Removal of micropollutants from municipal wastewater using different types of activated carbons

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Abstract

The water reservoirs are getting polluted due to increasing amounts of micropollutants such as pharmaceuticals, organic polymers and suspended solids. Powdered activated carbon (PAC) has been proved to be a promising solution for the purification of water without having harmful impacts on the environment. Parameters such as PAC dosing, wastewater hardness, the effect of coagulant and flocculant were evaluated in a batch scale study. These parameters were further applied on a pilot plant scale for the performance evaluation of PAC based removal of micropollutants concerning the contact time and PAC dosing with main focus on recirculation of PAC sludge. The obtained optimum dose was 10–20 mg/L providing 84.40 to 91.30% removal efficiency of suspended solid micropollutants (MPs) and this efficiency increased to 88.90–93.00% along with coagulant which further raised by the addition of polymer and recirculation process at batch scale. On pilot plant scale, the concentration in contact reactor and PAC removal effectiveness of dissolved air flotation, lamella separator and sedimentation tank were compared. Constant optimisation resulted in a concentration ranging from 2.70–3.40 g/L at dosing of PAC 10 mg/L, coagulant 2.00 mg/L and polymer 0.50 mg/L. PAC doses of 10–20 mg/L with 15-30 min contact time proved best for above 70–80% elimination. The recirculation system has also proved an efficient technique because the PAC's adsorption capacity was practically completely used. Small PAC dosages yielded high micropollutants elimination.

Keywords: Advanced wastewater treatment; Powdered activated carbon (PAC); Micropollutants (MPs); Suspended solids (SS); Coagulation; Flocculation; Sedimentation and recirculation.

1. Introduction

With the increasing technological advancements related to the production of desirable products, thousands of anthropogenic chemicals end up being discharged in the water resources. Commonly, these chemicals are referred to as micropollutants and are of paramount concern among stakeholders as their exposure may pose a significant risk to the aquatic ecosystem and human health due to their prevalence in the environment. The removal of anthropogenic micropollutants emitting from domestic, industrial, agricultural and urban sources are one of today's major global challenges (Alvarino et al., 2018b). Therefore these micropollutants (MPs) have been the subject of study for many years due to their severe biological impacts (Aschermann et al., 2018; Batel et al., 2020; Gautam and Anbumani, 2020). The quantities of organic micropollutants such as contraceptive medicines, aromatic hydrocarbons, antibiotics, personal care products and pesticides are increasing day by day and reaching to the alarming level (Mailler et al., 2016; Meza et al., 2020). These accumulate in plants and animals then reach to humans through the food chain (Lember et al., 2019).

The sustainable management of environment is only possible when the release of micropollutants is restricted and the removal of existing MPs is carried out efficiently. For this purpose, various wastewater treatment plants (WWTPs) are working. For example, municipal wastewater treatment plants are suitable for the removal of organic compounds, nutrient elements and solid particles providing clean water with improved quality. However, these conventional wastewater treatments are expensive or insufficient for decontamination (Ahmad et al., 2019) because some hazardous micropollutants are very difficult to be removed from the WWTPs due to their non-biodegradability, poor adsorption ability and complex nature (Benstoem et al., 2018; Chau et al., 2018). Moreover, some WWTPs are unable to remove MPs in very low concentration range such as ng/L to µg/L (Guillossou et al., 2019). Various technologies have been employed for MPs reduction. Frequently used technologies were reverse osmosis and nanofiltration (Vergili, 2013). However, due to their high cost, incomplete removal of salinity and MPs (Echevarría et al., 2020), these were replaced by advanced oxidation processes (Miklos et al., 2018), membrane processes (Garcia-Ivars et al., 2017; Lim et al., 2020) and activated carbon adsorption (Benstoem et al., 2017; Mellah and Harik, 2020) as these now proved to be efficient for their implementation (Sher et al., 2020b). Oxidation by-products, membrane pollution and high energy consumption were the main obstacles for large scale applications of membrane biological reactors (MBRs) and oxidation processes. Powdered activated carbon (PAC) has been proved to be the best due to its strong adsorption performance, mild reaction conditions, and limited by-products to achieve cheap, efficient and flexible adsorption of micropollutants (Mailler et al., 2016; Zhang et al., 2020).

Furthermore, the adsorption of micropollutants varies according to the type of adsorbent, dose of activated carbon (Kårelid et al., 2017b), quality or water composition and operational parameters (Streicher et al., 2016). Moreover, PAC is finely divided activated carbon that can be added into the wastewater for the adsorption of micropollutants onto the surface of its finely grounded particles. Therefore, after extensive wastewater treatments, PAC adsorption process has been approved as best for the removal of natural dissolved organic carbon (DOC), suspended solids (SS) (Mellah and Harik, 2020), chemical oxygen demand (COD), heavy metal ions, personal care products, dyes and pharmaceutical compounds (Wong et al., 2018).

After treatment process with PAC, the second important issue is the separation and disposal of PAC and adsorbed/precipitated particles of micro-level from cleaned treated water. Various separation processes are in use for this purpose like microsieve, sand filtration, sedimentation along with cloth filtration and advanced ultrafiltration (membrane filtration). The most suitable process among all is the sedimentation process of PAC treated wastewater using coagulants and flocculants because of the tiny size of PAC, allowing it to pass through filter media. Furthermore, the coagulants and flocculants are used for the change of physical state/size of dissolved or suspended matter followed by their removal by sedimentation. The most commonly used coagulants are either of aluminium or iron-based. For example, some metallic salts such as $AlCl_3$, $Na_2Al_2O_4$ $Fe_2(SO_4)_3$ and $FeCl_3$ are used along with or without organic polymers (Hu et al., 2020; Krahnstöver and Wintgens, 2018) to enhance removal efficiency. The disadvantage of using coagulants is their cost and high sludge production that can be overcome by using them in a small amount or along with flocculants (Alvarino et al., 2018a).

Although the PAC addition may contribute to an increase in the removal efficiency of dissolved contaminants, it may also affect the effluent turbidity (Wongcharee et al., 2020) and floc formation process at the same time. Hence, to overcome the effect caused due to PAC addition and to improve the removal efficiency of micropollutants, there is a need to increase the recyclability of partly loaded PAC for the enhancement of the removal efficiency. Thus, the removal of MPs from wastewater using PAC recirculation is undoubtedly the most economical and efficient technique. Also, the use of coagulants and flocculants increase the sludge formation that could be recovered back through recirculation and reduces the fresh input of PAC.

The micropollutants in the form of suspended solids also contribute largely towards water impurity (Amosa et al., 2016; Das et al., 2017). Therefore, this study focused on the evaluation of dosing strategies, nature of PAC, coagulant, cationic polymer and water hardness by suspended solids (SS) removal. The PAC recirculation along with coagulant ($FeCl_3$) have already been used for wastewater treatment, however, there is a lack of literature about their combined effect with flocculant even in the presence of water hardness. After lab scale analysis, these parameters are implemented on pilot plant scale for the optimisation of its operational units like contact reactor, lamella separator, sedimentation tank, recirculation tank and dissolved air flotation tank at various time intervals with different flow rates. To the best of our knowledge, the detailed study on the optimisation of operational units of WWTP using PAC recirculation process has been carried out for the first time. Therefore, this study also fills the research gaps by providing a suitable, flexible, simple and applicable method for the wastewater treatment.

2. Material and methods

2.1. Activated carbon characteristics

Activated carbons are made in finely divided powdered form (PAC) or granule form (GAC) of size less than 1 mm with the small diffusion surface distance due to which small molecules can diffuse into or on their surface easily. PAC is formed from the grounded or crushed particles of carbon that can be directly added into the process units such as rapid mixed basins, water intakes, clarifiers and gravity filters. Two main types of PAC were used for conducting all experiments named as Norit SAE-Super (Norit) and Donau Carbon Carbopal AP (Donau) made from different precursor materials and manufactured by different producers. As a result, they differed in particle size distribution, skeletal density and specific pore volume as described in Table 1. The size of PAC particles plays a vital role in the separation of micro-pollutants from wastewater either by sedimentation or precipitation processes. Due to this reason, determination of the particle size distribution is critical. The particle size distribution data analysed by laser diffraction is also shown in Table 1. D_{10} and D_{50} of the two PAC types are nearly equal while regarding D_{90}, Norit is bigger than that of Donau.

2.2. Lab-scale study

Different experiments were performed at laboratory scale for the evaluation of process parameters' impacts such as dosing of PAC, coagulant, flocculant, water hardness and recirculation of process in wastewater treatment. The basic jar testing was considered as a standard technique for the evaluation of adsorption, precipitation and coagulation processes in WWT (Sher et al., 2013). It was feasible to evaluate all these parameters by targeting one to two micropollutants at a time. Therefore, only suspended solid (SS) pollutants in the concentration range of 50–120 mg/L were targeted for the removal from influent. The jar tests were performed for the optimisation of dosing parameter for two kinds of PAC (Norit SAE Super and Donau Carbon Carbopal AP) by varying the PAC amount in the range of 10–40 mg/L. Then determination of micropollutants removal after 15 minutes stirring (120 rpm) at a constant temperature of 30 ^{o}C and filtration by the process as described by Zietzschmann et al., (2014).

