

Color removal from industrial wastewater with a novel coagulant flocculant formulation

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ABSTRACT: Chemically enhanced wastewater treatment is attracting substantial interest among the currently employed chemical unit processes in wastewater treatment. Coagulation-flocculation has received considerable attention for yielding high pollutant removal, especially color removal. This investigation presents a novel formulation of coagulation-flocculation for color removal from industrial wastewater and illustrates its efficiency, with aid of measurement of solid sludge content, suspended solid content, percentage of solid recovery, UV absorption in wastewater effluent from two automotive factories. The results show that the novel formulation can remove color content from wastewater efficiently. The treated wastewater had UV absorption close to distilled water and color was removed up to 96% by flocculation / coagulation treatment.

Key words: *Coagulation, flocculation, jar test, painting unit, wastewater, color removal*

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INTRODUCTION

Wastewaters contain particles with a wide variety of shapes, sizes, densities, etc, which influence their behavior in water and, therefore, their capacity to be removed. In industrial wastewater, the advanced treatment of color removal such as chemical coagulation may be used as pretreatment in order to enhance the biodegradability of wastewater during the biological treatments. A concentrated sludge may contain 10⁵ mg/L (10%) or more suspended solids; an untreated wastewater 100-1000 mg/L (0.01-0.1%); a treated wastewater 3-30 mg/L (0.0003-0.003%); a potable water less than 0.1 mg/L (0.00001%). These suspended particles are ordinarily polydisperse (range of different sizes), are nonspherical (fibers, irregular grains, amorphous shapes), and have variable densities (greater or less than that of water). The four class designations and the applicable size ranges of suspended particles listed in Table 1 (McKetta, 2004). The removal of particles and organic matter from wastewater is often achieved by coagulation, usually performed with iron or aluminum salts. Coagulation can be interpreted as the conversion of colloidal and dispersal particles into small visible floc upon addition of a simple electrolyte. Increasing the concentration of the electrolyte results in a compression

of the electrical double layer surrounding each suspended particle, a decrease in the magnitude of the repulsive interactions between particles and destabilization of the particles. The most common coagulant used in wastewater treatment is alum Al₂(SO₄)₃·4 H₂O and PAC (polyaluminum chloride), due to its effectiveness in treating a wide range of wastewater type and relatively low cost. Inorganic coagulants are simple electrolytes which are water-soluble, low-molecular weight acids, bases, or salts. Various inorganic coagulants are listed in Table 2.

The use of performed polymerized forms of Al has become more common as alternative coagulants, such as polyaluminum chloride and polyaluminum sulphate. These coagulants have the advantage of being more effective at lower temperatures and a boarder pH range than alum (Exall and Vanloon, 2003). Additionally, the higher charge density of polyaluminum chloride species often results in a decrease in the coagulant dose and the associated solids production. Alum, PAC and sodium aluminate function as a coagulant by initially forming positively charged Al species that adsorb to negatively charged natural particles resulting in charge neutralization. These species are thought to be primarily

Table 1: Relative sizes of suspended particles

Class	Diameter (mm)
Colloidal	0.000001-0.001
Dispersed	0.001-0.1
Coagulated	0.1-1.0
Flocculated	1.0-10.0

Table 2: Inorganic coagulants

Chemical name	Formula
Salts:	
Aluminum chloride	AlCl ₃
Aluminum sulfate	Al ₂ (SO ₄) ₃
Calcium chloride	CaCl ₂
Calcium oxide	CaO
Ferrous chloride	FeCl ₂
Ferric chloride	FeCl ₃
Ferrous sulfate	FeSO ₄
Ferric sulfate	Fe ₂ (SO ₄) ₃
Sodium aluminate	NaAlO ₂
Acids:	
Hydrochloric acid	HCl
Sulfuric acid	H ₂ SO ₄
Bases:	
Calcium hydroxide	Ca(OH) ₂
Sodium hydroxide	NaOH

