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Removal efficiency of endocrine disrupting chemicals through chemical coagulation using two different coagulants: $AlCl_3$ and $Al_2(SO_4)_3$

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ABSTRACT

Present study reports treatment of wastewater (WW) by two different coagulants, aluminum chloride ($AlCl_3$) and aluminum sulphate [$Al_2(SO_4)_3$]. *Batch coagulation experiments were conducted to evaluate the influence of initial pH (4.5-9) and coagulant dose (500-3000 mg L^{-1}) on chemical oxygen demand (COD), total suspended solids (TSS), ammonical nitrogen (NH_3-N), dissolved organic carbon (DOC), and turbidity removal from WW. Optimum pH and optimum dose was found to be 7.5 and 2000 mg L^{-1} respectively for both coagulants. Optimum pH was found to give 97 and 90% COD, 89 and 81% TSS 20.8 and 36.9% DOC, 96.5 and 93.4% turbidity and 93.6 and 92.5% NH_3-N removal efficiency (RE) by $AlCl_3$ and* [$Al_2(SO_4)_3$] *respectively from WW. The RE of the selected parameters at optimum dose was found almost similar to RE at optimum pH. Now the sample was treated at optimum pH and dose for 60 minutes and the characterization of sludge generated during coagulation process was done by FTIR analysis. Gas chromatography-mass spectrometry (GC-MS) analysis was also done for WW and treated water by selected coagulants. Selected compounds for this study are testosterone, progesterone, diethyl phthalate (DEP) and di-butyl phthalate (DBP). The RE of $Al_2(SO_4)_3$ was found to be good for phthalate compounds while the RE of $AlCl_3$ was good for all compounds. The average RE of testosterone, progesterone, DEP and DBP was found to be 39.5, 30.1, 64.7 and 57.7% by $Al_2(SO_4)_3$ and 59.4, 57.5, 67.2 and 61.3 % by $AlCl_3$, respectively in WW.*

Keywords: Endocrine disrupting chemicals (EDCs), Removal efficiency (RE), diethyl phthalate (DEP), di-butyl phthalate (DBP), GC-MS analysis.

INTRODUCTION

Water is used by human beings and all other aquatic and terrestrial communities for drinking and other purposes. It is the primary need of all living beings. There are so many natural resources of water but different activities of human beings make them contaminated. Although rapidly growing industrial activities make human's life more comfortable but all these practices have generated various hazardous chemicals **[1]** including heavy metals like lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr) etc.

[2,3] which affect water cycle causing a global disturbance and show their eventual impact on human being and wild life. Some of them are carcinogenic, mutagenic and toxic to aquatic organisms as well as human beings **[4]**. The quality of wastewater can be determined with the help of physicochemical and microbiological parameters **[5]** and removal of the hazardous chemicals require specific techniques. Coagulation is a physicochemical method used in wastewater treatment plants (WWTPs), to remove suspended solids (SS) and colloidal material from the WW **[6, 7, 8]**. It involves addition of chemicals, known as coagulants, coagulation of SS to alter the physical state of suspended and dissolved solids followed by flocculation which produce microflocs through aggregation mechanisms and elimination of floc aggregates through sedimentation **[9]**. This process has been applied in WW treatment to remove pathogens and to decrease turbidity and total suspended solids **[10]**. Coagulation is also used for treatment of endocrine disrupting chemicals (EDCs) present in WW. There are a large number of different classes of EDCs from which we select only two i.e. steroid hormones and phthalates for this study.

