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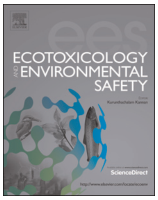

Response surface-optimized removal of Reactive Red 120 dye from its aqueous solutions using polyethyleneimine enhanced ultrafiltration

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ABSTRACT

Retention of toxic dyes with molecular weights lower than the molecular weight cut-off (MWCO) of the ultrafiltration membranes can be improved through selective binding of the target dyes to a water-soluble polymer, followed by ultrafiltration of the macromolecular complexes formed. This method, often referred to as polymer enhanced ultrafiltration (PEUF), was investigated in the present study, using polyethyleneimine (PEI) as the chelating agent. Model azo dye Reactive Red 120 was selected as the poorly biodegradable, target contaminant, because of its frequent recalcitrant presence in colored effluents, and its eventual ecotoxicological impacts on the environment. The effects of the governing process factors, namely, cross flow rate, transmembrane pressure polymer to dye ratio and pH, on target dye rejection efficiency were meticulously examined. Additionally, each parameter level was statistically optimized using central composite design (CCD) from the response surface methodology (RSM) toolkit, with an objective to maximize performance efficiency. The results revealed high dye retention efficiency over 99%, accompanied with reasonable permeate flux over 100 L/m^2 h under optimal process conditions. The estimated results were elucidated graphically through response surface (RS) plots and validated experimentally. The analyses clearly established PEUF as a novel, reasonably efficient and economical route for recalcitrant dye treatment.

1. Introduction

Dyes are considered as one of the major and most obnoxious contaminants present in untreated industrial discharge, such as textile and tannery effluents (ElDefrawy and Shaalan, 2007; Khandegar and Saroha, 2013; Verma et al., 2012). The discharged effluents from various dye generating or consuming industries are often marked by the presence of residual color in dauntingly high proportions, which emerges as a parameter of encumbrance for the industries, and environmentalists alike, owing to the perceived ecotoxicological impacts of these dyes on the aquatic as well as terrestrial flora and fauna, including their effects on human health, which are abominable and at times, fatal. Apart from being aesthetically repulsive, these dyes are mutagenic and carcinogenic. Besides, they also provoke allergy, dermatitis and severe skin irritation (Absalan et al., 2011; Cardoso et al., 2012). Moreover, these residual dyes adversely affect the aquatic ecosystems by severely occluding light penetration, which, in turn limits the photosynthetic rates of aquatic flora (Cardoso et al., 2012). Additionally, the chance discharge of unfixed or poorly fixed dyestuffs into the terrestrial environment along with the industrial waste stream distorts the nutrient balance of soil and affects the toxicology of the soil in agricultural fields, thereby hindering seed germination and plant growth (Paul et al., 2013). In this context, the reactive azo dyes, in particular, are worth mentioning. The azo dyes constitute the most widely applied class of synthetic dyes on commercial scale, accounting for over 70% of the dyes used in industries, such as textiles (Absalan et al., 2011; Naveen et al., 2011; Subash et al., 2013). However, over 30% of these dyes are discarded during the dyeing operations owing to the relatively high level of hydrolysis exhibited by these reactive dyes in the alkaline problem environment as compared to other dye classes; these dyes are hence discharged into the aquatic environment as toxic colored contaminants (Cardoso et al., 2012; Paul et al., 2011). The problem of azo dye disposal is further exacerbated by the excellent water

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Abbreviations: PEUF, polymer enhanced ultrafiltration; PEI, polyethyleneimine; MWCO, molecular weight cut-off; RSM, response surface methodology; CCD, central composite design; RS, response surface; ANOVA, analysis of variance; C.V.%, coefficient of variation; S/N, signal to noise ratio; Std. Dev., standard deviation

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Nomenclature

J_w	the pure water flux (L/m^2 h)
Q	the quantity of permeate collected (L)
Δt	the sampling time (h)
A	the membrane area (m^2)
R_e	rejection efficiency (%)
C_p	the solute concentrations in permeate solutions (mg/L)
C_f	solute concentrations in feed solutions (mg/L)
Y	response
x_i, x_j	the coded values of the independent input factors
β_o	the constant regression coefficient
βi	the linear regression coefficients
β_{ij}	the interaction regression coefficients
β_{ii}	the quadratic regression coefficients
n	total number of independent design variables
N	total number of experimental trials
n_c	central runs
$Y1$	predicted Reactive Red 120 dye rejection efficiency response (%)
A	RSM symbol for coded level of pH cross-flow rate cross flow rate (L/h)
B	RSM symbol for coded level of polymer to dye ratio
C	RSM symbol for coded level of transmembrane pressure (bar)
D	RSM symbol for coded level of cross-flow rate cross flow rate (L/h)
R^2	coefficient of multiple determination
R	correlation coefficient
R^2_{adj}	adjusted R^2 statistic
K_p	a constant of protonation

