. 7 and 8 show that the present data for the conditions:
1461 < *Re* < 54466, and 1428 < *Sc* < 1536, fit the equations:
For four blades flat turbine

$$Sh = 4.75 \ Sc^{0.33} \ Re^{0.607}, \qquad (9)$$

with an average deviation of ± 22.3%

For four blades 45° pitched turbine

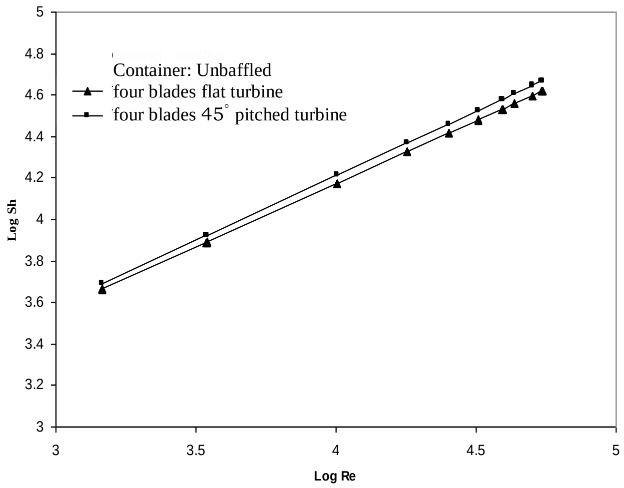


Fig. 5. Log *Sh* versus log *Re* for cementation of Cu^{++} on four blades flat and four blades 45° pitched Zn turbine of unbaffled agitated vessel.

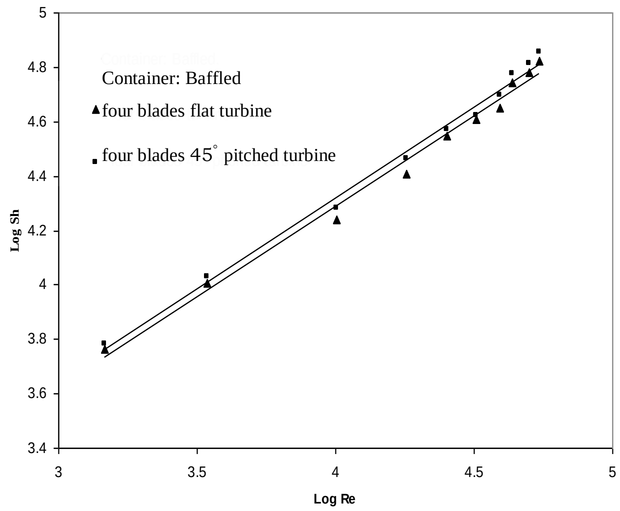


Fig. 6. Log *Sh* versus log *Re* for cementation of Cu^{++} on four blades flat and four blades 45° pitched Zn turbine of baffled agitated vessel.

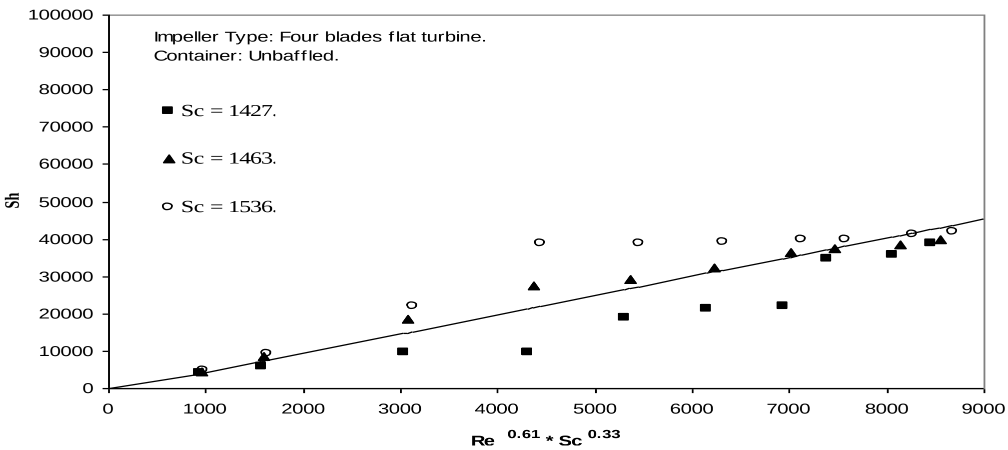


Fig. 7. Over all mass transfer correlation for cementation of Cu^{++} on four blades flat Zn turbine of unbaffled agitated vessel.

$$Sh = 5.17\ Sc^{0.33}\ Re^{0.605}, \quad (10)$$

with an average deviation of ± 11.2%.