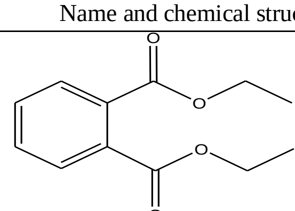
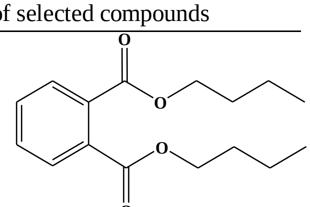
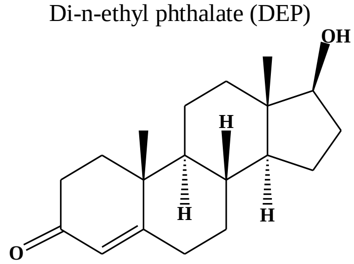
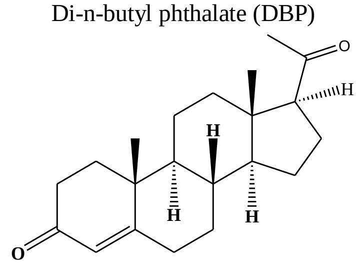
Steroid hormones are a large class of lipophilic molecules that acts on various target sites to regulate multiple physiological functions and are therefore essential in normal physiology. The inappropriate activation or inhibition of receptors of these steroids causes endocrine disruption of an endocrine system i.e. reproductive system **[11]**.

Phthalates are incorporated as fixative agents **[12, 13]**, commonly used as plasticizers in plastics to make them flexible, transparent, and workable **[14, 15]**. They are not chemically bonded to polymer products and can easily seep out and migrate into the environment during the manufacture, consumption and disposal processes **[16]**. Dibutylphthalate (DBP) and diethylphthalate (DEP) are suspected as endocrine disruptor because these interfere with hormone function, causing reproductive and developmental problems. Insufficiently treated municipal WW discharge and industrial effluents are the major sources of these compounds discharged into the aquatic environment **[17, 18, 19, 28]**.

It is concluded from literature survey that these chemicals are “emerging contaminants”, in aquatic environment having endocrine disrupting activity **[20]**. It is therefore necessary to identify the concentration and removal efficiency of these compounds in WW.

The objective of this study was to investigate EDCs removal during coagulation process using two type of coagulants $AlCl_3$ and $Al_2\,(SO4)_3$ at the optimum pH and dose. Dissolved organic carbon (DOC) was measured to assess the effect of coagulant on the removal of EDCs. Therefore Batch experiment including the influence of coagulant dose and pH on initial COD, TSS, turbidity, DOC, NH_3-N and alkalinity, were conducted to study the removal of EDCs. Sludge generated during coagulation was characterized by FTIR analysis. The selected compounds from above two classes of EDCs are given in table 1.

Table 1: Selected EDCs for analysis

Name and chemical structures of selected compounds	
 Di-n-ethyl phthalate (DEP)	 Di-n-butyl phthalate (DBP)
 Testosterone	 Progesterone

MATERIALS AND METHODS

Chemicals and sample collection: The standards of DEP (CAS 84-66-2), DBP (CAS 84-72-2), testosterone (CAS 58-22-0) and progesterone (CAS 57-83-0) bearing high-purity (>99%) were purchased from Sigma Aldrich Chemie GmbH (Germany). Other organic solvents & reagents required for this study were of analytical grade. All glassware was washed carefully and dried in oven. Filter papers used for extraction were also dried before use. WW was collected in clean 2L plastic bottles from activated sludge process (ASP) based WW treatment plant located in jagjeetpur, Hardwar (Uttarakhand). The sample was preserved at 4^oC before analysis.