The coagulant is used to enhance the coagulation effect to attain bigger flocs for easy removal of micropollutants. Therefore, the above process was repeated with the addition of coagulants, ($FeCl_3$, $FeClSO_4$ and $Na_2Al_2O_4$), a dose of 2 mg each along with both PACs and extending the stirring period for 3 minutes. To check the effect of water hardness parameter on the treatment process, the wastewater samples were collected from two different industries, these samples showed a difference in their hardness (11.40 ^{o}dH and 17.30 ^{o}dH) due to the presence of Ca^{2+} or Mg^{2+} metal ions as determined by photometry test, where 1 ^{o}dH is equal to 10 mg CaO/L. Furthermore, these water samples were named as middle and hard water. Another set of experiments was performed, focusing on water hardness and flocculant nature (K10-14, K14-15) for the evaluation of the combined effect of flocculants in the presence of water hardness.

In each of the two 1 L jars (middle and hard wastewater) PAC, $FeCl_3$ and polymer were added in the sequence as mentioned in Table 2 and stirred by a magnetic mixer.

After mixing, solutions were allowed to settle down, and results were calculated. Another factor that affects floc formation is the activated sludge (AS) / PAC ratio achieved by the recirculation process, which is used to enhance the process efficiency and reusability of PAC and other added chemicals. The PAC, coagulant and flocculant were added sequentially after sludge in jars as described in Table 3 and mixed for 30, 3 and 1 minute respectively for each. Afterwards, they were put in Imhoff cones in order to determine the sludge volume index (SVI) in mL/g as per method used by Canziani and Spinosa, (2019) in the study of sludge from wastewater treatment plants. The calculations of SVI indicated the amount of SS settling effected by recirculation of AS. Finally, the observations were undertaken to evaluate the sedimentation process of formed compositions.

2.3. Pilot plant reactor description

The process flow diagram of pilot plant experimental set-up with four different schemes is shown in Fig. 1. All experiments conducted with grab samples taken from the secondary sedimentation tank outflow of wastewater treatment plant (WWTP). PAC with 50% cut diameter of 25 μm was dosed at different concentrations in all the phases. $FeCl_3$ is added as coagulant along with PAC at different doses (Table 4). In general, cationic polymer K14-15 was used and mixed with groundwater with the help of Reifomat device. Two types of contact reactor were used in the process namely; rectangular stainless steel tank and circular stainless tank. The former type of reactor with a maximum volume of approximately 8 m^3 was used in the first scheme of wastewater treatment. It consists of two chambers with water in the first chamber that was transferred to the second by gravity flow and the second chamber consisting of provision to adjust the overflow.

Desirable contact time can be achieved by regulating the height of overflow in the tank and the wastewater inflow. The latter type of reactor was used in the other wastewater treatment schemes except for the one in Fig. 1(a). Although the maximum volume is approximately 1 m^3, however, the circular geometry contributes for better mixing allowing no solids to settle at the edges (Sher et al., 2016). Therefore, the contact reactor of circular stainless steel type was used to achieve better and desirable results. The PAC addition tank was a circular stainless steel tank from which PAC was delivered to the contact reactor via cavity progressive pump and $FeCl_3$ was added from the vessel using a diaphragm pump as in previous studies (Krahnstöver and Wintgens, 2017; Sher et al., 2020a). The cationic polymer was added as a flocculant mixed with groundwater from the vessel to the outflow of the contact reactor or polymer mixing tank depending upon the type of set-up.

The circular stainless steel settling tank was used to achieve high settling velocity in the suspended solids. Lamella separator was used to increase the sedimentation area leading to the formation of more compact sedimentation. Furthermore, dissolved air floatation (DAF) tank was used to adjust the recirculation of outflow. One important thing to add here is that ST, LS and DAF operational units have two types of outflow discharge; one is called "outflow concentration" or simply "outflow" that represents the concentration of treated water after the removal of SS. The other is called "sludge concentration" or simply "sludge" that is formed by the accumulation of PAC, coagulant, flocculant and SS. A recirculation tank consisted of a stirrer that was used to mix the sludge outflows from the settling tank, lamella separator and DAF in a manner that equalises the sludge concentration in the tank thus avoiding sedimentation of suspended solids. A pump was connected to the recirculation tank that carries the outflow to the contact reactor. Polymer mixing tank was provided with a stirrer for constant stirring during the addition of polymers to increase the recirculation ratio.

2.4. Pilot plant process description

The full-scale wastewater treatment plant (WWTP) was simulated at pilot plant scale for analysing adsorption zone treatment. Four different schemes were tested in order to determine the effective efficiency of adsorption. Based on the concentration of PAC, Fe^{3+} coagulant, and polymer addition or removal of operational units, the four schemes were further bifurcated into different phases. The different inflow and outflow concentrations of each operational units were measured using online sensors installed with each unit operation.

First scheme (Fig. 1(a)) was divided into five different phases from A to E with a fixed concentration of PAC and Fe^{3+} while varying polymer concentration (Table 4). The phase E has same polymer concentration as that of phase D but experienced removal of canal pump due to inherently installed water level protection in the overflow vessel in contact reactor, hence avoiding danger during the drawing of water in the case of recirculation pump failure. The wastewater flow from the secondary sedimentation tank to the recirculation tank has been represented schematically in Fig. 1(a). Moreover, from the recirculation tank to the contact reactor using a pump was a measurable parameter for the required recirculation efficiency during wastewater treatment.

In the second scheme (Fig. 1(b)), there was an addition of polymer mixing tank and removal of the dissolved air flotation tank. The type of contact reactor tank was changed from rectangular to circular to avoid settling of suspended solids. The second scheme was divided into two phases F and G that differ only in coagulant concentration (see Table 4). Third scheme or phase H (Fig. 1(c)) involved further removal of recirculation tank from the second scheme.

Furthermore, the sludge from sedimentation tank and lamella separator was directly recirculated to the contact reactor tank. Fourth scheme or phase I (Fig. 1(d)) was a simplified version of the process keeping in account the time constraint and the cost limitations. The removal of lamella separator and lower PAC dosing were the characteristic features of this phase. The results of all schemes were calculated and compared for the selection of the best scheme providing nearly 100% efficiency.

3. Results and discussion

3.1. Evaluation of micropollutants removal at lab scale

3.1.1. Impact of PAC dosing

The dosing impacts were evaluated by varying PAC dose concentration in the range of 10–40 mg/L into wastewater. Two kinds of PACs (Norit and Donau) were used for wastewater treatment (WWT) and results were compared based on performance. The experiments were performed on three alternate days with three types of wastewater samples with each type of PAC and named as NW1 (wastewater sample 1 with Norit SAE Super), NW2 (wastewater sample 2 with Norit SAE Super) and NW3 (wastewater sample 3 with Norit SAE Super) for Norit PAC. In all cases, by increasing PAC dosing amount, the percentage removal of suspended solids also increased. Fig. 2 shows that in the case of Norit, the removal efficiency increased from 35.65 to 91.30 % with an increasing dose concentration from 10 to 20 mg/L, and decreased from 91.30 to 54.79 % as the concentration was raised to 40 mg/L.

Similarly, when the Donau PAC was used, the removal efficiency increased from 39.79 to 84.40% and decreased to 7.77% that can be seen from Fig. 3. The same dosing effect was observed by Platz et al., (2012). One of the reasons for the decrease in removal efficiency can be as by increasing dosing amount from 10–20 mg/L range, the availability of active sites on PAC surface also increases. However, after a specific limit, PAC may start contributing to the solid content of wastewater that starts competing with suspended solids for adsorption on active sites. Hence affecting negatively, similar results were found from previous studies (Boehler et al., 2012; Guillossou et al., 2020; Zietzschmann et al., 2014). The other reasons could be that by increasing PAC dose, the particle could accumulate or form aggregates thus exposing less active sites for adsorption (Noreen et al., 2020).

The Donau has somewhat different characteristics from Norit regarding its particle size diameter, skeletal density and originating material. While comparing the results from Fig. 2 and Fig. 3, it is evident that the removal efficiency of Donau was quite less than Norit for all samples. The lesser amount of adsorption was because of lesser amount of finer and coarser particles around the median. Furthermore, better performance of Norit is due to the smaller specific pore volume (cm^3/g) on its surface than the other one (Rúa-Gómez et al., 2012) due to which small suspended micropollutants get entangled inside the pores on Norit surface and become unable to release. The laboratory experiments mostly performed with powdered activated carbon have provided a fundamental understanding of adsorption mechanisms also stated in previous studies (Hu et al., 2016; Kårelid et al., 2017b; Margot et al., 2013).

Based on these experiments, the optimum dose of both PACs was selected as 20 mg/L for further use. Norit provided higher removal efficiency of 91.30% as compare to Donau with 84.40% (Fig. 2 and Fig. 3). These lesser amounts of adsorption for Donau is because of its different internal structure, size and production material. These results agreed well with previous findings based on pilot-scale PAC wastewater treatment system with PAC dosage between 10 to 20 mg/L (Margot et al., 2013). Hu et al., (2016) was able to remove micro-pollutants from wastewater up to 60% with an optimum PAC dosing concentration of 10–20 mg/L. Therefore, the present study results proved better than from the previous studies.

3.1.2. The combined effect of PAC and coagulant

In many separation processes, an increased particle or floc size facilitates micropollutants' removal. The particles in wastewater are typically negatively charged, therefore they repel each other and stay dispersed in a stable suspension. By adding specific chemicals, particle suspensions can be destabilised and the formation of larger aggregates and flocs can be promoted. In a satisfactory flocculation process, particle counts <10 µm should be reduced, while particle counts >10 µm are expected to increase. For this purpose, either inorganic coagulants or polymeric flocculants are used which absorbed on the particle surface neutralising their charge and facilitating PAC to attain a point of zero-charge. Thus the point of zero-charge was attained and coagulation of particles formed flocs (Krahnstöver and Wintgens, 2018).