The above equations can be used to predict the rate of cementation under a given set of conditions, it can also be used to design industrial agitated vessels working with four blades flat or four blades 45° pitched turbine.

Fig. 9 shows that, for the same impeller velocity, the rate of mass transfer obtained in the present study is higher than that obtained by Mubarak [8] who studied the rate of removal of Cu^{++} by cementation on the walls of baffled-agitated vessels stirred with four blades 45° pitched turbine. This is consistent with the fact that the level of turbulence at the impeller zone is higher than that elsewhere in the agitated vessel and intensity of turbulence, generated by the axial flow induced by the impeller at high rotation speed, decreases as the distance from the impeller to the vessel wall increases.

Figs. 10 and 11 show that the dimensionless group (*Sh*) increased by an amount varying from 32% to 78% in case of four blades 45° pitched turbine, and from 39% to 94% in case of four blades flat turbine as a result of fixing four baffles to the wall of the agitated vessel depending on the rotation speed. This may be attributed to the fact that baffles improve the mixing conditions in agitated vessel by inhibiting the ineffective swirl (tangential) flow and promoting the more effective axial and radial flow [13, 14, 15].

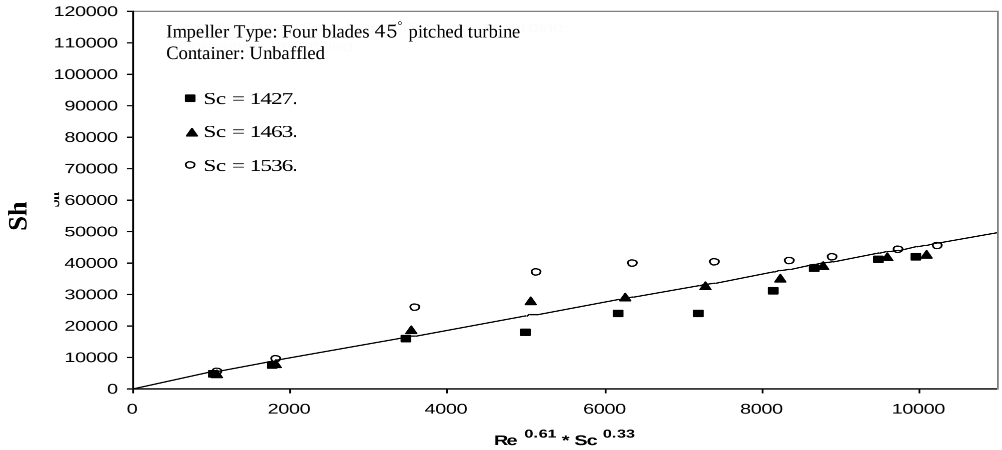


Fig. 8. Over all mass transfer correlation for cementation of Cu^{++} on four blades 45° pitched Zn turbine of unbaffled agitated vessel.