Experimental methodology: Coagulation tests were performed with the help of Flocculator (a Jar test apparatus) by using actual municipal sewage. A known amount of the coagulant was introducing into a beaker containing 1 L WW (municipal sewage) of known initial pH, COD, TSS, and turbidity. For optimization of the initial pH, the coagulation of WW by the coagulants was studied over a pH range of 4.5-9 at the coagulant dosage (m) of 2 g L^{-1} for both $AlCl_3$ and $Al_2(SO_4)_3$. The pH of the WW was adjusted using 1 N solution of either H_2SO_4 or NaOH. To optimize coagulant dose, coagulation experiments were carried out by varying values of coagulant dose in the range of 0.5-3 g L^{-1}. The mixture was allowed for rapid mixing at 200 rpm for 5 min and then speed was reduced to 20 rpm and the system was kept at this condition for 120 min. Thereafter, the solution was kept for settling for 15 min and the supernatant was filtered through Whatman filter paper grade No. 1 and analyzed for all above parameters. For gas chromatography–mass spectrometer (GC-MS) analysis the supernatant was filtered through Millipore Whatman filter paper 0.45μm and extracted with a solvent mixture of dichloromethane and n-hexane in the ratio of 85:15. For extraction of 500 mL of water sample, 50 mL of extraction solvent was added into a separating funnel. The sample was taken for mechanical shaking for 20 min and the formed cloudy solution was allowed to stand uninterrupted until the two layers separated, then the organic layer was collected and another 30 mL of extraction solvent in same ratio was added into the same water sample for further extraction and separate similarly. The two organic layers of the two times were collected and concentrated under a gentle stream of nitrogen to 1mL followed by GC–MS analysis **[12]**. Finally the WW was treated at the optimum pH (7.5) and optimum dose (2 g L^{-1}) at 180 rpm for one hour and the sample was taken out at 15, 30, 45 and 60 min. The collected samples and the sludge obtained from the coagulation process were used for FTIR studies.
The REs of selected EDCs were calculated by using the following formula:

$$\text{RE (\%)} = \frac{(X_{in} - X_{ef})}{X_{in}} \times 100$$

Where X_{in} = Measured conc in the influent of the plant
X_{ef} = Measured conc in the final effluent of the plant

RESULTS AND DISCUSSION

Determination of optimum pH and coagulant dose: To determine optimum pH and coagulant dose we run the experiment at different range of pH (4.5-9) and coagulant dose (0.5-3g L^{-1}) for WW. From fig 1a it is found that at pH 7.5 maximum REs were found for COD and TSS and further increase in pH do not show significant removal of these parameters indicating that pH 7.5 is optimum pH for removal of COD and TSS. Similarly optimum dose of coagulants defined as the values above which there is no significant increase in the RE with further addition of the coagulants **[21]**. The effect of coagulant dose was observed by comparing the turbidities of the treated samples. The minimum turbidity and maximum removal efficiency of COD and TSS was found at coagulant dose 2g L^{-1}.

Now after observation of optimum pH and coagulant dose the sample is treated at optimum pH and dose by following the experimental procedure for 60 min. The initial sample and final effluent was taken for GC-MS analysis to know about the concentration of EDCs and their RE in this process. The sample is also collected at the time interval of 15 min i.e. at 15, 30, 45, and 60 min along with the sludge sample generated during the coagulation process by $AlCl_3$ (Being more efficient in comparison of $[Al_2(SO_4)_3]$ for FTIR analysis.

Effect of pH and coagulant dose: Fig. 1a represents the effect of initial pH and coagulant dose on the COD and TSS removal. It is observed that as the initial pH of WW was increased, the COD removal increased up to 7.5 giving maximum COD RE of 89 and 81% with aluminium chloride ($AlCl_3$), aluminium sulphate ($Al_2(SO_4)_3$), respectively, and above pH 7.5, COD removal decreased. Hence pH 7.5 was optimum pH for both coagulants. Similarly maximum removal of COD and TSS was given at 2g L^{-1} of coagulant dose for both coagulants (Fig. 1b). After the determination of optimum pH and dose further experiments were conducted at optimum conditions.