The settling velocity sequence of wastewater samples with different coagulants ($FeCl_3$, $FeClSO_4$ and $Na_2Al_2O_4$) after a simultaneous stirring in all jars, was observed. In $FeCl_3$ jar, settling velocity appeared higher than the other two coagulants. The concentration of flocs was a visually differentiating factor among three coagulants. Moreover, $FeCl_3$ coagulant selection was the best option (Platz et al., 2012). In order to have better settling performance, more coagulant and flocculant should be added. However, this was not affected due to increased cost on large scale plants and charge reversal of micro flocs leading to the restabilisation of particles‘ suspension. Further procedure was the same as used for simple Norit and Donau dosing except that the coagulant $FeCl_3$ was added to study the combined effect of PAC and coagulant to the wastewater.

Furthermore, the samples named as NW1Fe (wastewater sample 1 with Norit and $FeCl_3$), NW2Fe (wastewater sample 2 with Norit and $FeCl_3$) and NW3Fe (wastewater sample 3 with Norit and $FeCl_3$) were treated to determine the amount of total adsorbed, precipitated and coagulated solids inside the wastewater. The optimum dosing range remained the same as 10–20 mg/L along with $FeCl_3$ but with higher percentage removal efficiency. Fig. 4 shows the removal efficiency of Norit treated samples was raised from 91.30 to 93.60% by the addition of $FeCl_3$ coagulant. The reason behind this removal percentage increment was the addition of coagulant, which affects the conversion of smaller particles to larger aggregates in two ways. When optimum dose (2 mg/L in this case) of $FeCl_3$ is added into the wastewater, the Fe^{3+} and its hydrolysed products interacted with negatively charged smaller suspended solids (SS) particles (nearly all water impurities were negatively charged) and converted them into relatively larger aggregated particles.

Because of this precipitation of aggregated particles became easy and lead towards the feasible removal of micropollutants from water. While in a second way, coagulant interacted with the negatively charged colloids (PAC particles with adsorbed negatively charged suspended solids) and neutralised their charges. That made colloids destabilisation leading to the aggregation of colloidal particles and their sedimentation by the increment of their molecular weights and size. Furthermore, colloidal dispersion may also occur if the coagulant dose exceeds the optimum level due to the charge reversal process (Li et al., 2010; Suopajärvi et al., 2013). Consequently, SS removal percentage increases with the combined effect of PAC and coagulant rather than the use of PAC alone.

The testing procedure and measuring parameters were same in the case of Donau. The percentage removal efficiency was increased from 84.44 to 88.95% in the case of Donau treated wastewater with the $FeCl_3$ addition (Platz et al., 2012). By comparing the results of Norit and Donau treated wastewater samples along with the $FeCl_3$, it is easier to conclude that Norit samples showed higher removal efficiency (93.60%) than Donau (84.40%).

A previous study employed the use of alum ($Al_2(SO_4)_3.18H_2O$) as a coagulant, enhanced the removal efficiency of ACZ from 42 to 89% with the combined effect provided the support for the use of coagulants with PAC (Wongcharee et al., 2020). Moreover, It is observed that the addition of PAC and Fe^{3+} as combined adsorption and coagulation agents improved effluent water quality concerning dissolved organic pollutants, total suspended solids (TSS) and turbidity in comparison to a WWT plant operated without the addition of Fe^{3+} based coagulant. Sufficient micropollutant (MP) removal around 80% was achieved Löwenberg et al., (2016).

3.1.3. Influence of water hardness and flocculant addition

No apparent difference in the results with a middle and high level hardness water was observed. The floc size was similar with approximately equal settling time and the suspended PAC particles were not settled or remained attached to the jar walls. Even by increasing the concentration of $FeCl_3$ to 6 mg/L, no big difference was observed. This behaviour is because the concentration of Ca^{2+}/Mg^{2+} ions affects the sedimentation process only at a high level. Dong et al., (2012) also described as the presence of Ca^{2+} ions do not have any effect on the floc formation leading to the removal of humic acid (HA) from wastewater even in the concentration range of 3.5 to 10 mg/L of poly aluminium chloride coagulant (PAC). Although the water hardness did not affect sedimentation process significantly.

Nevertheless, the SS removal efficiency was increased due to K14-15 polymer addition as a flocculant, that facilitated the size increment of flocs thus increasing the settling velocity of the flocs and removal efficiency was increased up to 95.43%. Moreover, flocculation is mostly implemented in addition to coagulation to further increase in the particle size. The resulting flocs are larger, denser and more stable than flocs obtained by coagulation only but also observed positive results by using metal chloride coagulants in combination with a cationic polymer in combination (Chong, 2012; Irfan et al., 2017; Lee et al., 2014).

3.1.4. Influence of PAC recirculation process

The activated sludge (AS) produced was again added into the contact reactor to enhance the removal efficiency of suspended solids (SS). The jar tests determined the effects of AS/PAC ratio or recirculation of PAC. The process was evaluated at the beginning (t = 0 min) and the end of the test (t = 35 min). After 30 minutes of mixing PAC with AS, the sedimentation velocity in jar A was greater than the others probably because of low AS concentration. After 35 minutes, big amounts of suspended PAC particles in A and AS suspended particles in E were observed. However, D seemed to be the most clearly observed in Imhoff cones. The AS sludge concentration assumed to affect PAC removal (Jafarinejad, 2017). Furthermore, the microscopic SS and PAC particles were covered and dragged to the bottom by large AS flocs. The combination of PAC and AS provided better results than obtained without recirculation process and similar results were obtained by Lübken et al., (2018) for the removal of micropollutants (MPs) by the recirculation of AS. The next step was to investigate the settling performance of AS, wastewater and PAC mixture after the addition of coagulants and flocculants. Stirrers were turned on again during the addition of $FeCl_3$ followed by polymer addition.

The results were visible after 5 minutes of setting time. In all samples, floating suspended solids remain dispersed and on the surface. In sample A, the PAC particles were still suspended in water. By moving in the direction from A to E, the treated water became more clear. Afterwards, they were mixed again and poured to Imhoff cones to examine the settling behaviour and determined the sludge volume index (SVI). The SVI calculations indicated the amount of SS settling effect and removal by recirculation of AS. The increasing amount of SVI from A–E showed that more amount of suspended solids has been settled down and can be removed. The SVI obtained from each sample is shown in Fig. 6.

The lower is the AS/PAC ratio, the microflocs of PAC remains floating and attached with the walls. Due to an increase of AS, flocs get larger in size and as they settle, they engulf floating PAC particles and other suspended solids. Higher the ratio AS/PAC, fewer sediments would be attached to the walls. The most transparent water appears to be D (30% PAC, 70% AS) with the removal efficiency of 98.65% because of less floating sludge. These results proved that high activated sludge concentration assists sedimentation due to the reusability of PAC and other chemicals added initially for wastewater treatment. However, the flocs of AS remained unsettleable if it is higher than 70%. The possible reason is that repeated adsorption in multi-stage PAC reuse results with similar equilibrium concentrations as single-stage adsorption. Thus, a single relationship between solid and liquid phase suspended solids concentration appeared valid throughout all stages (Zietzschmann et al., 2015; Zietzschmann et al., 2019). Therefore, the recirculation system represents an efficient technique, because PAC's adsorption capacity increased in comparison to PAC application without recirculation (Meinel et al., 2016a).

3.2. Evaluation of micropollutants removal at pilot plant scale

3.2.1. PAC recirculation analysis

The main objective of pilot plant scale treatment is to maximise the sludge formation by increasing PAC based adsorption of suspended solids from wastewater, leading to their settlement to form sludge. So that this sludge can be used for recirculation, providing cleaned treated water with multiple uses of PAC. In phase A, with a flash of 30 times per hour and total discharge of concentrate outflow (0.072 L/h), the recirculation outflow was measured as 444 L/h. The concentration in the contact reactor did not change after repetitive experiments, and high values in recirculation concentration (255±53 mg/L) were observed only two times (Table 5). The high values measured in the outflow of the secondary sedimentation tank depicts the relation between settling velocity and concentration of suspended solids. In dissolved air floatation (DAF) tank, the average concentration of clear outflow (47±4 mg/L) becomes too high than typical values (36±3 mg/L) indicating a loss of suspended solids as can be seen from Fig. 7 and a possible reason for low concentration in the contact reactor (Table 5).

The variation in inflow and outflow rate indicates the presence of dry solids sticking on the walls or floating in ST, LS or DAF units. Due to fluctuations in the contact reactor, high variations in outflow concentration were observed, that affects the separation efficiency of sludge forming. In phase B, to overcome the low sludge concentration obtained in the previous phase, polymer dosing is increased to form bigger flocs and to trap more dissolved air in DAF. As a result of which floating sludge foam was created at the surface of ST and LS. Since the source of air inflow was the pumps that dragged air from the CR overflow. Another source of air inflow might be the connections between the pump inflow and outflow. The rubber in the connection point has open spaces, where the air could trap and as the water drawn the air was also dragged.

