

Supporting information

Synthesis and characterization of a few amino functionalized co-polymeric resins and their environmental applications

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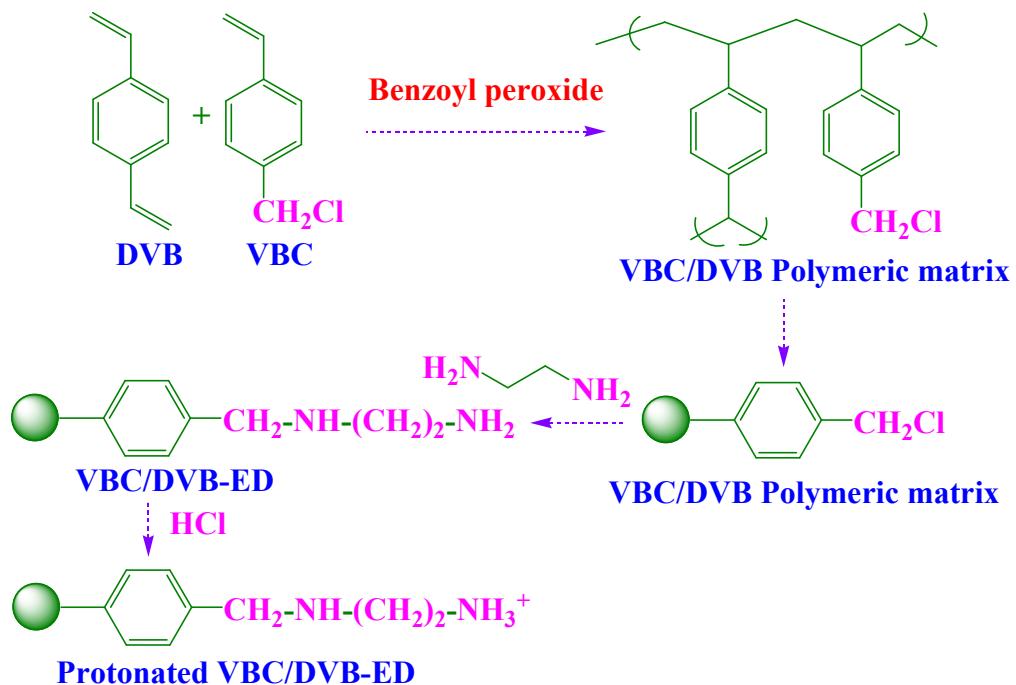
Synthesis of polymeric resins

1. Synthesis of VBC/DVB-ED resin

The vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer cross-linked with 10 % of DVB were prepared by suspension polymerization technique in the presence of the porogen i.e. mixture of toluene and n-heptane (T/H 1:9 v/v). Benzoyl peroxide was used as initiator (0.5 wt % in relation to the monomers). The volume ratio of monomer mixture to porogens is 2.3:1 and the ratio between the aqueous phase and the organic phase was 1.5:1. Reactions were carried out in a 1 L three neck glass reaction vessel equipped with a speed controlled mechanical stirrer, a reflux condenser and a nitrogen gas inlet. The aqueous medium containing PVA and CaCl_2 were mixed in a reactor for 2 h at room temperature. Before monomers and the initiator were added, the dissolved oxygen was removed by bubbling nitrogen gas for 10 min through water phase (500 ml) at room temperature. This procedure of removing oxygen was applied to

the organic phase just before the monomers and porogens were added to the reactor. Polymerisation was first carried out at 60 °C for 1h, then at 70 °C for 1h, after that at 85 °C for 2 h and then at 90 °C for 6 h. The stirring speed was maintained at 200-400 rpm. After cooling, the polymeric beads were separated from the polymerisation mixture. Then, they were washed with water and acetone.

The amino groups were grafted to the VBC/DVB copolymer by following procedure. About 5 g of poly(vinylbenzyl chloride) copolymer, VBC/DVB was made swollen overnight in 70 ml of 1,4-dioxane in 250 ml three-necked flask with a reflux condenser. Ethylenediamine was added into the swollen polymer and the mixture was refluxed for 2-24 h and left undisturbed for 7 days at room temperature. The resultant product was filtered. After amination, the resin beads were washed successfully with cold and hot water until the pH of the eluate was near neutral. Then the resin was washed with 1M HCl, water and 1M NaOH. This procedure was repeated for 3 times and finally the resin was washed with 0.001 M HCl and dried at 60 °C in a vacuum oven and used for sorption studies. The proposed synthesis of VBC/DVB-ED resin is shown in Scheme S1a.