solubility, unusually high chemical as well as photolytic stability, and recalcitrancy demonstrated by the residual dyestuff, which inadvertently result in prolonged persistence of these dyes in the environment and their eventual resistance to microbial degradation (Kittinaovarat et al., 2010; Naveen et al., 2011). A maximum color level of 400 Hazen units has hence been prescribed by in regard to the discharge of dye effluents discharged from various dye and dye intermediate industries (CPCB, 2014). Reactive Red 120 (RR 120), an anionic dye widely applied in textile industries, has often been regarded as an appropriate paradigm of an azo dye in archival literature (Paul et al., 2011; Subash et al., 2013). Given the consequent acute aquatic toxicity, progressively stringent environmental regulations regarding discharged effluent quality and the necessity for uncontaminated process water usage in the water stressed national and global milieu, textiles and allied industries are currently confronted with the arduous task of engineering ingenious and cost-effective techniques, which can concomitantly bring about appreciable decolourization of the dyestuff-loaded industrial process streams, appreciable reclamation of treated process water and sizable recovery and reuse of unutilized resources in the primary facilities (Chakraborty, 2010; Cooper, 1995).

Various treatment processes have been applied over the years in an effort to mitigate the dye levels in industrial wastewaters and ensure environmental sustainability. However, these treatment processes suffer from some serious limitations. For instance, the biological methods often demonstrate process inflexibilities in the rapidly fluctuating problem environment (ElDefrawy and Shaalan, 2007; Khandegar and Saroha, 2013). Other treatment techniques, such as ozonation, suffer from short half-life and relatively high costs, while the potential of effective adsorbents are largely untapped owing to the difficulty faced in spent adsorbent regeneration and disposal. Coagulation and cost-intensive Fenton treatments generate huge volume of sludge, yielding mediocre dye remediation results, while chlorination leads to the formation of secondary pollutants (Dasgupta et al., 2014b). Assiduous exploration of competent and environmentally benign alternatives to conventional techniques, with limited disadvantages, has led to the evolution of membrane technology, with numerous advantageous features that can adequately overcome the limitations of the traditional treatment analogs. The membrane based treatment techniques have attracted the attention of researchers and industries alike, owing to their simplicity, environmental benignity and most importantly, their effectiveness in retaining recalcitrant dye. Furthermore, these methods can also satisfactorily bring about sizable recovery of chemicals, unused resources and reclamation of treated process water, which satisfies the criteria for reuse in primary industrial processes, such as dyeing facilities of textiles. Besides, periodic cleaning of membranes also leads to substantial membrane fouling abatement (Dasgupta et al., 2014b; Koltuniewicz and Drioli, 2008). These aspects are thus successful, albeit partially, in offsetting the initial capital costs. Out of the various membrane based techniques, ultrafiltration has been found to be the most economically attractive treatment option, principally owing to relatively low transmembrane pressure as compared to other cost-intensive membrane based methods such as nanofiltration and reverse osmosis. Despite being immensely successful in handling a wide spectrum of industrial effluents, its application, as a treatment technique for effecting dye removal from highly colored effluents, is rather limited. This is primarily due to the fact that the molecular weights of the spent dyes are considerably lower than the molecular weight cut-off (MWCO) of the ultrafiltration membranes (Dasgupta et al., 2014a; Ouni and Dhahbi, 2010). Consequently, the reclaimed permeate quality usually fails to satisfy the stipulations mandated in regard to innocuous disposal of treated effluents or effective process water reuse in principal industrial processes. This trade-off between operation cost and dye retention efficiency can be substantially resolved by employing a hybrid process involving complexation and ultrafiltration, wherein the target contaminants are bound by water-soluble polymers or polymeric macroligands to form macromolecular complexes, which can be effectively retained by the subsequent ultrafiltration process. This process has been termed as polymer enhanced ultrafiltration (PEUF) and its applicability in removing contaminants such as heavy metal ions from industrial wastewaters has been explicitly reconnoitered in the recent scientific investigations (Chakraborty et al., 2014; Shao et al., 2013; Zamariotto et al., 2010), although studies on the usage of PEUF in dye contaminated wastewater remediation is still relatively limited, as revealed in the appraisal of archival literature (Fradj et al., 2014; Mondal et al., 2012; Ouni and Dhahbi, 2010). A meticulous survey of the PEUF based scientific investigations available in archival literature has, moreover, revealed the fact that most of these have employed classical methods to appraise the effects of various process parameters, such as pH, polyelectrolyte concentration, and transmembrane pressure, on the retention of the target solutes from their respective aqueous solutions (Fradj et al., 2014; Ouni and Dhahbi, 2010). The application of a flexibile statistical tool, such as response surface methodology (RSM) in such cases, reduces the time expended on the required analyses by resorting to the formulation of a robust design matrix, that is engineered to yield precisely configured experimental trials within the dictated ranges of variables. Additionally, the empirical models developed