A solution could be water-tight connections. Furthermore, the air bubbles might originate from the "cavitation" phenomenon due to different diameters in hydraulic equipment connections. Anaerobic conditions in ST might contribute to air bubble production, however, at a slower rate than the previous causes. Therefore, as a result dissolved air was lifting flocs to the surface. Aggregations were accumulated as well as bioreactions were happening to form an increasing floating foam surface layer. In LS, the inflow was driven to that foam and new aggregations stick to the floating, engulfing new air bubbles and not settling down. The coagulants and flocculants were binding that foam. The Fig. 8 results conclude lower concentration in the outflow from LS (14±3 mg/L) than the LS ideal outflow concentration (23±3 mg/L) and from ST (16±3 mg/L) as well.

In phase C, due to excess polymer loading in the previous phases (A and B), suspended solids become stacked on the walls and therefore lamella separator with a rabble rake was installed and the polymer dosing was lowered down to 0.30 mg/L. The rabble rake cleans only bottom of the LS but not the walls as a result the concentration was initially increased to a certain point and then decreased gradually. Therefore, the CR suspended solids concentration remained low and fluctuating (132±42 mg/L) in comparison to phase A and B also shown in Table 5. Furthermore, in DAF the sludge loss increased due to an increased outflow concentration (49±3 mg/L) than DAF ideal values (36±3 mg/L) as shown in Fig. 9. Although, effluent quality from LS improved as compared to the previous phase. The peaks representing the outflow of LS matches well with the ideal values (see Fig. 9).

In phase D, the low concentration of contact reactor remained still a problem due to sludge loss in DAF, therefore the polymer dosing was raised again up to 0.50 mg/L to compensate the loss (Krahnstöver and Wintgens, 2017). This phase focussed mainly on the concentrations of recirculation tank which did not rise well enough and lead to loss suspended solids. The outflow concentration of ST varied between 10±3 mg/L and 16±3 mg/L while LS varied between 19±4 mg/L and 21±4 mg/L. In phase E, canal pump was removed, and the outflow of SST to the contact reactor was reduced to 3.50 m^3/h (Behin and Bahrami, 2012). Since the flocs were too heavy to be carried by air bubbles and due to low surface area of flocs, they were unable to engulf air bubbles. As a result, the flocs settled and dragged to the outflow pipe leading to higher concentrations of suspended solids into the DAF clear outflow (49±7 mg/L) than DAF ideal outflow (36±3 mg/L). It was found that DAF affects the process negatively.

From phase F onwards, DAF is removed since it affects the process and lowers the concentration in the contact reactor. Further, a polymer mixing tank was provided rather than the direct addition of polymer in the outflow of contact reactor stream. The results revealed unstable and low concentration in RT (235±19 mg/L) than RT ideal concentration (436±10 mg/L) as shown in Fig. 10. High concentration was achieved only when rabble rake was used in RT. Nevertheless, in this phase the recycling tank suffered an overflow due to which there was a loss of suspended solids. The peaks represented a deviation of RT concentration from their ideal values. Moreover, to solve this problem in phase G, the coagulant concentration was increased to 4 mg/L but the CR concentration did not rise. Repetitive experiments and laboratory investigations revealed that the sludge loss was due to overflow in the recirculation tank. Looking at previous phase results, the recirculation tank was removed in phase H to avoid PAC loss from RT overflow. The recirculation rate was increased from 25 to 50% for high settling velocity and high suspended solids concentration in recirculation outflow. Therefore, coagulant concentration was lowered to 2 mg/L. The results of this phase proved a significant rise in contact reactor concentration.

In phase I, due to time and cost limitations, the process was simplified by removing LS. Again, the PAC addition was lowered to 10 mg/L (Mailler et al., 2015; Zietzschmann et al., 2019) because the efficient recirculation can be obtained with low PAC dosing amount (Meinel et al., 2016b). It is not necessary to obtain a higher removal of micropollutants with an increased amount of dose. However, optimum quantity resulted with desirable removal (Margot et al., 2013). The CR concentration remained stable between 2 and 3 g/L for long and hence resulted in a favourable result. The observations also confirmed from the previous studies (Meinel et al., 2016a; Zhang et al., 2018) indicated that high removal efficiency of micropollutants was obtained by optimisation of wastewater treatment pilot plant with main focus on PAC recirculation.

3.2.2. Recirculation efficiency

The degree of recirculation of different phases was calculated by the ratio of output flowrates from the recirculation tank and secondary sedimentation tank respectively. The higher degree of recirculation resulted in better effluent quality. Fig. 11 shows output flowrates of two tanks as well as the effects of different unit operations on recirculation rate. The recirculation tank and secondary sedimentation tank output flowrate at 0.50 m^3/h and 4.00 m^3/h respectively resulted in a constant recirculation efficiency with the other parameters such as PAC, Fe^{3+} and polymer concentration being changed significantly. In phase E, the reduction in output flow rate to 3.50 m^3/h from the secondary sedimentation tank resulted in a slight increase in the recirculation efficiency from 2–4 %. In phase F and G, the output flow rate from SST was further reduced to 1.50 m^3/h, that resulted in a sudden rise in recirculation efficiency of 33.33 %.

In phase H and I, the removal of recirculation tank and reduction in output flow rates from SST to 1 m^3/h and 0.50 m^3/h respectively resulted in approximately 100% recirculation efficiency that can be seen from Fig. 11. Thus the pilot plant`s optimisation has proved to be a suitable process to obtain required removal efficiency focusing on recirculation of PAC as also supported by previous studies (Kårelid et al., 2017a; Meinel et al., 2016b). Under the current scenario of environmental pollution (Güleç et al., 2019; Kausar et al., 2020), there is need to develop and apply eco-benign technologies (Rashid et al., 2020; Sehar et al., 2020) to avoid the environmental pollution (Rasheed et al., 2020) and activated carbons (Sher et al., 2020a) are excellent adsorbents for the treatment of diverse types of toxic and micropollutants from the wastewater.

4. Conclusions

This study deals with the wastewater treatment using PAC along with coagulant, flocculant, in the presence of heavy metal ions at lab scale and pilot plant scale. The recirculation of PAC sludge was examined and a variety of performance parameters were tested. The results were obtained by a comparison of water entering the set-up from the secondary sedimentation tank and getting out of it after treatment. After the evaluation of parameters at lab scale, the process was tested at a pilot plant scale for the optimisation of its operational units. The results revealed best recirculation efficiency when the dosing concentration of PAC was 10–20 mg/L while the dose of Fe^{3+} and polymer were 2 and 0.50 mg/L respectively being unaffected by water hardness. The suspended solids based micropollutants removal percentage obtained by using only PAC was 84.40 to 91.30% that raised to 88.90–93.60% by the addition of $FeCl_3$ coagulant. This process became more efficient by the addition of flocculent (polymer) as that enhanced the size of flocs and made an easy separation. The selected amounts of adsorbents were further used to optimise the operational units (ST, LS and DAF) of pilot plant set up to minimize the energy inputs and cost. Constant optimisation and recirculation of sludge resulted in elimination rate of about 100% at the flow rate of wastewater stream from the secondary sedimentation tank and outlet from the sedimentation tank at 0.50 m^3/h in the presence of limited operational units (ST) of pilot plant set-up making it cost-effective and practically applicable. The benefits were greater for small PAC dosages. Small PAC doses lead to higher recirculation efficiency. Based on the operating conditions and removal efficiencies of all setups, recommendations are compiled for efficiently designing and operating PAC separation stages and further monitor their quality for multi-stage micropollutants adsorption other than suspended solids (SS). Nevertheless, future research should be undertaken for the reactivation of multi-stage recirculated PAC by thermal recovery and its implementation on the WWT process to obtain economic benefits.

Acknowledgement

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List of Tables

Table 1. The physical properties of tested PAC types; Norit SAE super and Danau Carbon Carbopal AP.

Parameter	**Norit SAE Super**	**Donau Carbon Carbopal AP**
PAC	Norit	Donau
Precursor material	Peat	Brown coal
Skeletal density (g/cm^3)	2.32	2.33
Specific pore volume (cm^3/g)	0.52	0.69
Particle size distribution (µm)		
D_{10}	3.92	4.78
D_{50}	25.35	25.68
D_{90}	98.41	68.61

Table 2. Impact of wastewater hardness and polymer addition on the removal of SS from wastewater.

Water hardness	**Middle**	**Hard**	**Middle**	**Hard**
PAC (mg/L)	20.00	20.00	20.00	20.00
Coagulant (mg/L)	2.00	2.00	2.00	2.00
Polymer K14-15 (mg/L)	0.50	0.50	-	-
Polymer K14-10 (mg/L)	-	-	0.50	0.50

Table 3. Different combinations of AS/PAC ratio for the evaluation of recirculation process.

Parameter	**A**	**B**	**C**	**D**	**E**
AS (mg/L)	4.00	6.00	10.00	14.00	4.00
PAC (mg/L)	16.00	14.00	10.00	6.00	16.00
Fe $^{3+}$ (mg/L)	2.00	2.00	2.00	2.00	2.00
K14-15 (mg/L)	0.50	0.50	0.50	0.50	0.50
Accumulative AS/PAC ratio (%)	(20 : 80)	(30: 70)	(50: 50)	(70 : 30)	(80 : 20)

Table 4. The concentration of PAC, Fe^{3+} and polymer in different phases of wastewater pilot plant.