In most cases, the aluminum hydroxide sols are formed so rapidly (1-2 sec). These amorphous solid species are responsible for the charge neutralization of natural particles also contribute to the formation of larger floc (Delgado, *et al.*, 2003). Aggregates formed predominantly

by bridging of particles with a coagulant or polymer partially recover after shearing to a steady state floc size, whereas when charge neutralization is the dominant aggregation mechanism, there is a higher degree of recovery. Generally as aggregate size increases in natural water using Al based coagulants, fractal dimension decreases. Under typical wastewater treatment conditions particles are unable to penetrate the interior of aggregates and tend to attach on the exterior, which forms a more open, less dense structure. However, it has also been proposed that increasing aggregate size may correspond to increasing fractal dimensions as a result of break up and reaggregation of larger aggregates into denser, more compact structure (McCurdy *et al.*, 2004).

Flocculation is usually interpreted as the further agglomeration of slowly-settling coagulated particles into large rapidly-settling (or floating) floc upon the addition of an organic polyelectrolyte. Flocculant molecules attach and bridge between particles to form larger agglomerates. Some characteristic properties of different type of polyacrylamide (PAM) as flocculant agent are given in Table 3 (Bersa *et al.*, 2004). Polyelectrolyte flocculants are linear or branch chain organic polymers which form complex ions in solution. Polyelectrolytes have high molecular weights and are fully water-soluble. Various types of polyelectrolyte flocculants are listed in Table 4 (Heimer, 2004).

Table 3: Characteristic properties of different type of polyacrylamide (PAM)

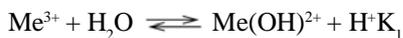
Ionic type	M.W (g/mol)	Charge density (C/g)	Percentage charge monomer
Anionic PAM	$5.5 - 7 \times 10^6$	-260	30.0
Cationic PAM	$6.0 - 7 \times 10^6$	+150	19.0
Non-ionic PAM	5.0×10^6	-1.07	-

Table 4: Polyelectrolyte flocculants

Type	Ionic charge	Examples
Anionic	Negative	Poly(acrylamide), partially hydrolyzed (>5-40%) Poly(acrylic acid) and salts Poly(acrylamide/acrylic acid) copolymers Poly(styrene sulfonic acid) and salts Poly(vinyl alcohol)
Cationic	Positive	Poly(alkylene polyamine) Poly(epichlorohydrin) Poly(ethylenimine) Poly(dimethyl aminomethylacrylamide) Poly(diallyldimethyl ammonium chloride)
Nonionic	Neutral	Poly(acrylamide), partially hydrolyzed (<1-5%)
Miscellaneous	Variable	Alginate acid, Cellulose, Dextran, Glues, Gums, Starch, Other natural products and derivatives

The presence of organic matter generally increases the required coagulant dosage. It has been suggested that Al hydrolysis products from insoluble aluminum-humates or -fulvates with humic substances, producing a colloidal sol that settles very slowly. At higher coagulant doses, the aluminum-organic complexes may be removed by incorporation into $\text{Al}(\text{OH})_3$ flocs (Aguilar *et al.*, 2003).

Bach and Papavasiliopoulos draw together information on factors which influence the conditioning and dewatering behavior of an alum sludge gained from the coagulation of low-turbidity colored water. In their research, they focused on potential impact of aluminum hydroxide on the sludge character. They found that, there were strong similarities in the behavior of different solution, indicating the potential impact of the hydroxide. They showed also, that, there were common features being displayed by both the organic fractions and the hydroxide. They studied effects of pH and alum concentration in color removal as described in Fig.1 (Bache and Papavasiliopoulos, 2003). Duan and Gregory investigated on coagulation by hydrolyzing aluminum and iron salts and their dependence on pH and coagulant dosage. They illustrated the hydrolysis constants for successive deprotonations in terms of following equations.



And for solubility constant:



Table 5 gives the hydrolysis and solubility constants for aluminum and iron at 25 °C (Duan and Gregory, 2003). But, for practical purpose, product of monomeric hydrolysis of Fe(III) and Al(III) can be presented as Fig. 1. Kan, Huang and Pan employed a photometric dispersion analyzer (PDA) to monitor clay coagulation by alum and polymeric aluminum chloride (PAC).