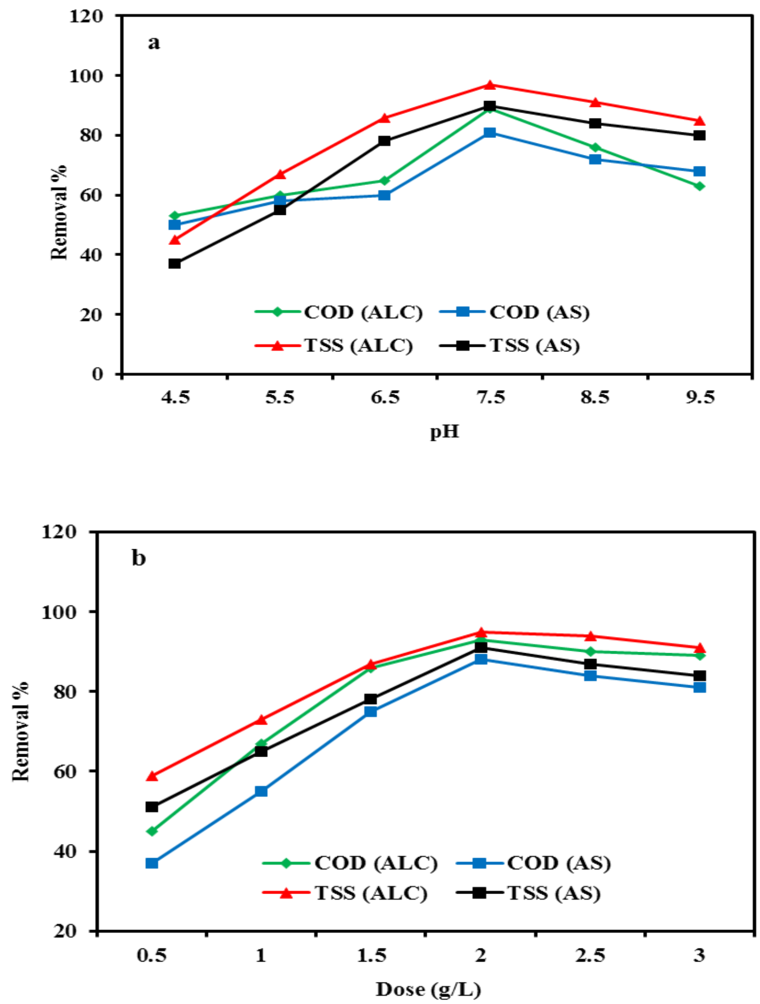


Figure 1. Removal % of COD and TSS with respect to a) pH and b) dose variation

The initial and final concentration of other selected parameters i.e. alkalinity, NH_3-N, DOC, and turbidity at optimum pH and dose are given in (Table 2).

Table 2. Initial and final concentration of selected parameters

	Initial Conc.	Coagulant $AlCl_3$	Coagulant $Al_2(SO_4)_3$
Alkalinity (mg/L)	298	60	76
NH_3-N (mg/L)	18.7	1.2	1.4
DOC (mg/L)	53	42.0	33.4
Turbidity (NTU)	28.6	1.0	1.9

Fourier transforms infrared (FTIR) spectroscopy of samples: The RE of compounds in coagulation process by $AlCl_3$ (being more efficient in comparison of $Al_2(SO_4)_3$) can be understood by FTIR analysis of sludge sample generated after the treatment **[22]**. Fig. 2 shows the FTIR graph of supernatant samples at 15, 30, 45, and 60 min of the treatment process along with sludge generated during the treatment process at optimum pH and dose.. Absorption band at 609 and 1142 cm^{-1} in sludge sample was shows the presence of C-H stretching frequency of -CH_3 group indicating the presence of alkane residues. Peak at 1646 cm^{-1} is characteristic peak of C=C stretching of aromatic ring. Peaks at 2852, 2926, 2960 cm^{-1} and 1332 to 1353 cm^{-1} indicate the presence of C-H stretching in aliphatic methylene groups **[23]**. Stretching and bending vibration frequencies of FTIR spectra of supernatant and sludge samples were summarized in table 3.

The bands at 1406, 1465 cm^{-1} are also assigned the presence of aromatic ring and at 3423.86 cm^{-1} assigned the presence of -NO_2 group in the sludge sample. On comparing the results of FTIR with GC-MS analysis we found that during coagulation process phthalates convert into acids & phenols under aerobic conditions while steroid hormones get adsorbed to SS and subsequently removed from WW through sedimentation **[24]** and consequently removed from WW. The peaks observed in the FTIR spectra may also be due the presence of some other compounds like carbohydrate, proteins, lipid, fats, etc. because these compounds remain present in WW **[25]**.