Phase	**PAC (mg/L)**	**Fe^{3+} (mg/L)**	**Polymer (mg/L)**
A	20.00	2.00	0.15
B	20.00	2.00	0.40
C	20.00	2.00	0.30
D	20.00	2.00	0.50
E	20.00	2.00	0.50
F	20.00	2.00	0.50
G	20.00	4.00	0.50
H	20.00	2.00	0.50
I	10.00	2.00	0.50

Table 5. Mean values and standard deviations of outflow concentrations from different units in phase A, B and C.

Secondary sedimentation tank	**Contact reactor**		**Recirculation tank**	**Sedimentation tank**		**Lamella separator**		**Dissolved air floatation**		**Ideal values**		
Outflow	Sensor	Outflow		Outflow	Sludge	Outflow	Sludge	Outflow	Floatation	ST	LS	DAF
Phase A												
73±6	57±5	88±7	255±53	18±2	218±48	21±4	246±50	47 ±4	251±51	15±3	23±3	36±3
Phase B												
61±5	45±4	70±7	182±41	16±3	219±35	14±3	97±31	33±4	50±15	15±3	23±3	36±3
Phase C												
58±5	43±4	81±8	132±42	16±3	156±27	18±3	176±32	49±3	96±39	15±3	23±3	36±3

*SST: Secondary Sedimentation Tank, RT: Recirculation Tank, CR: Contact Reactor, ST: Sedimentation Tank, LS: Lamella Separator, DAF: Dissolved Air Floatation

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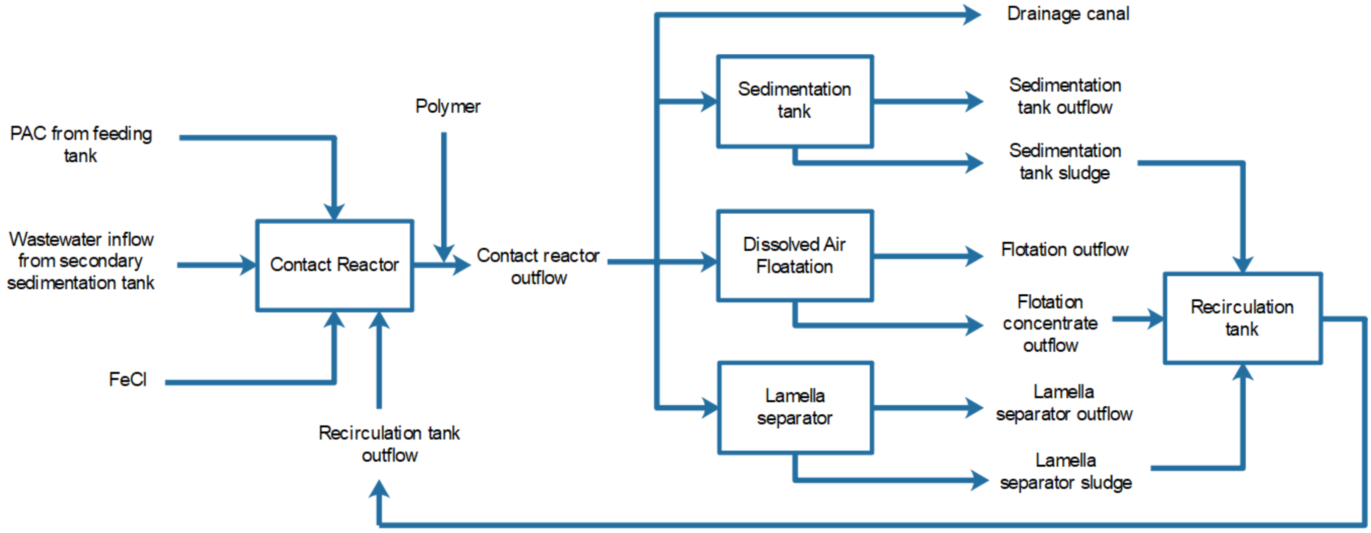
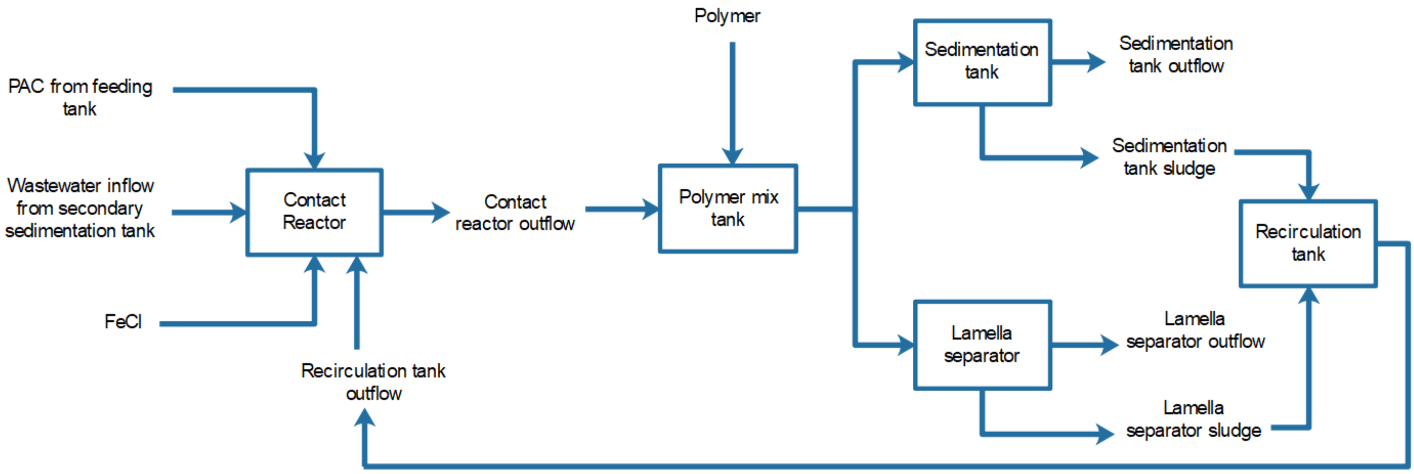
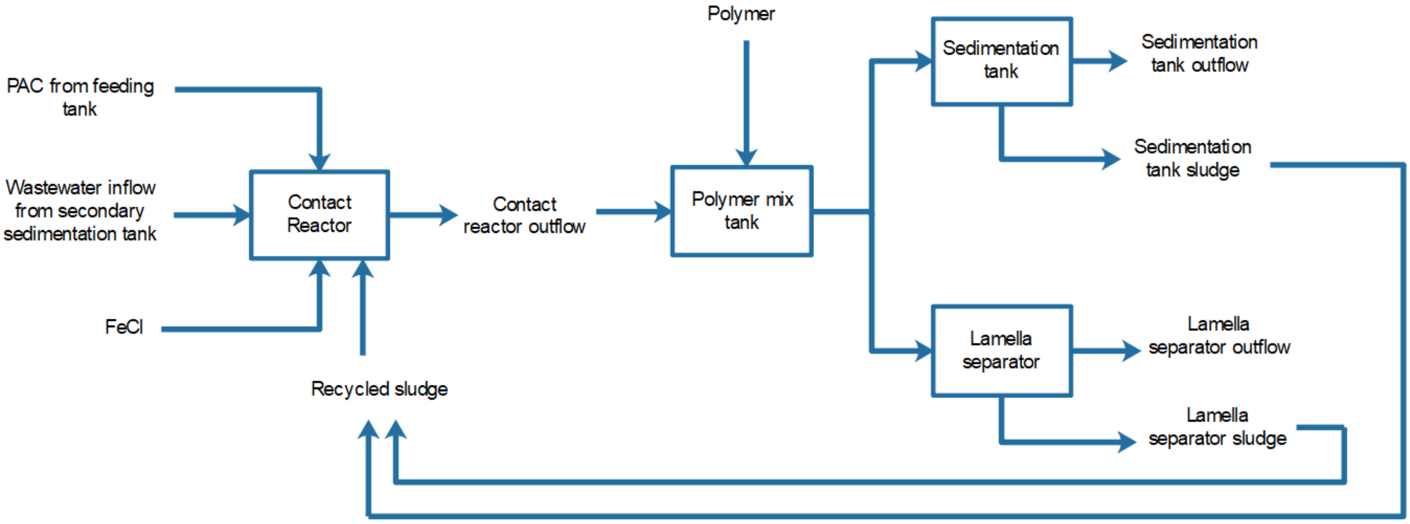
(a)



(b)



(c)