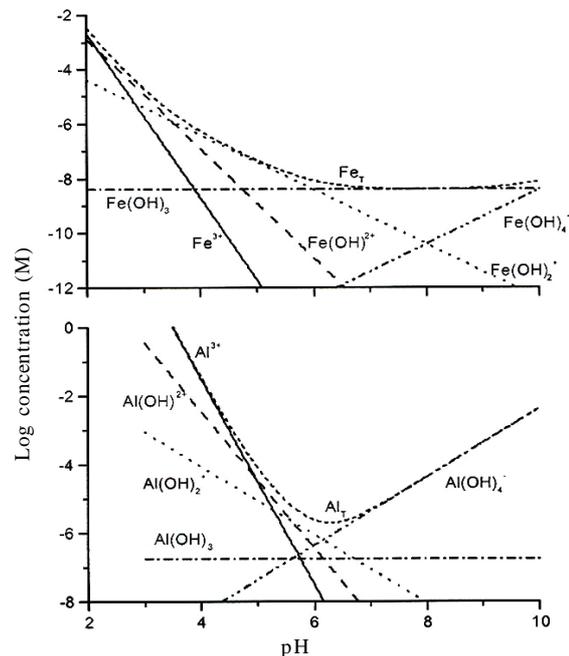


Fig. 1: Concentration of monomeric hydrolysis products of Fe and Al in equilibrium with the amorphous hydroxides at zero ionic strength and 25 °C.

They studied the effect of rapid mixing time on particle removal. They proposed adequate mixing times by PDA and mixing test methods (Kan *et al.*, 2002).

Larsson, Walldal and Wall investigated the flocculation of large cationic polymers and nanosized particles. They found that the molecular architecture of the polymer (linear or branched) is essential for the flocculation behavior. Only in the case of the linear polymer, the degree of aggregation of the particle is important (Larsson *et al.*, 1999).

Liu and Liang studied the effect of recirculation of chemical sludge and integrated sludge on enhancement of color removal in integrally industrial wastewater plant. They showed that with sludge recirculation the process of coagulation for the color removal has up to 35% enhancement in comparison with no sludge recirculation (Liu and Liang, 2004). Delgado, Diaz, Garcia and Otero compared effectiveness of three inorganic coagulants-aluminum sulphate, ferric chloride and polyaluminum chloride (PAC)- in reducing

Table 5: the hydrolysis and solubility constants for aluminum and iron at 25 °C

	K_1	K_2	K_3	K_4	K_5
Al^{3+}	4.95	5.6	6.7	5.6	31.5
Fe^{3+}	2.2	3.5	6	10	38

the turbidity of secondary effluents from a conventional wastewater treatment plant. They showed that the optimal conditions are 50 mg/L corresponded to pH = 6 and a dose of PAC of 20 mg/L, but the recommended conditions are 50 mg/L for pH = 6 to obtain a turbidity reduction of 90% (Delgado *et al.*, 2003). In present investigation, a novel formulation of coagulant/flocculant has been introduced and treated on effluent of two automotive factories. The concentration of color in the effluent wastewater was up to 5 g/L. The efficiency of color removal from the wastewater as floated sludge was evaluated by determination of suspended solid content, sludge solid content, solid recovery percentage and UV absorption of treated wastewater. This research carried out in chemistry department of Islamic Azad University, north branch with cooperating of Iran Khodro and Mehrkam Pars companies.

MATERIALS AND METHODS

The wastewater samples were obtained from painting unit of two Iranian vehicle-manufacturing companies, Iran Khodro and Mehrkam Pars. For better comparison, three samples of each wastewater tank were taken for treatment.

In this investigation, a novel formulation as powder, which consists of coagulant, flocculant, coagulant aid and pH adjusters, have been applied for color removal from industrial wastewater. The formulation has been treated to the wastewater taken from sludge reservoir of two grand automobile painting units. The ingredients of coagulant / flocculants formulation are listed in table 6 in weight percentages.