Scheme S1a. Synthesis of VBC/DVB-ED resin

2. Synthesis of ST/DVB/VBC-ED resin

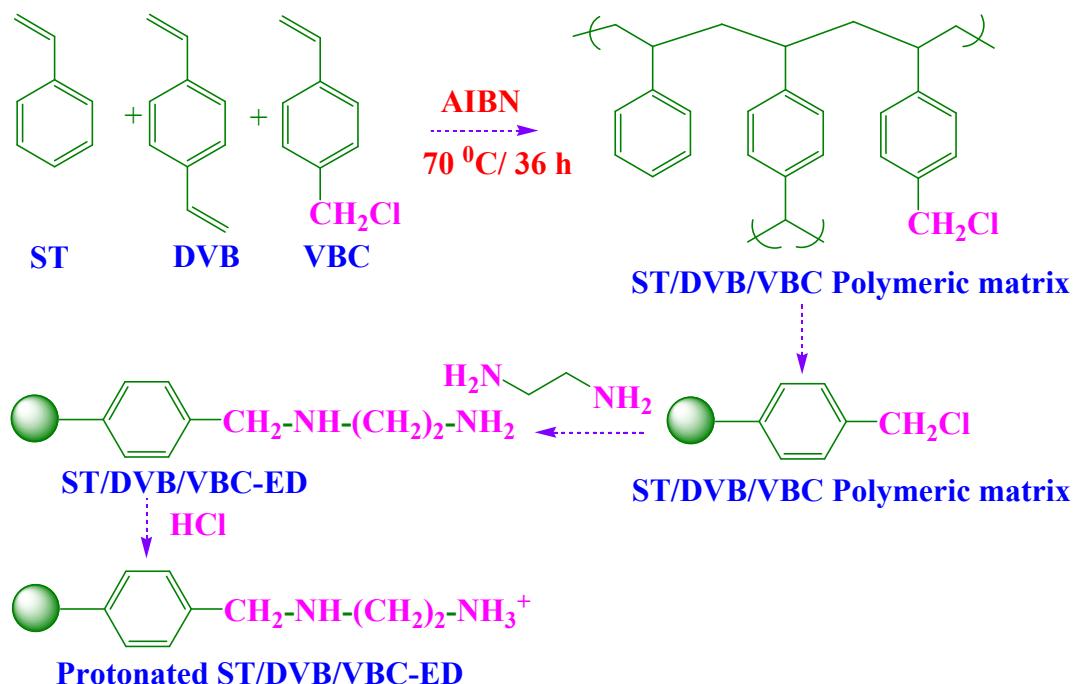
In 450 ml deionized water, 2.70 g gelatin was dissolved in 120 ml of water at 50-60 °C with magnetic stirring. In the remaining water 5.10 g boric acid and 4.50 g PVA were dissolved at room temperature. The pH of the latter solution was adjusted to 10.0 by the addition of 25 % aqueous sodium hydroxide solution to maintain the conformation of gelatin. The hot gelatin solution was added to the rest of aqueous phase and mixed thoroughly. The entire mixture was added to a 2-L three-necked round-bottomed flask fitted with reflux condenser and a mechanical stirrer.

A solution of 117.75 g styrene, 41.25 g vinylbenzyl chloride (25 %-active-site), 6.10 g divinylbenzene (2 % cross-linking) and 0.825 g AIBN was added slowly and carefully to the reaction flask containing the aqueous phase so that the organic phase floats over the aqueous

phase. Nitrogen was passed through the flask to remove atmospheric oxygen for about 45 min at room temperature and a slight positive pressure of nitrogen was maintained throughout polymerization. The teflon blade level of the stirrer was adjusted so that the tips were in organic phase and most of the blade in aqueous phase. The reaction mixture was stirred at room temperature for two minutes and stopped to examine visually the size of the droplets. This operation was repeated several times to get the desired droplet size by increasing the stirring speed. The mixture was stirred for at least 10 min at room temperature before it was heated to 70 °C over a period of 40-60 min. The polymerization mixture was observed for at least the first 2-3 h at 70 °C till it reached the gel point. The 36 h hold period at 70 °C was done by keeping it overnight. After 36 h, polymer beads were transferred from the three-necked flask to a beaker and washed with hot water repeatedly till all the PVA got removed. It was then filtered through a buckner funnel and washed with hot water, acetone and methanol. It was dried at 60 °C in a vacuum oven.

