



Influence of hydrodynamic size and zeta potential of a novel polyelectrolyte poly(acrylic acid) grafted guar gum for adsorption of Pb(II) from acidic waste water



Abhijit Pal, Arindam Giri, Abhijit Bandyopadhyay*

Department of Polymer Science and Technology, University of Calcutta 92, A.P.C. Road, Kolkata-700009, India

ARTICLE INFO

Article history:

Received 8 December 2015
Received in revised form 26 February 2016
Accepted 29 February 2016
Available online 2 March 2016

Keywords:

Graft copolymer
Guar gum
Zeta potential
Polyanion
Pb(II)
Chi-square (χ^2) test

ABSTRACT

This article describes the influence of zeta potential and hydrodynamic size of a polyanion, poly(acrylic acid) grafted guar gum (GG-g-PAA) for adsorption of Pb(II). The copolymers were synthesized through surfactant mediated free radical polymerization technique. Aqueous dispersion of the copolymers were directly added to the contaminated water and the parameters such as copolymer grade, pH, adsorbent-adsorbate concentrations, adsorption time and temperature were varied to maximize the adsorption efficiency. The copolymer synthesized with 1:10, GG:AA mole composition and 0.5 wt% initiator content produced maximum adsorption (89.62%) at a pH of 4.5, which was further raised to 95.32% on manipulation. Regression analysis showed the polyanion chemically interacted with Pb(II) and formed a monolayer (Langmuir adsorption) while Chi-square (χ^2) test indicated possibility of multilayer formation (both Langmuir and Freundlich isotherm models as well). The process followed pseudo second order kinetics alike all adsorption processes.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Pollution of aquatic environment has alarmingly increased of late mainly due to contamination of non-degradable toxic compounds through direct discharge of effluents from various industries [1–4]. Often unplanned disposal of municipal waste, especially in the urban areas, is also responsible for the contamination [5,6]. Organic dyes and heavy metal ions are among the major components of toxic contaminants. Presence of organic dyes could be detected in naked eyes and precautions can be taken [2], however, silent risk remains with the soluble heavy metal ions like Hg(II) and Pb(II) as their soluble salts are completely colorless [2,7]. These, along with other metal ions such as Cd(II), As(III), Cr(VI) and anion like F(I) have a higher tendency towards accumulation in the biological bodies [8]. Various techniques like electro deposition [9], membrane processes [10], solvent extraction [4], chemical precipitation [11], reverse osmosis [12] and ion exchange [13] have been applied so far for removal of both metal and non-metal ions from waste water, however, the adsorption has emerged as the most convenient and commercially viable process so far for both the types of contaminants [4,9,11–16].

Pb(II) has been reported as the major contaminant in the recent time because of its heavy demand in both consumer and chemical industry. The global demand of Pb(II) has now reached to 11.6 Mt per annum and is likely to go further up in the coming years owing to the steep growth in human population [17]. Most of the chemical industries in the third world countries generally do not follow the prescribed effluent treatment process and thus the Pb(II) rich effluents are directly discharged into the surrounding areas. A recent incident reported in Nigeria shows how aquatic and human population could be severely affected from the contamination of Pb(II) [18]. Soluble salts of Pb(II) precipitate in alkaline pH due to the formation of $\text{Pb}(\text{OH})_2$ but remains soluble in the acidic pH. The effluents are mostly acidic and thus the discharged Pb(II) is directly adsorbed in the aquatic lives as well as in the soil. It further transmits deep into the soil and gradually contaminates the underneath water reserve with time.

Water is used in our daily life for cooking, drinking, washing, bathing, cooling machines and cultivating crops. Mainly cooking, drinking and cultivation requires high quality water thus should be properly treated before use [19]. According to WHO, the concentration limit of Pb(II) in the drinking water should be 0.05 ppm or less [20]. However, for other primary uses, the tolerance could be little higher than that. According to the latest literature report, various disposable solids like almond shell [21], clay [22], grape stalks [23] and waste maize bran [24] were used as

* Corresponding author.

E-mail address: abpoly@caluniv.ac.in (A. Bandyopadhyay).

adsorbents. The adsorption capacity of almond shell was found to be very low, only 0.08 mg g^{-1} , followed by 49.7 mg g^{-1} by grape stalks, 104.28 mg g^{-1} by clay and 142.86 mg g^{-1} by the waste maize bran. Many semi-synthetic polymers [25–27] and their nano-composites [11,12,14,28] were employed as adsorbents which elucidated moderate to high adsorption capacity. The latter (polymeric adsorbents) displays polyanionic character which, more than often, led to a sharp increase in sorption efficiency of Pb(II) through strong electrostatic interaction as compared to the disposable solid adsorbents.

Polysaccharides are efficient polyelectrolyte due to the presence of high density of tunable hydroxyl ($-\text{OH}$) groups [29]. We have previously explored the role of neat GG as adsorbent for Pb(II) through direct addition into the contaminated water instead of using it in conventional packed bed or column [13]. The direct addition approach yielded high removal capacity (408 mg g^{-1}) and the efficiency was found to be controlled by both hydrodynamic size and zeta potential of the GG molecules in the aqueous phase. To work on this technology further, we have synthesized poly (acrylic acid) grafted GG, designated as GG-g-PAA in this article, in anticipation to prepare an even stronger polyelectrolyte than GG through introduction of the pendant acid chains. The carboxyl ($-\text{COOH}$) group is a stronger pH responsive unit than $-\text{OH}$ and thus likely to influence both the polyanionic character and the hydrodynamic size of the copolymer, as the pH is increased. The copolymer was synthesized using surfactant mediated free radical polymerization of AA in the presence of GG. The surfactant resisted the run-away reaction of AA into PAA by arresting the acid in the aqueous phase. GG-g-PAA was purified and the percent grafting was calculated using gravimetry. Infrared spectroscopy was used for determination of the microstructure. Aqueous dispersion of the copolymers was prepared for the adsorption study. Experiments were carried out with different grades of copolymer, at variable pH, adsorbate and adsorbent concentrations and at different temperatures to determine the best possible condition for maximum adsorption of soluble Pb(II).