Table 6: Ingredients of coagulant / flocculant formulation

Role	Component	wt %
pH adjuster	KOH	8
coagulant	PAC	37
coagulant	NaAlO ₂	40
coagulant	Na ₂ SiO ₃	4
pH adjuster	Na ₂ CO ₃	4
coagulant aid	Polyvinyl alcohol	6
flocculant	PAM	1

Each component in the formulation has the specific character, which permits to have more efficiency in color removal. Their roles can be gathered in four classifications as below:

- Coagulants: Polyaluminum chloride (PAC), sodium aluminate (NaAlO₂) and sodium silicate are poly electrolyte materials and play the role of coagulant. PAC is a polymer which has low molecular weight, high charge density and short chain length.
 - Flocculant: Polyacryl amide (PAM), has long chain length, low charge density and high bonding ability.
 - Coagulant aid: Polyvinyl alcohol with long chain length that permits air penetration into molecules and increasing of flocculation action.
 - pH adjusters: Potassium hydroxide and sodium carbonate have the role of pH adjuster for maintaining pH of solution in range of about 8.5 – 10.
- The operation condition and speed of stirring during the each step are presented in Table 7.

Treatment method

The specifications of the wastewater treatment tanks are presented in Table 8 and Fig. 2. The settling time for each experiment was 2 h. For evaluation of efficiency of formulation in color removal, three samples of 1 L of treated wastewater in 1m depth of vessel were taken.

Then, sludge solid content can be calculated using the following formula:

$$\text{Sludge solid} = \frac{z - x}{y - x}$$

that:

x = weight of the container in grams

y = weight of the container and sludge in grams

z = weight of the container and sludge after 2hr at 105°C in oven

with considering that total solid which exists initially in the solution:

C = color + coagulant / flocculant material

Thus, the suspended solid in solution and solid recovery percentage are calculated as:

$\text{Suspended solid} = C - \text{sludge solid content}$

$$\% \text{solid recovery} = \frac{\text{sludge solid content}}{C} \times 100$$

Table 7: operational conditions for different formulations used

Agitation speed in coagulation/flocculation step (rpm)	400
Time of coagulation/flocculation step (sec.)	900
Agitation speed of Settling (rpm)	200
Settling time (sec)	90

Table 8: The specification of Iran Khodro and Mehrkam Pars wastewater treatment tanks

	Volume (m ³)	Height (m)	The value of primary color (kg)	The value of powder that added to the tank (kg)	Impeller type
Iran Khodro	150	5	5	150	Turbine
Mehr	95	5	5	150	Turbine
Kam Pars					

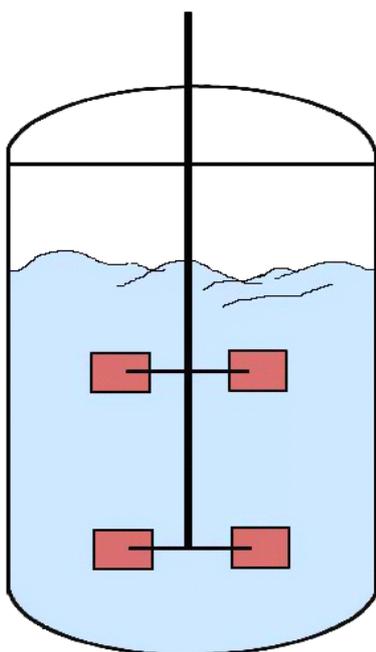


Fig. 2: Wastewater treatment tank

Treatment method

The specifications of the wastewater treatment tanks are presented in Table 8 and Fig. 2. The settling time for each experiment was 2 h.

RESULTS

Figs. 3, 4 and 5 show the sludge, suspended solid contents and the solid recovery percentages for three samples obtained from IranKhodro. Figs. 6, 7 and 8 also, present the results for three samples obtained from Mehrkam Pars and show the high efficiency of treatment in separation of solids. Ultra Violet absorptions of solution after treatment for all of samples are presented in Figs. 9 and 10.