The amino resins were prepared by the following procedure. About 5 g of ST/DVB/VBC copolymer was made swollen overnight in 70 ml of 1,4-dioxane in 250 ml three-necked flask with a reflux condenser. Ethylenediamine was added into the swollen polymer and the mixture was refluxed for 2-24 h and left undisturbed for 7 days at room temperature. The resultant product was filtered. After amination, the resin beads were washed successfully with cold and hot water until the pH of the eluate was near neutral. Then the resin was washed with 1M HCl, water and 1M NaOH. This procedure was repeated for 3 times and finally the resin was washed with 0.001 M HCl and dried at 60 °C in a vacuum oven, sieved into uniform particle size

and used for sorption studies. The proposed synthesis of ST/DVB/VBC-ED resin is shown in Scheme S1b.



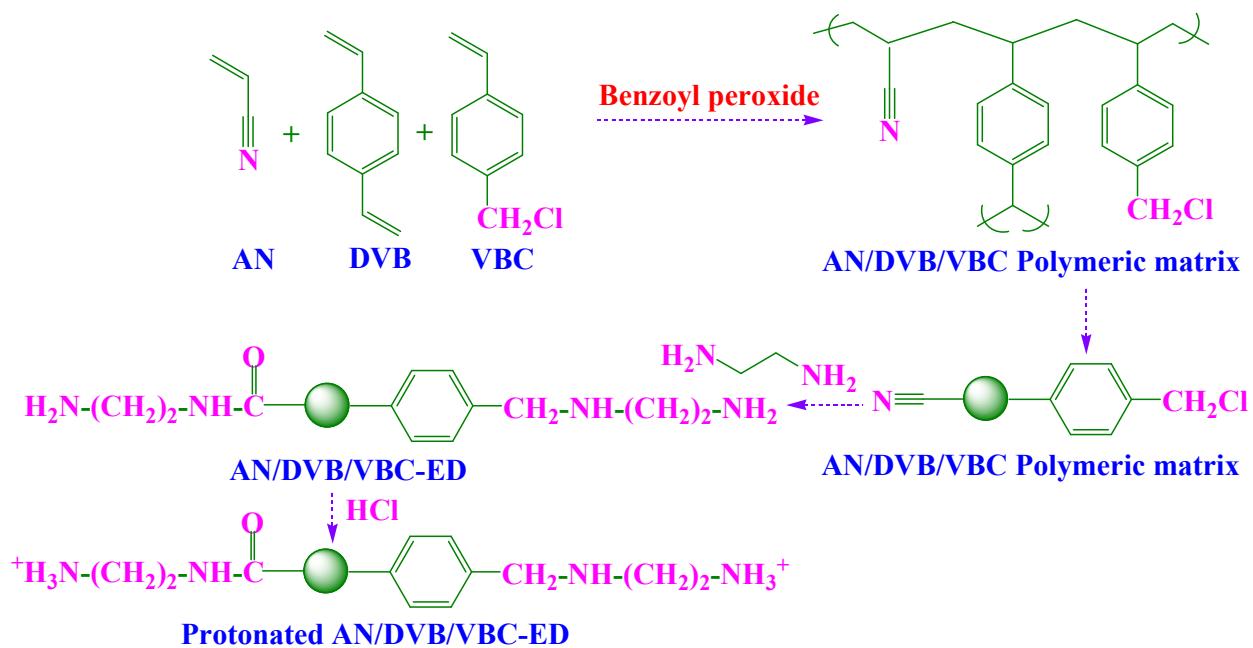
Scheme S1b. Synthesis of ST/DVB/VBC-ED resin

3. Synthesis of AN/DVB/VBC-ED resin

The polymeric matrix acrylonitrile/divinylbenzene/vinylbenzylchloride (AN/DVB/VBC) copolymer containing 2 wt % of cross-linker (DVB) and 20 mol % of acrylonitrile was obtained by suspension polymerization method using 0.5 wt % of benzoyl peroxide as the initiator. Polymerisation was carried out in the presence of toluene (50 wt % with respect to the monomers mixture) in order to obtain a polymeric material with an expanded gel structure. The mixture of monomers and toluene was suspended in an aqueous phase composed of calcium chloride and

PVA (as stabilizer of suspension). The mixture of monomers and diluents was suspended in aqueous phase (7 wt % solution of CaCl_2 , containing 1.5 wt % (in respect to organic phase) of PVA. The temperature was kept at 60 $^{\circ}\text{C}$ for 1 h, at 70 $^{\circ}\text{C}$ for 1 h at 85 $^{\circ}\text{C}$ for 2 h and finally at 95 $^{\circ}\text{C}$ for 6 h. After polymerization, the polymeric beads were washed with hot water, acetone and then dried.