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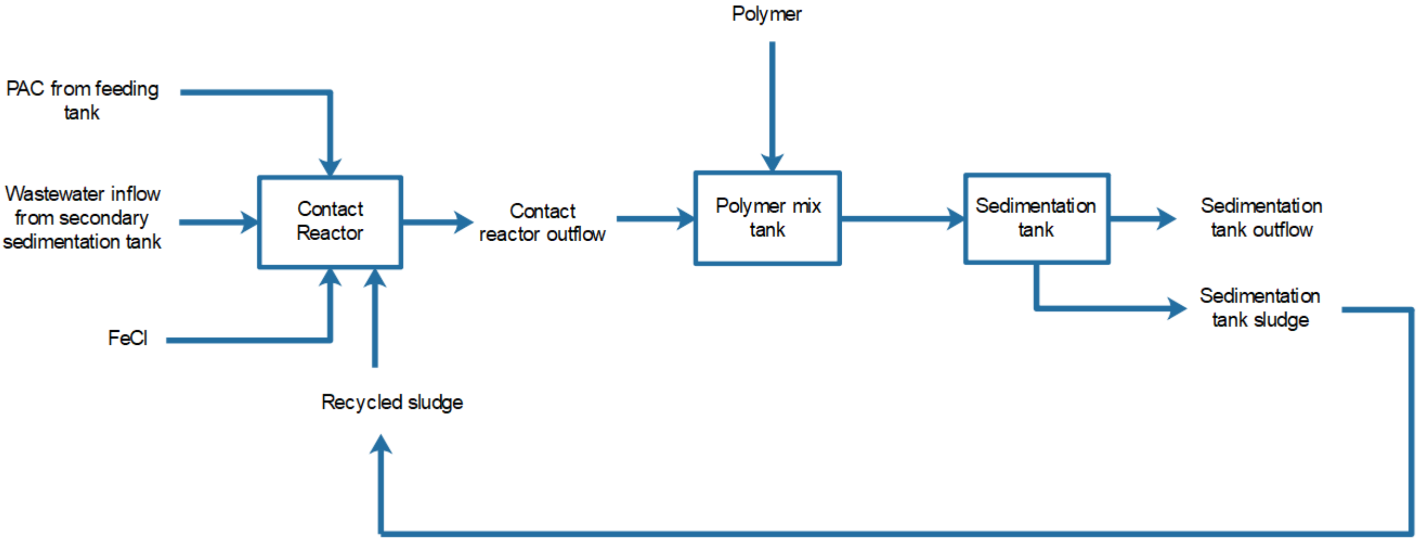

Fig. 1. Process flow diagrams of different wastewater treatment schemes; (a) all unit operations, (b) after the removal of DAF tank, (c) after the removal of DAF and recirculation tank, and (d) after removal of LS, DAF and recirculation tank.

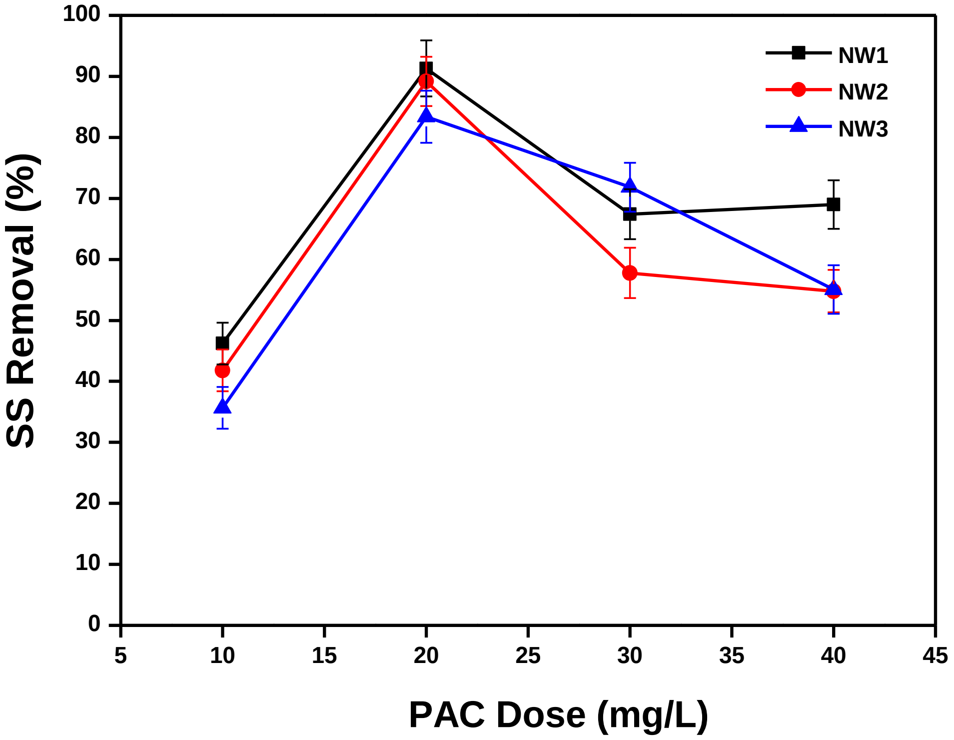

Fig. 2. Effect of Norit PAC dosage on suspended solids (SS) removal from different wastewater samples at 120 rpm and 30 ºC.

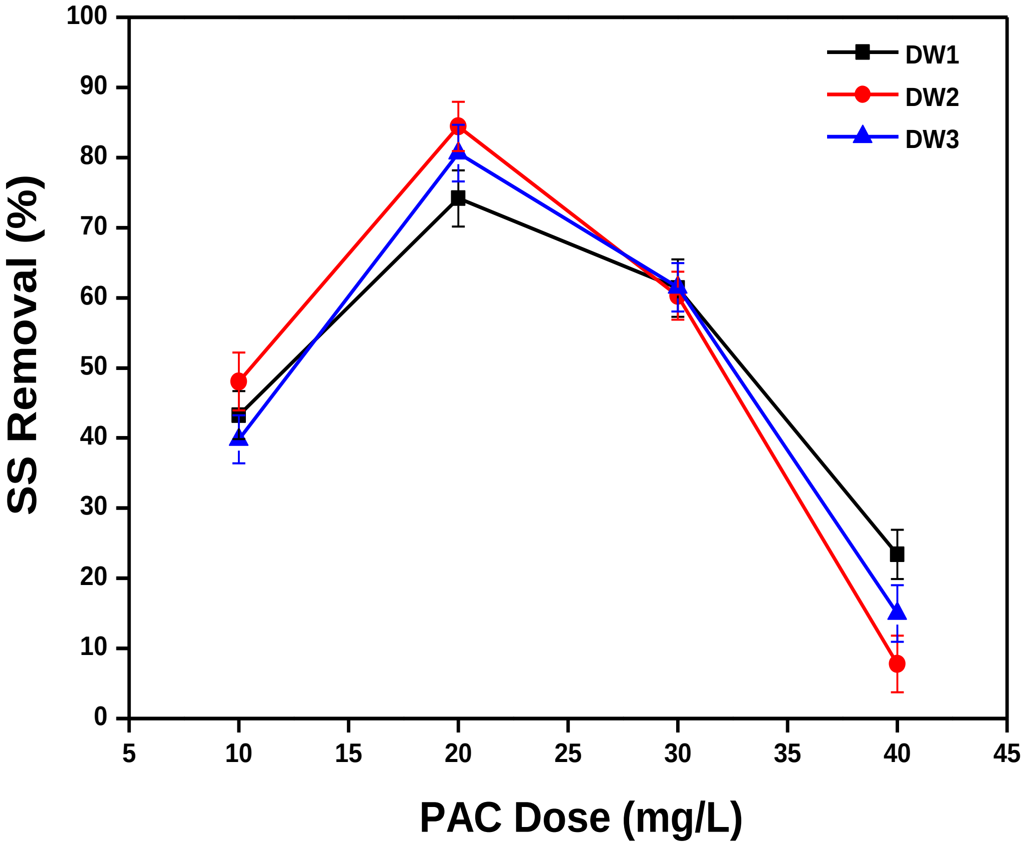

Fig. 3. Effect of Donau PAC dosage on suspended solids (SS) removal from different wastewater samples at 120 rpm and 30 ºC.

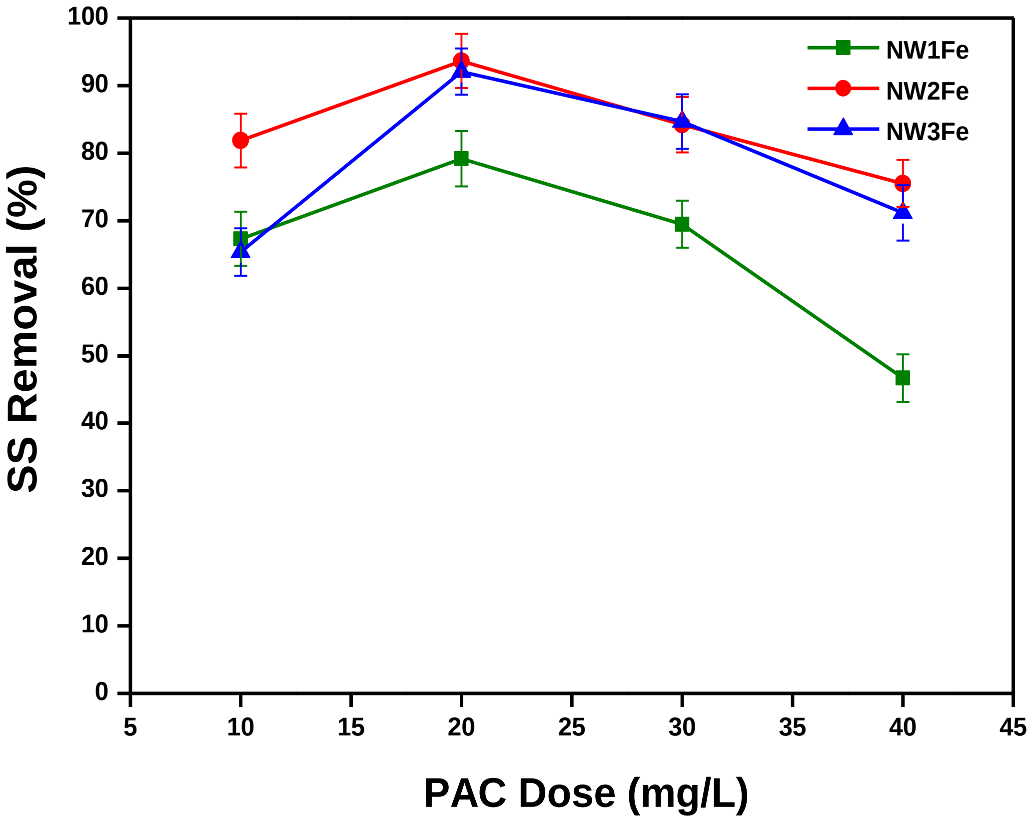

Fig. 4. Effect of Norit PAC dosage with FeCl3 coagulant on suspended solids (SS) removal from different wastewater samples at 120 rpm and 30 ºC.