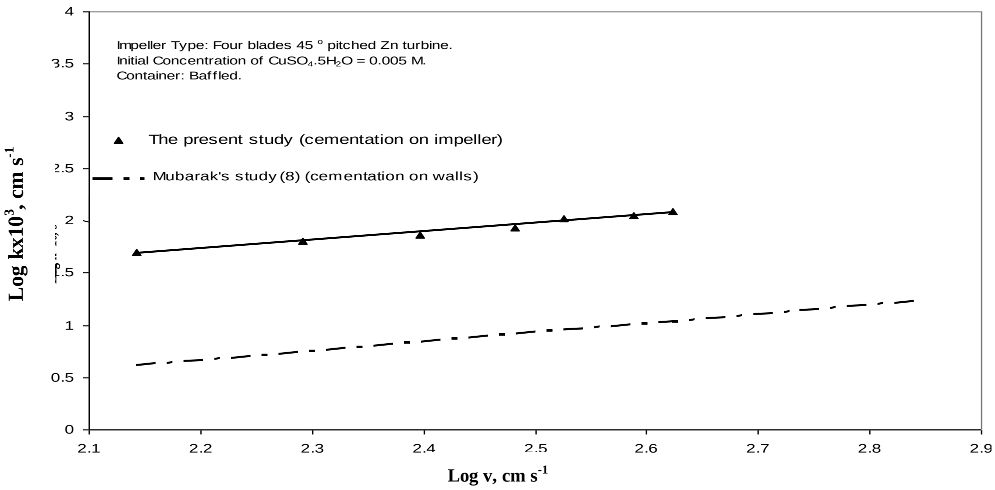


Fig. 9. Comparison for the cementation of Cu^{++} on both the impeller and the walls of baffled agitated vessels.

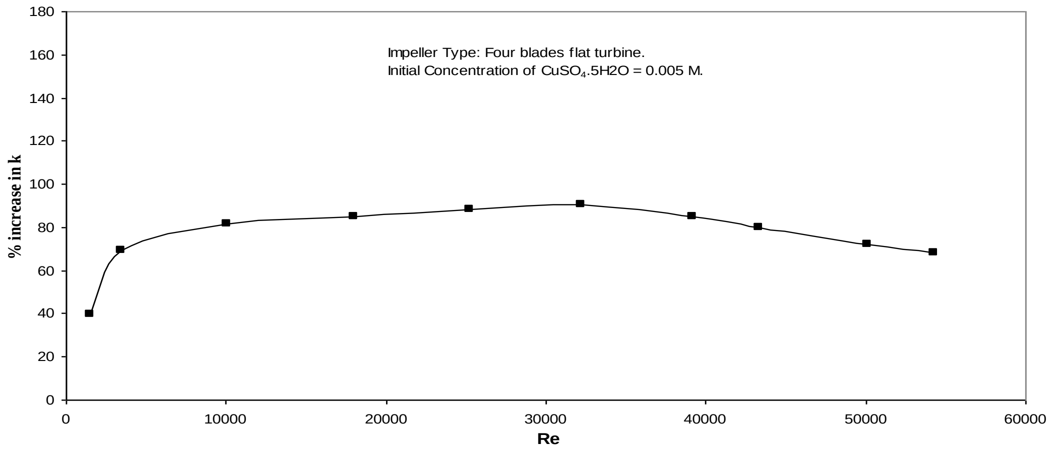


Fig. 10. The percent increase in mass transfer coefficient of the cementation of Cu^{++} on four blades flat Zn turbine due to baffles effect.

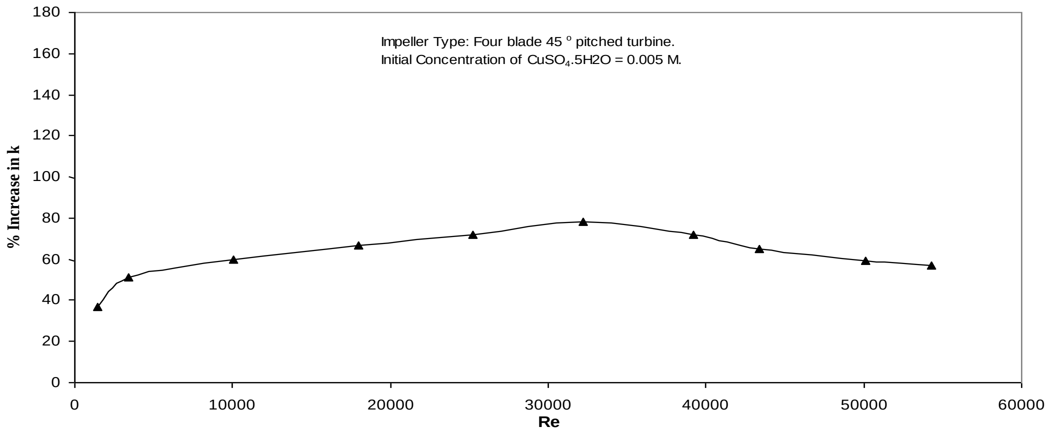


Fig. 11. The percent increase in mass transfer coefficient of the cementation of Cu^{++} on four blade 45° pitched Zn turbine due to baffles effect.