2. Materials and methods

2.1. Materials

GG was a gifted sample from Hindustan Gum and Chemicals Ltd., Haryana, India. AA, Ammonium persulphate (APS, the initiator), sodium lauryl sulphate (SLS, the surfactant) and

hydroquinone (the chain terminator)—used for the synthesis of graft copolymers, were purchased from Merck, India. Lead nitrate (MW: $331.24 \text{ g mol}^{-1}$) for generating Pb(II), sodium acetate and acetic acid—for buffering, hydrochloric acid and sodium hydroxide—for adjustment of pH and ethylene diamine tetra acetic acid (EDTA) and xylenol orange indicator – for the titrimetric determination of concentration of Pb(II)—were purchased from indigenous sources and were used without further modification. All experiments were carried out using double distilled water.

2.2. Surfactant mediated graft copolymerization: protocol for synthesis

Table 1 shows the complete recipe for the synthesis of the copolymers. Prescribed amount of GG, SLS and APS were dissolved in 90 ml double distilled water in a three necked flask at room temperature under constant stirring. On dissolution, the pH of the medium was adjusted to 7.0 and nitrogen was purged inside to drive off the air from the reaction vessel. The temperature was raised to 70°C and AA was added drop wise into the vessel from a dropping funnel. The addition was completed within 30 min. The reaction was allowed to stand for 2.5 hrs at $70 \pm 5^\circ\text{C}$ since the addition of AA was complete. A thermostat was used to maintain the range of temperature variation. After 2.5 h, saturated solution of hydroquinone was added to quench the reaction. The vessel was cooled to room temperature and allowed to stand overnight. After 24 h, the viscous mass was poured into excess volume of acetone (LR grade) under stirring to precipitate out the graft copolymer. The residue was filtered, washed thrice with acetone and then with double distilled water and finally dried in an air oven at 50°C to constant weight. The hard mass was crushed into white powder and characterized. The percent of grafting was determined following Eq. (1) [30]:

$$\text{Grafting percentage (GP\%)} = \frac{\text{Weight of grafted copolymer}}{\text{Initial weight of back bone polymer}} \times 100 \quad (1)$$

2.3. Batch experiment for adsorption study

Adsorptions were studied in a batch process. About 0.399 g of lead nitrate was dissolved in adequate amount of double distilled

Table 1
Copolymer composition, percent grafting, hydrodynamic and molecular parameters and their effect on percent adsorption at pH 4.5.

Sample designation	GG in mol	AA in mol	Molar ratio of GG:AA	APS in mol w.r.t AA (wt%)	GP (%)	Carbonyl Index (CI)	Average hydrodynamic size (d.nm)	Zeta potential (mV)	Adsorption (%)
GG	–	–	–	–	–	–	1781	-6.29	57.8
GG-g-PAA _{5/0.5}	0.0061	0.0305	1:5	0.5	71.53	0.99102	1531	-9.61	47.36
GG-g-PAA _{5/1}	0.0061	0.0305	1:5	1	80.28	0.99788	1766	-30.4	62.15
GG-g-PAA _{5/2}	0.0061	0.0305	1:5	2	78.60	0.99347	1706	-21.7	58.64
GG-g-PAA _{10/0.5}	0.0061	0.061	1:10	0.5	85.37	0.9985	1873	-47.6	89.62
GG-g-PAA _{10/1}	0.0061	0.061	1:10	1	75.32	0.99513	1516	-40.8	79.62
GG-g-PAA _{10/2}	0.0061	0.061	1:10	2	63.26	0.99334	1276	-36.1	73.38
GG-g-PAA _{15/0.5}	0.0061	0.0915	1:15	0.5	62.35	0.99572	1153	-27.3	54.62
GG-g-PAA _{15/1}	0.0061	0.0915	1:15	1	58.84	0.99107	976	-24.7	51.26
GG-g-PAA _{15/2}	0.0061	0.0915	1:15	2	38.21	0.99702	864	-29.7	60.02
GG-g-PAA _{20/0.5}	0.0061	0.122	1:20	0.5	71.03	0.9953	702	-19.1	47.67
GG-g-PAA _{20/1}	0.0061	0.122	1:20	1	59.32	0.99516	1303	-16.4	42.63
GG-g-PAA _{20/2}	0.0061	0.122	1:20	2	47.67	0.99218	1448	-15.7	38.29
GG-g-PAA _{25/0.5}	0.0061	0.1525	1:25	0.5	54.63	0.99303	1458	-11.5	38.39
GG-g-PAA _{25/1}	0.0061	0.1525	1:25	1	47.98	0.99119	1247	-17.6	32.64
GG-g-PAA _{25/2}	0.0061	0.1525	1:25	2	43.31	0.99223	1024	-10.3	26.34

Anhydroglucose unit (AGU) of Guar gum is considered as 167 g for the entire synthesis protocol. Concentration of SLS was maintained at 0.1 wt% with respect to AA during each grafting reaction. Temperature was fixed at 30°C .

The figures mentioned in bold indicate the best condition within that particular set of parameters that produced the best result.

Download English Version:

<https://daneshyari.com/en/article/221654>

Download Persian Version:

<https://daneshyari.com/article/221654>

[Daneshyari.com](https://daneshyari.com)