DISCUSSION AND CONCLUSION

The results of the sludge, suspended solid content and the solid recovery percentages for these samples obtained from Inrankhodro and Mehrkam Pars (Figs. 3 to 8) illustrate that treatment of coagulant/ flocculant has the similar efficiency for all of samples (with maximum 0.1% difference among results) and separates their solid contents very well. The amounts of absorption of the solution (Figs. 9 and 10) for different samples are close to absorption of distilled water. That means the treated wastewaters have the behavior of distilled water in point of view of UV absorption. In explaining of the results, it must be mentioned that aluminum ions are released in wastewater by PAC and sodium aluminate which surrounds the color and neutralizes it as shown in Fig. 11. Sodium silicate enhances this action. Then, the coagulated particles flocculate by chain S of PAM and float toward free surface of wastewater (Fig. 12). Polyvinyl alcohol as coagulant aid agent produces air bubbles among physical bandings (hydrogen bonds) and therefore, reinforces the floatation of color as sludge (Fig. 13). Entire results show that, the novel composition of the coagulant / flocculant can separate the color from industrial wastewater concentration up to 5g/L. After addition of coagulant / flocculant composition to wastewater treatment tanks, PAC and sodium aluminate neutralize the color and PAM flocculate it. The sludge, which is produced within treatment, is floated by polyvinyl alcohol and removed. By this composition, the color can be separated up to 96% from industrial wastewater. The industrial wastewaters after treatment with coagulant / flocculant composition have UV absorption close to absorption of distilled water.

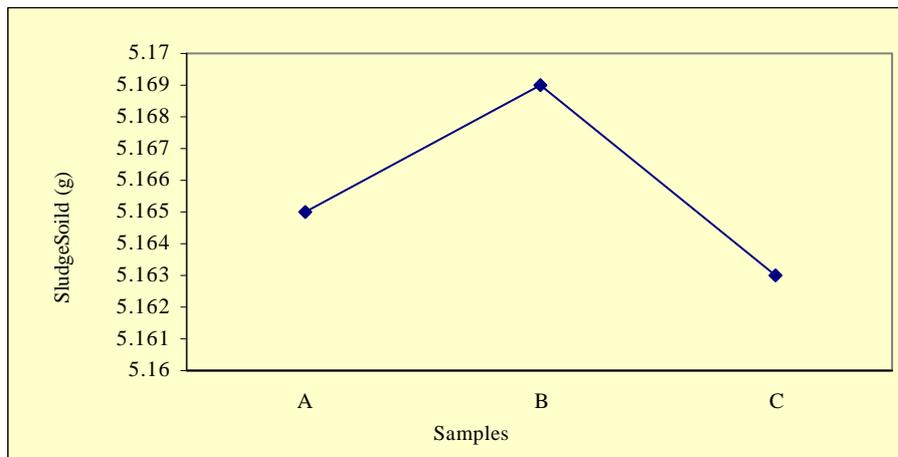


Fig. 3: Sludge solid content for different samples obtained from Iran Khodro Co.

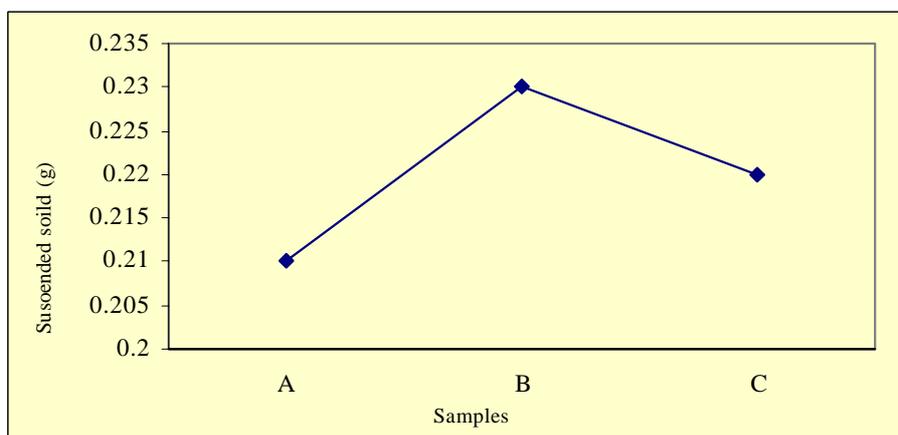


Fig. 4: Suspended solid content for different samples obtained from Iran Khodro Co.