Figs. 12 and 13 show that, for the same *Re*, the rate of increase in the rate of mass transfer due to baffles was higher in case of four blades flat turbine than that in case of four blades 45° pitched impeller, this may be explained by the higher degree of swirl flow which prevails in case of four blades flat turbine in the absence of baffles [14, 15].

3.1. Effect of drag reducing polymers on the rate of cementation of Cu^{++} on Zn turbines

Figs. 14 and 15 show that the addition of polyethelene oxide drag reducing polymer (Polyox WSR-301) reduces the mass transfer coefficient of Cu^{++} cementation on Zn impellers by an amount ranging from 2% to 40% for the four blades flat turbine and from 1% to 37% for the four blades 45° pitched turbine, depending on the polymer concentration and impeller rotational speed. The decrease in the mass transfer coefficient in the presence of Polyox drag reducing polymer is attributed to the ability of the polymer molecules to damp small scale high-intensity eddies responsible for energy dissipation by polymer molecules, these eddies exist in the buffer layer of the hydrodynamic boundary layer formed at the impeller surface with a consequent increase in the thickness of the laminar sublayer and the diffusion layer across which Cu^{++} diffuses through to reach the Zn blades of the impeller. This leads to a decrease in the rate of mass transfer and rate of cementation [16].

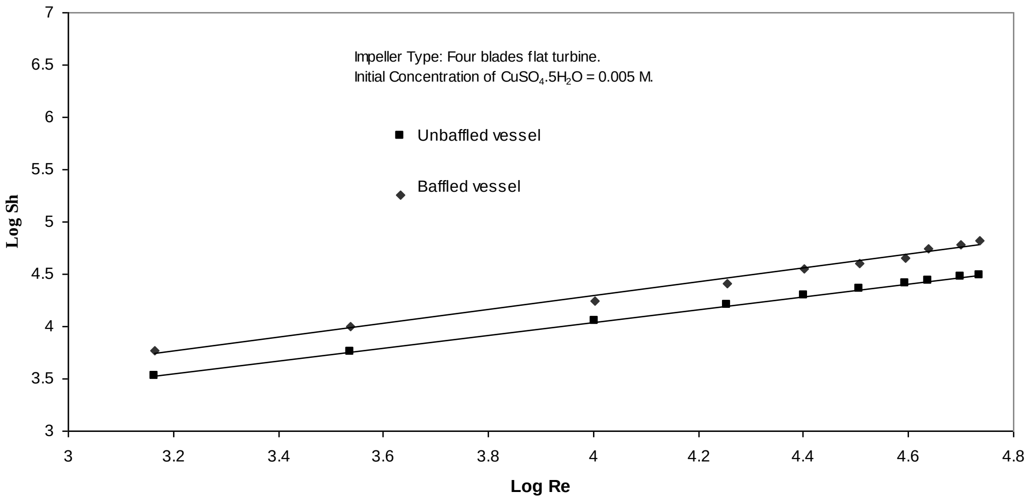


Fig. 12. Log *Sh* versus log *Re* for cementation of Cu^{++} on four blades flat Zn turbine of both unbaffled and baffled vessels.