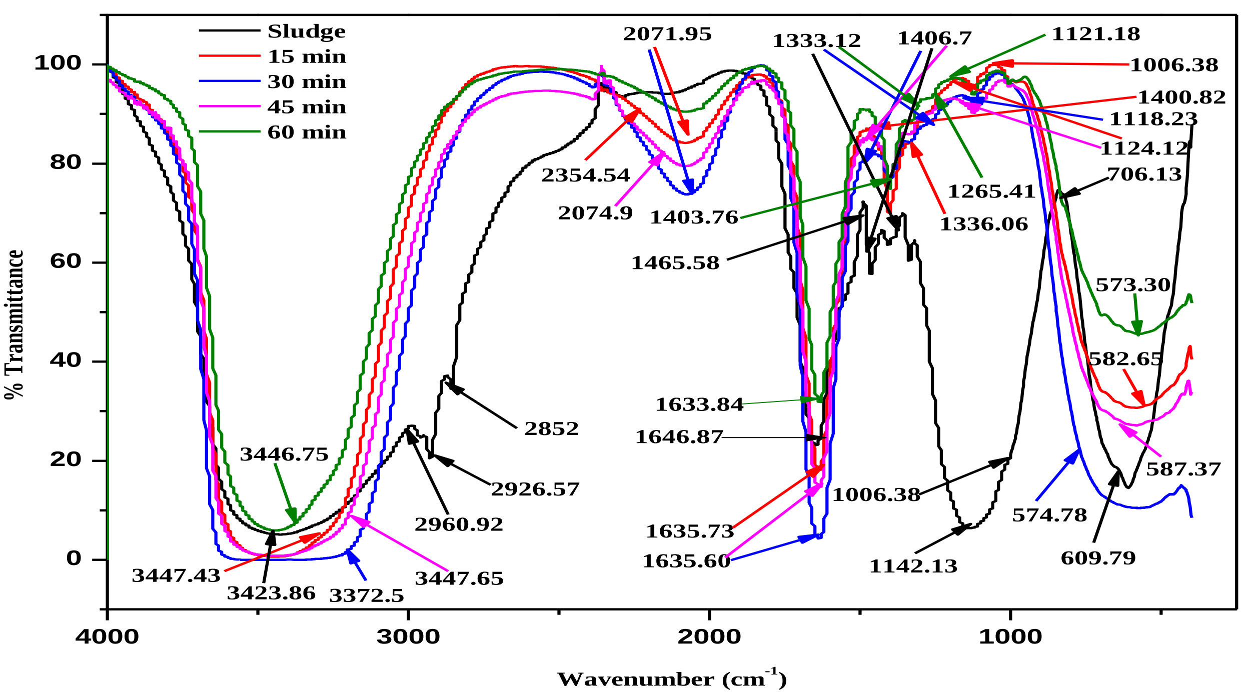


Figure 2: FTIR analysis of sludge and supernatant samples

Table 3. Band assignments obtained in Fourier transforms infrared (FTIR) spectroscopy

Band Assignment	Frequency (cm^{-1})				
	15 Min	30 Min	45 Min	60 Min	Sludge
$O\text{-}H_{str}$	3447.43	3372.50	3447.65	3446.75	3423.86
$C\text{-}H_{str}$ in aliphatic methylene group	2071.95, 2354.54	2071.95	2074	-	2852, 2926.57, 2960.92
$C{=}C_{str}$ in aromatic ring	1635.73	1635.61	1635.60	1633.84	1646.87
$C\text{-}H_{def}$	1400.82	1406.70,	1406.70	1403.76	1406.70, 1465.58
$C\text{-}C_{str}$	1336.06	1332.12	-	1265.41, 1333.12	1333.12
$C\text{-}O_{str}$ in C-O-C group coupled with adjacent C-C stretching	1006.38, 1124.12	1118.23	1124.12	1006.38, 1121.18	1142.13
$C\text{-}H_{def}$	582.65	574.78	587.37	573, 706	609.79

Removal of phthalate compounds: The effectiveness of a coagulation unit depend on several factors including coagulant type and dosage, mixing conditions, temperature, pH and alkalinity as well as nature of compounds **[26]**. The use of [$Al_2(SO_4)_3$] as a coagulant was proven to be highly effective in removing certain hydrophobic EDCs such as phthalate plasticizers **[5]**. Plasticizers like DEP and DBP showed the good removal efficiency 64.7 & 67.2% (DEP) and 54.6 & 61.3% (DBP) by [$Al_2(SO_4)_3$] and $AlCl_3$ respectively (Fig. 3). The removal of these compounds during coagulation process take place, because due to high hydrophobicity, these compounds associate with the suspended solids in wastewater and removed during treatment through sedimentation **[10]**.