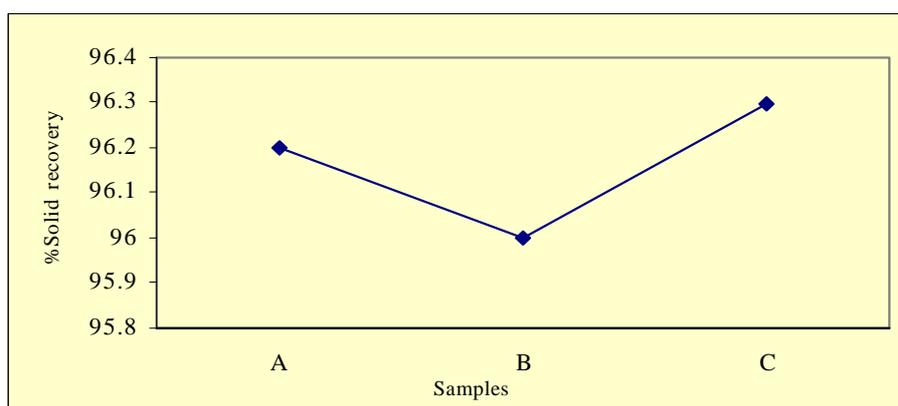


Fig. 5: %Solid recovery for different samples obtained from Iran Khodro Co.

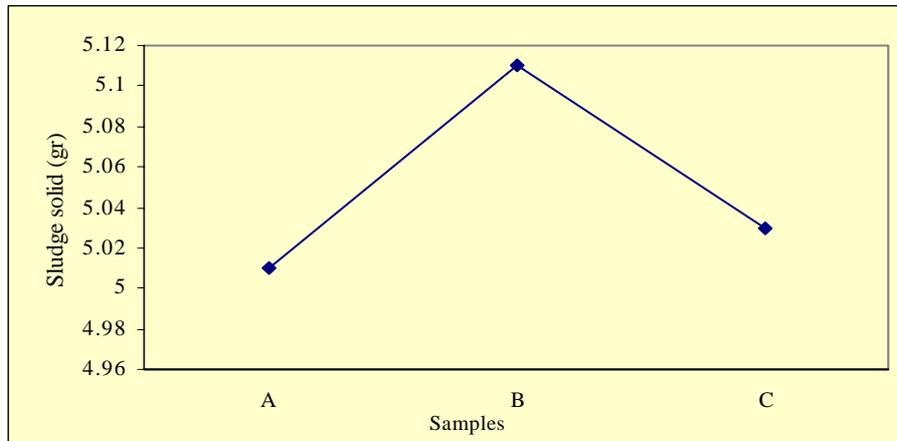


Fig. 6: Sludge solid content for different samples obtained from Mehrsam Pars Co.