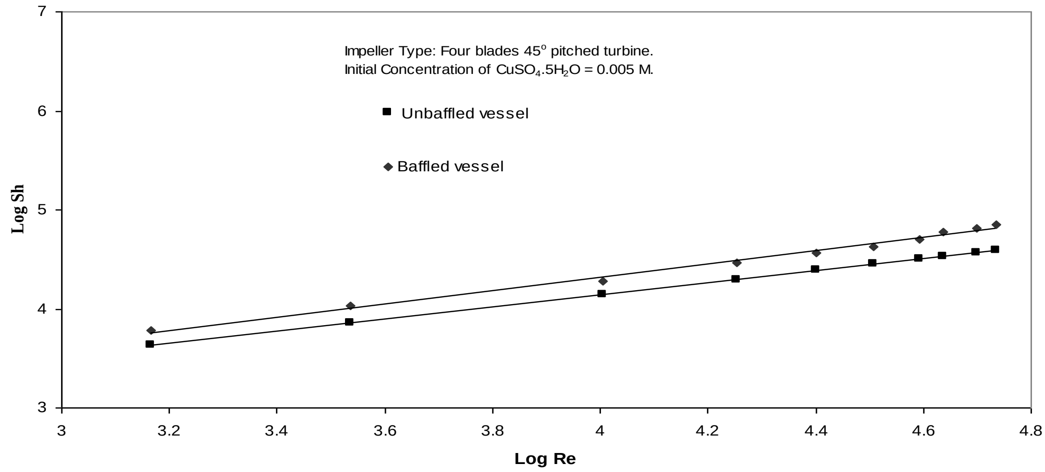


Fig. 13. Log *Sh* versus log *Re* for cementation of Cu^{++} on four blades 45° pitched Zn turbine of both unbaffled and baffled vessels.

Figs. 14 and 15 also show that, for a given polymer concentration, the percent decrease in the mass transfer coefficient tends to increase with increasing *Re*, reach a maximum value, and then decrease with further increase in *Re*. The initial increase in the percent reduction in mass transfer coefficient with increasing *Re* may be ascribed to the increase in the degree of stretching of the polymer molecule under the influence of the shear stress which prevails at high *Re*, and the ability of the polymer molecule to damp high-intensity eddies increases with increasing the degree of polymer stretching. The subsequent decrease in the percent reduction in mass transfer coefficient after reaching a maximum may be attributed to mechanical (shear) degradation of the long chain polymer molecules by the high shear stress to low molecular weight ineffective breakdown products [17].

Figs. 14 and 15 show that, for a given *Re*, the percent reduction in the mass transfer coefficient tends to increase with increasing polyox concentration and this may be attributed to the increase in the number of polymer molecules which are able to damp small scale high frequency eddies which are responsible for enhancing the rate of mass transfer [13].

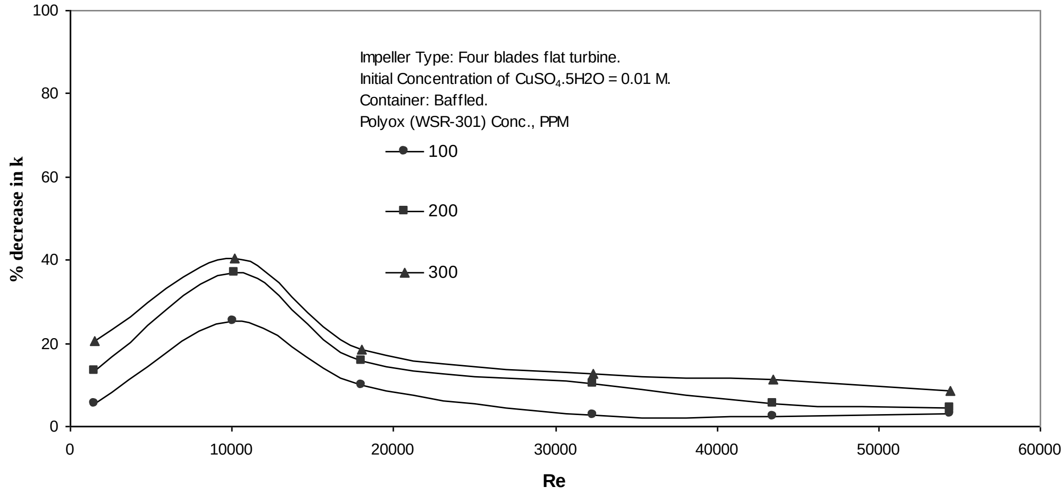


Fig. 14. Effect of polyox cementation on the percent decrease in the mass transfer coefficient at different *Re* for the cementation of Cu^{++} on four blades flat Zn turbine.