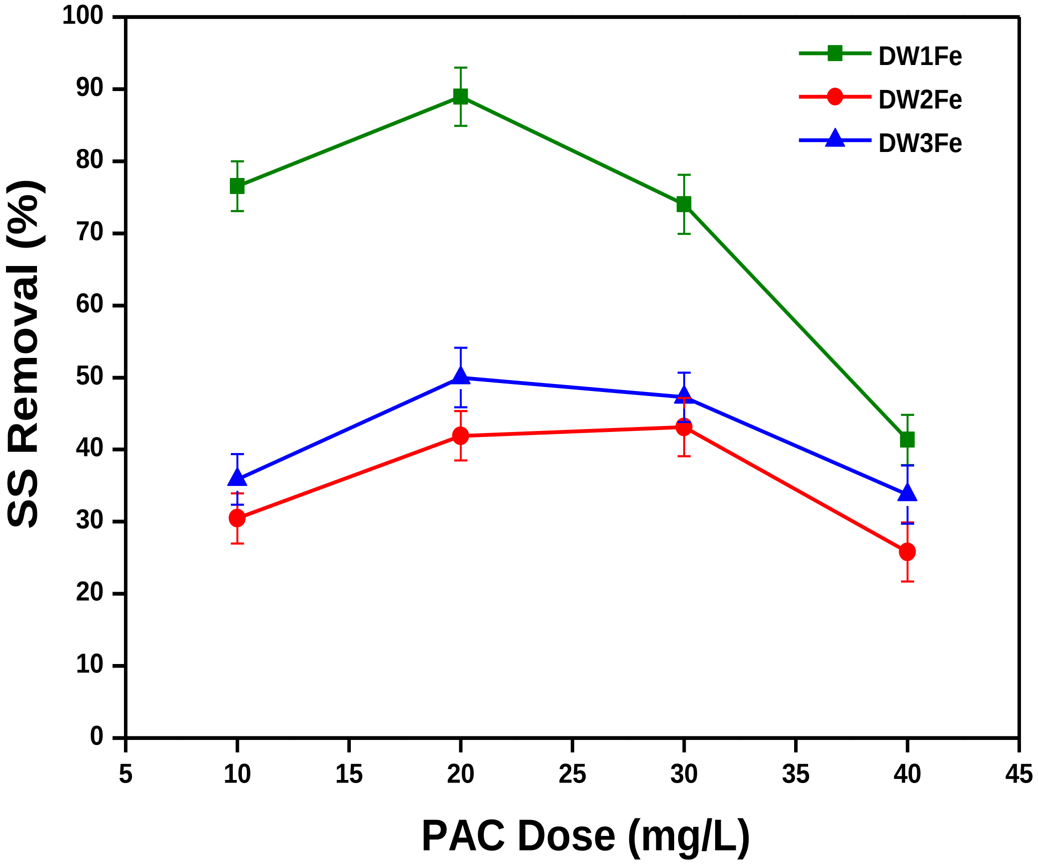

Fig. 5.Effect of Donau PAC dosage with $FeCl_3$ coagulant on suspended solids (SS) removal from different wastewater samples at 120 rpm and 30 ºC.

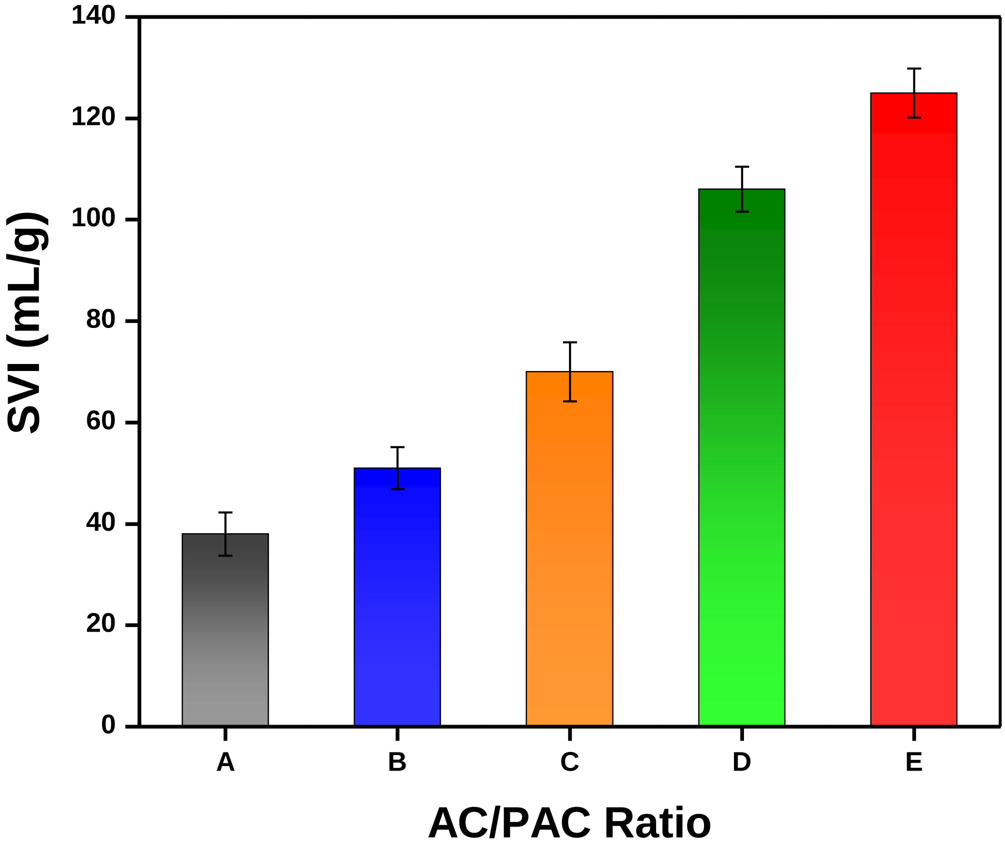

Fig. 6.Sludge settling concentration corresponding to AS to PAC ratio during different phases at 30 °C.

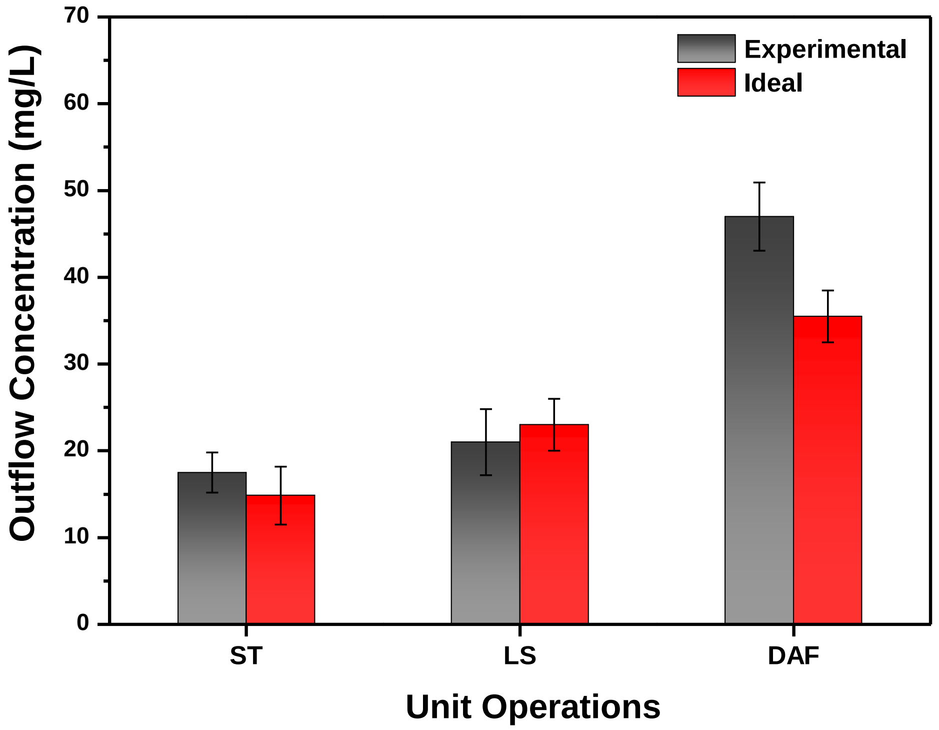

Fig. 7. Comparison of experimental and ideal values from phase A unit operations of recirculation reactor at 30 °C.