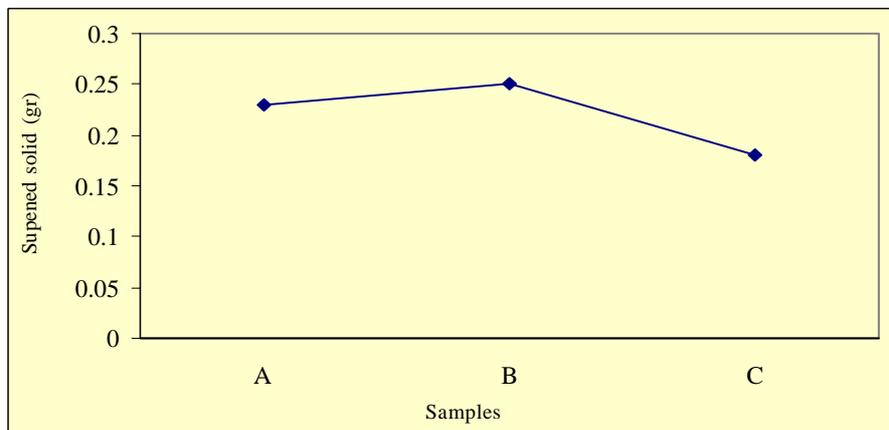


Fig. 7: Suspended solid content for different samples obtained from Mehrsam Pars Co.

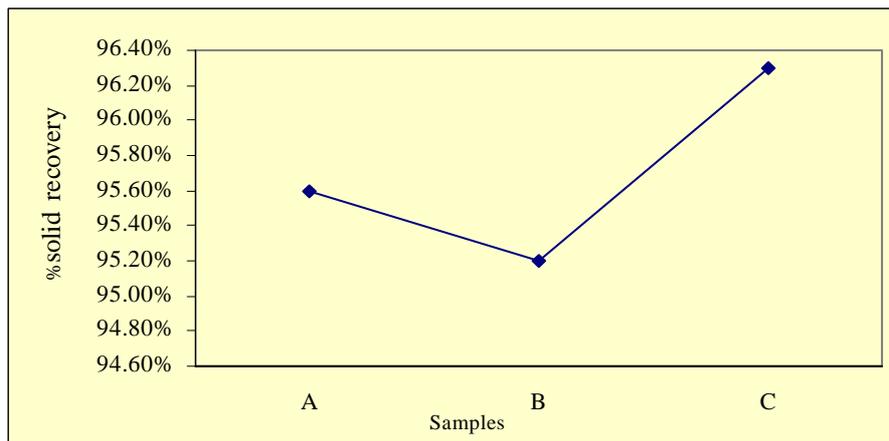


Fig. 8: % Solid recovery for different samples obtained from Mehrsam Pars Co.

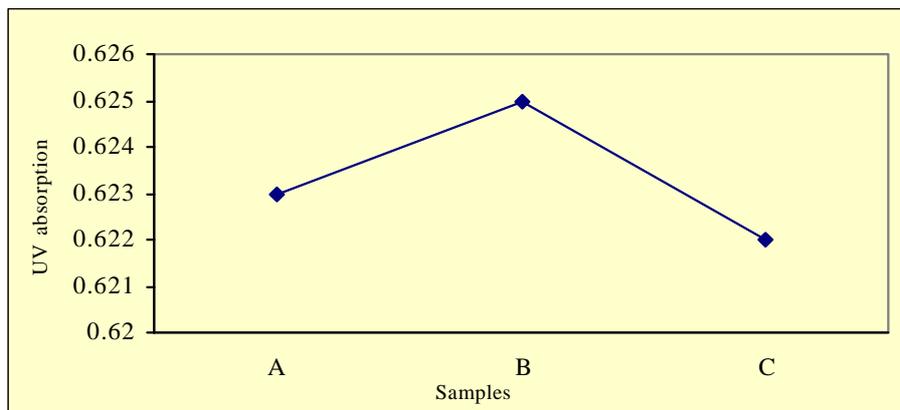


Fig. 9: UV absorption for different samples obtained from Iran Khodro Co.