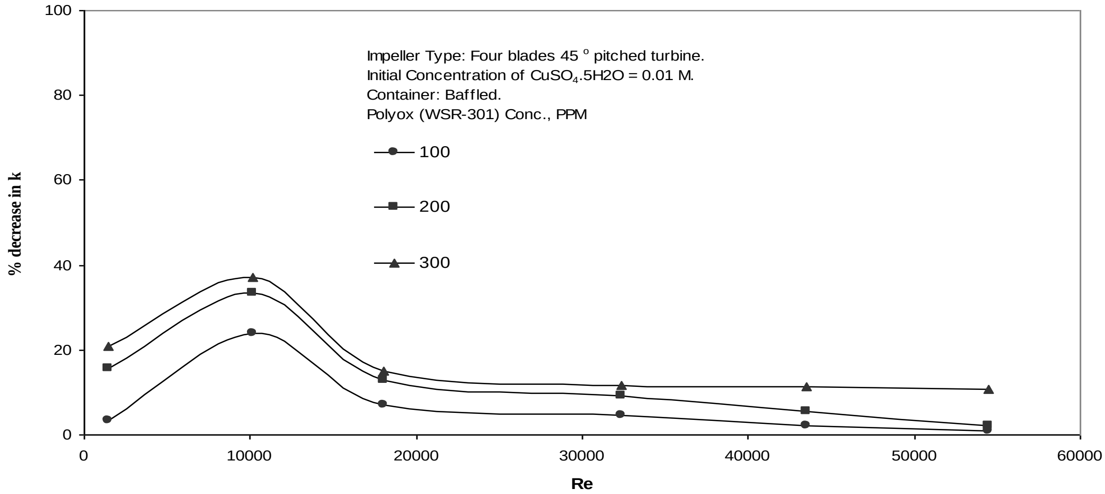


Fig. 15. Effect of polyox cementation on the percent decrease in the mass transfer coefficient at different *Re* for the cementation of Cu^{++} on four blades 45° pitched Zn turbine.

In view of the present finding that the drag reducing polymers decrease the rate of mass transfer at the transfer surface with a consequent decrease in the rate of cementation process, polymer addition to cut down mechanical power consumption should be carried out with caution as the benefits of energy saving should outweigh the decrease in the rate of cementation. The best situation for which drag reducing polymer can be used advantageously without any reservation is when the main process taking place in the agitated vessel is not controlled by liquid phase mass transfer, e.g., chemically controlled reactions or physical processes which are not controlled by liquid phase mass transfer such as cementation of Cu^{++} on Ni. In this case drag reducing polymers would reduce energy consumption without reducing the rate of copper production [18, 19].

4. Conclusions

1- Cu^{++} can be effectively removed from wastewater by cementation on Zn impellers of agitated vessels. The rate of cementation was found to be a function of impeller rotation speed, type of impeller, and physical properties of the solution. The rate of cementation was found to increase with increasing rotation speed; this confirms the diffusion controlled nature of the cementation reaction. Four blades 45° pitched turbine was found to be more effective than four blades flat turbine with regard to the higher rate of mass transfer obtained on the former type. The rate of cementation of Cu^{++} on Zn impeller of unbaffeled agitated vessels was related to the controlling variables by dimensionless equations. These equations can be used in practice to design industrial large scale agitated vessels, they can also be used to predict the rate of cementation on impellers of agitated vessels under a given set of conditions.

2- Installing baffles on the walls of agitated vessels was found to increase the rate of Cu^{++} cementation on rotating Zn impellers by an amount ranging from 39% to 94% in case of four blades flat turbine, and ranging from 32% to 78% in case of four blades 45° pitched turbine.

3- Drag reducing polymers (polyox WSR-301) were found to inhibit the rate of Cu^{++} cementation on rotating Zn impellers of agitated vessels by an amount ranging from 2% to 40% % in case of four blades flat turbine, and ranging from 1% to 37% in case of four blades 45° pitched turbine, depending on the rotation speed and polymer concentration. In view of the present finding, drag reducing polymers should be used only in agitated vessels if the benefit of reducing power consumption outweights the disadvantage of reducing the rate of mass transfer.

4- In view of the limited area of single impeller, further studies on the use of multi impeller agitated vessel in conducting cementation reactions are needed to increase the productivity of the reactor.

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