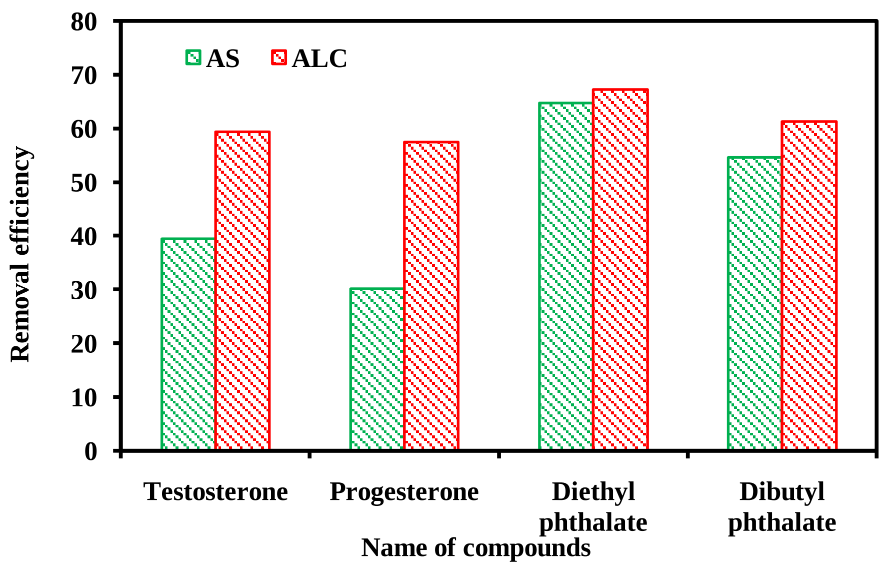


Figure 3: Removal efficiency of selected compounds by $Al_2(SO4)_3$ and $AlCl_3$

Removal of steroid hormones: The selection of an appropriate coagulant is a challenging step because the presence of different contaminants in the wastewater along with the different functional groups, molecular weight and hydrophobicity affect the applicable use for different coagulants for treatment **[27]**. In addition of hydrophobicity EDCs can be adsorbed to particles by interactions of polar functional groups with charged particles and mineral surfaces by ion exchange **[19]**. Steroid hormones are found to be poorly removed by $Al_2(SO_4)_3$ (39.5% testosterone & 30.1% progesterone) but shows the good removal efficiency by $AlCl_3$ (59.4% testosterone, and 57.5% progesterone) coagulant (Fig. 3) because nature of compound also influence the removal efficiency of a particular compound **[5]**. A major factor influencing the removal of pollutant from wastewater is their ability to interact with solid particles and added to the medium used because these facilitate their removal by physical, chemical and biological processes.

APPLICATIONS

This type of treatment process is useful because with the help of this technique level of contamination can be reduced before discharge of wastewater into natural water bodies which ultimately reduce the hazardous effects of these contaminants on aquatic organisms and consequently on human beings.

CONCLUSIONS

On the basis of the present studies, the following conclusions can be described:

- Physicochemical analysis of wastewater confirmed that decrease in concentration of COD and others parameters indicates that the concentration of organic contaminants (Steroid hormones and Phthalates) decrease during coagulation process.
- FTIR analysis of sludge generated during coagulation process at optimum conditions of pH and dose was also confirmed that steroid hormones and phthalate compounds were adsorbed on suspended matter of WW and easily removed from WW during the treatment.
- GC-MS analysis of WW and treated water samples was found that RE of Testosterone, Progesterone, DEP and DBP was found to be satisfactory by both the coagulants while the more efficient coagulant was $AlCl_3$.

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