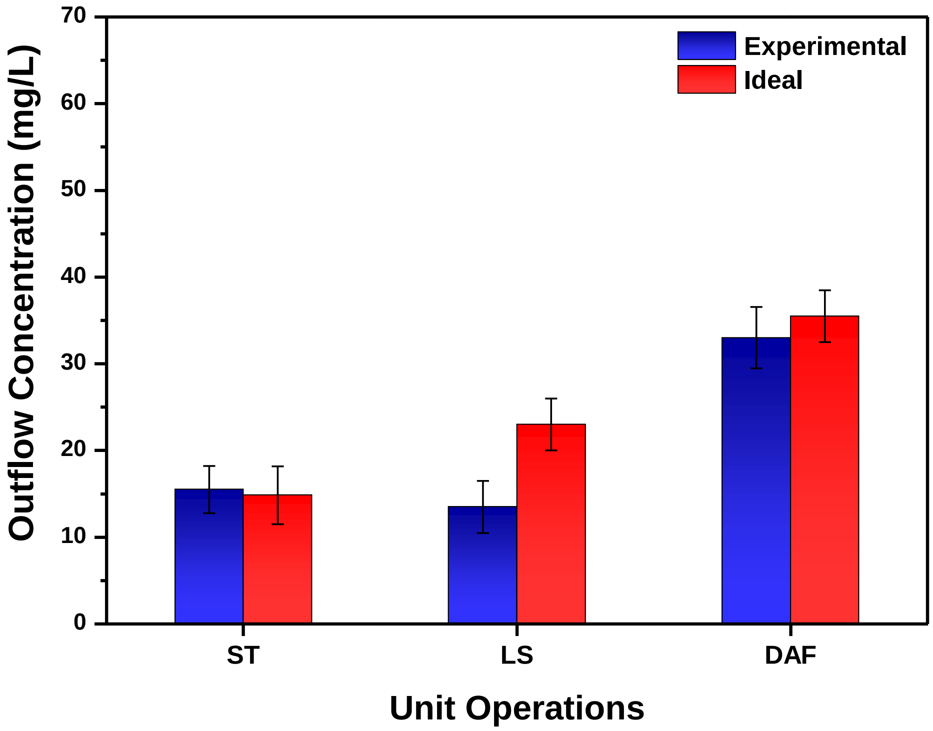

Fig. 8. Comparison of experimental and ideal values from phase B unit operations of recirculation reactor at 30 ºC.

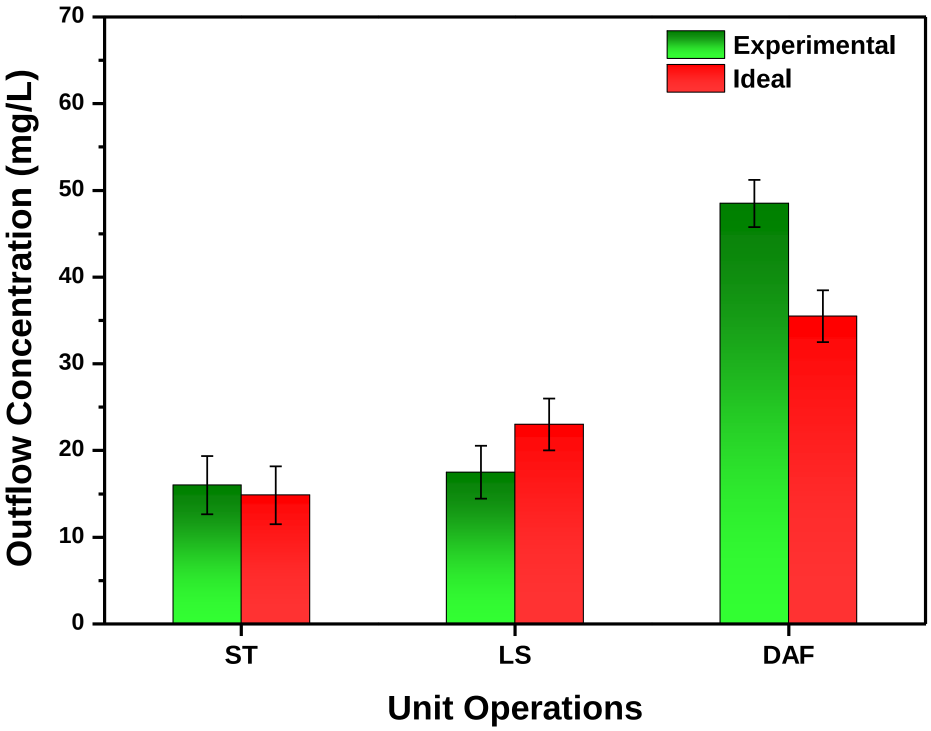

Fig. 9. Comparison of experimental and ideal values from phase C unit operations of recirculation reactor at 30 ºC.

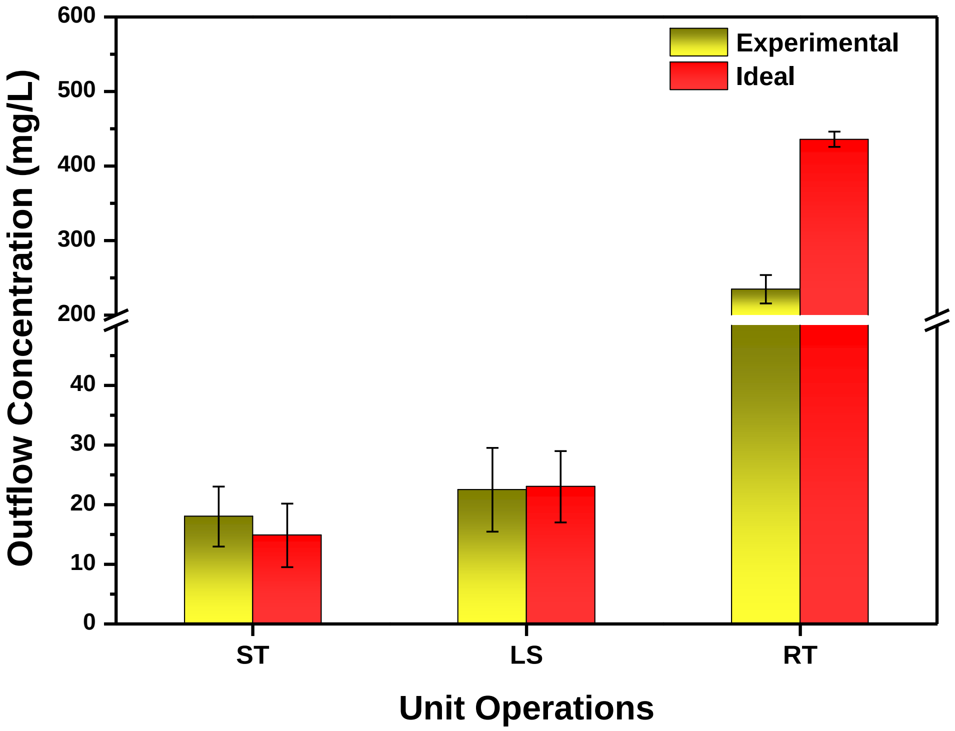

Fig. 10. Comparison of phase F unit operations of recirculation reactor at 30 °C.

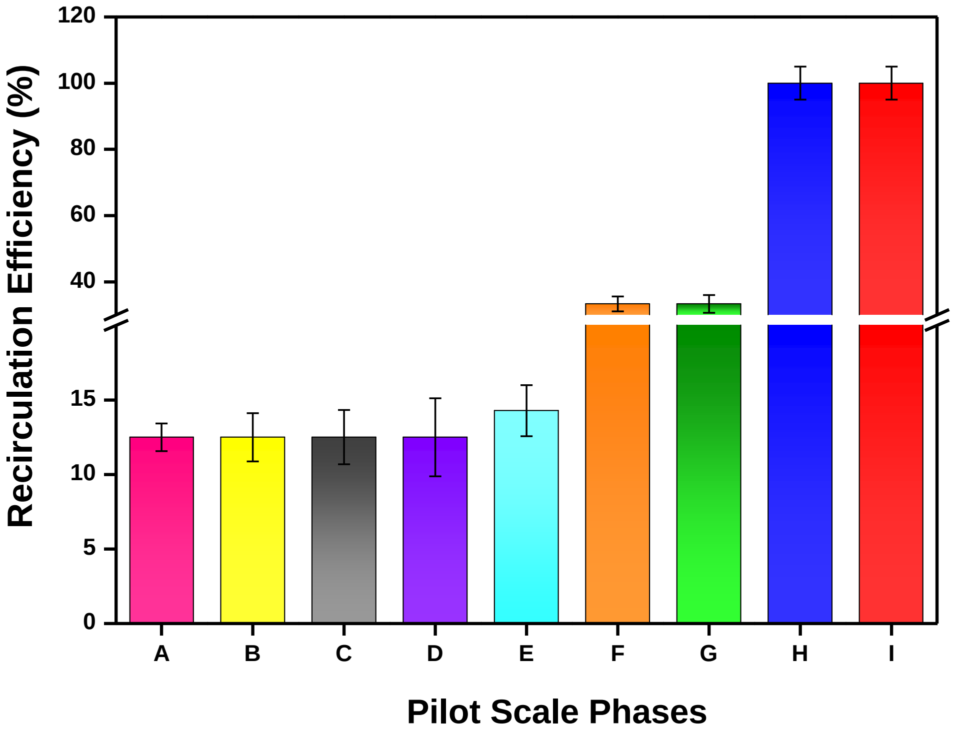

Fig. 11. Comparison of recirculation efficiency in different pilot-scale phases at 30 ^{o}C.