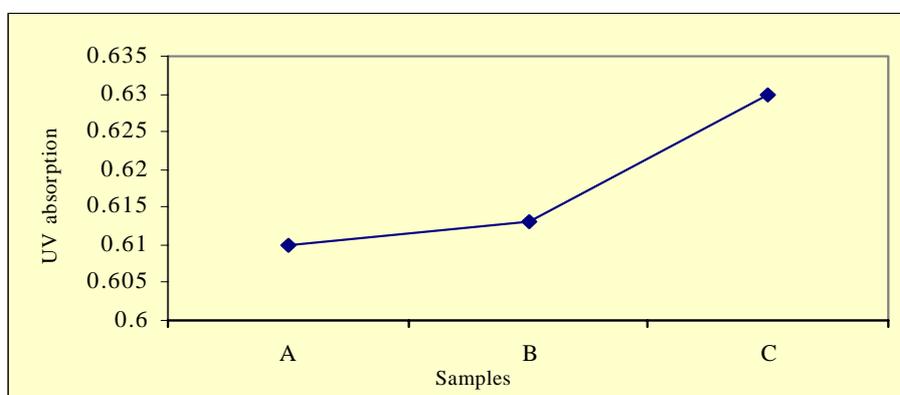


Fig. 10: UV absorption for different samples obtained from Mehrsam Pars Co.

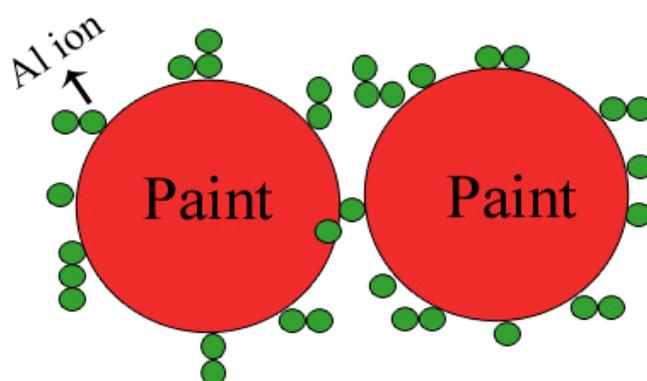


Fig. 11: Deposition of metal hydroxide species on oppositely-charged particles, showing charge neutralization

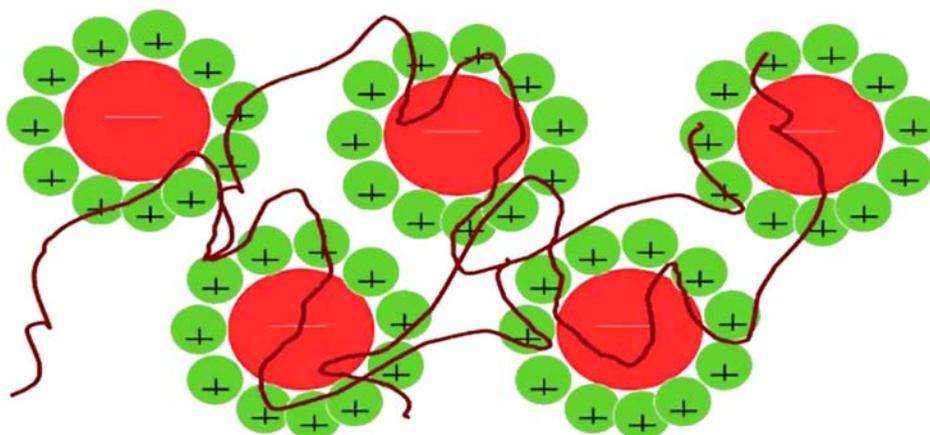


Fig. 12: Mechanism of paint flocculation

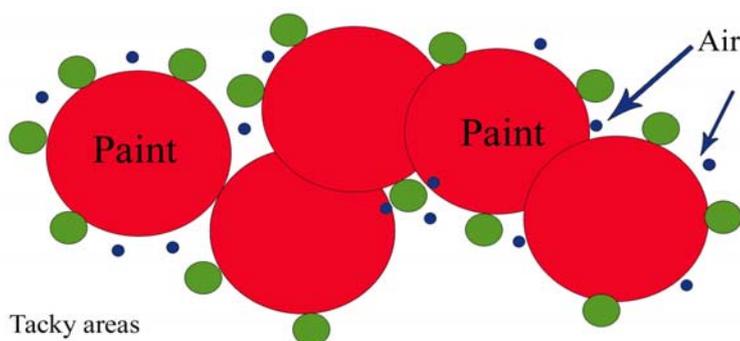


Fig. 13: Mechanism of paint floatation (as sludge) by coagulant aid

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