The AN/DVB/VBC copolymeric beads were swollen in DMF for 24 h and then aminolysed with ethylenediamine. The reaction mixture was kept at room temperature and stirred for 19 days. Finally the modified resins were filtered, washed, alternatively with water, 1 M HCl, 1 M NaOH and dried under vacuum at 40 $^{\circ}\text{C}$ to the constant mass and were sieved into uniform particle size and subjected for sorption studies. The proposed synthesis of AN/DVB/VBC-ED resin is shown in Scheme S1c.



Scheme S1c. Synthesis of AN/DVB/VBC-ED resin

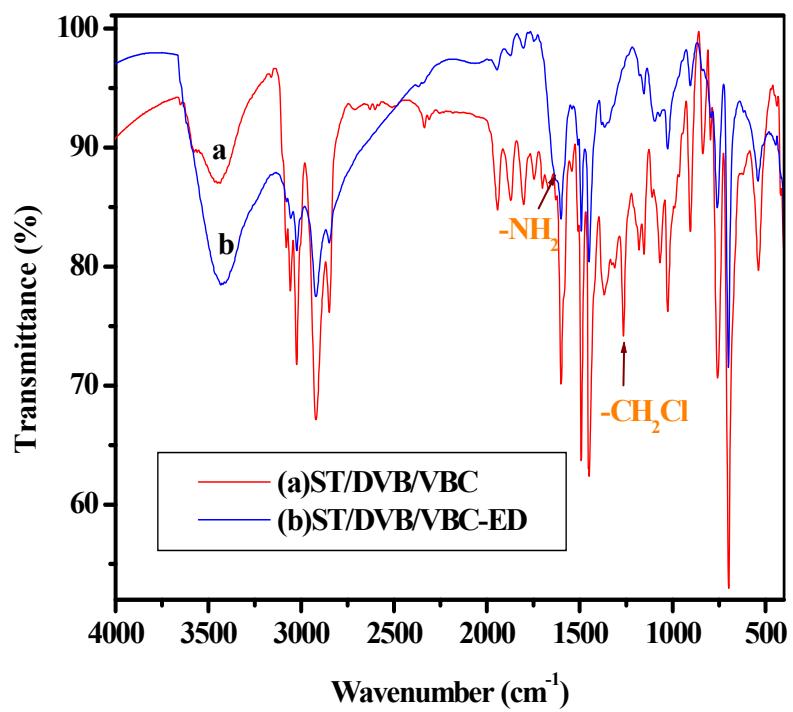


Figure S1. FTIR spectra of (a) ST/DVB/VBC and (b) ST/DVB/VBC-ED

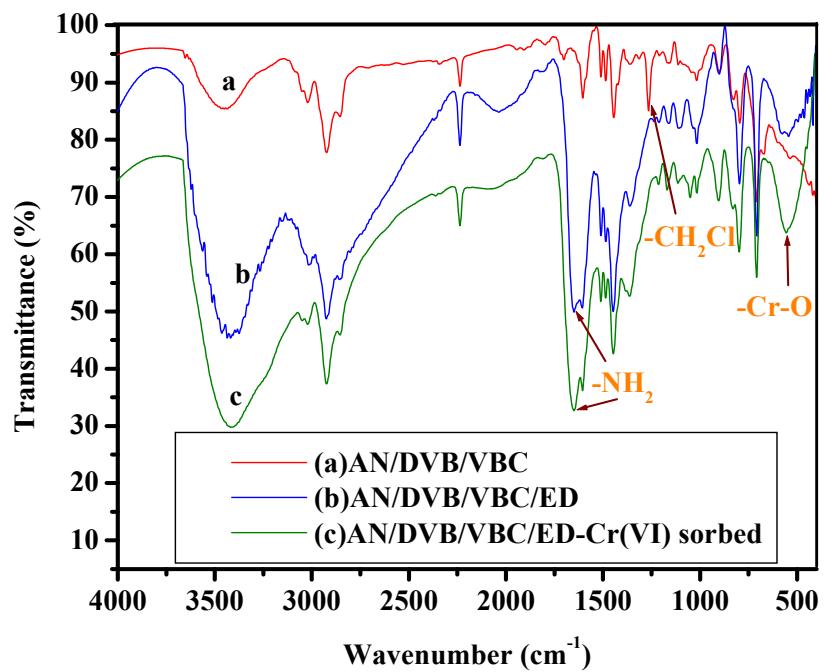


Figure S2. FTIR spectra of (a) AN/DVB/VBC (b) AN/DVB/VBC-ED and (c) chromium-sorbed AN/DVB/VBC-ED.

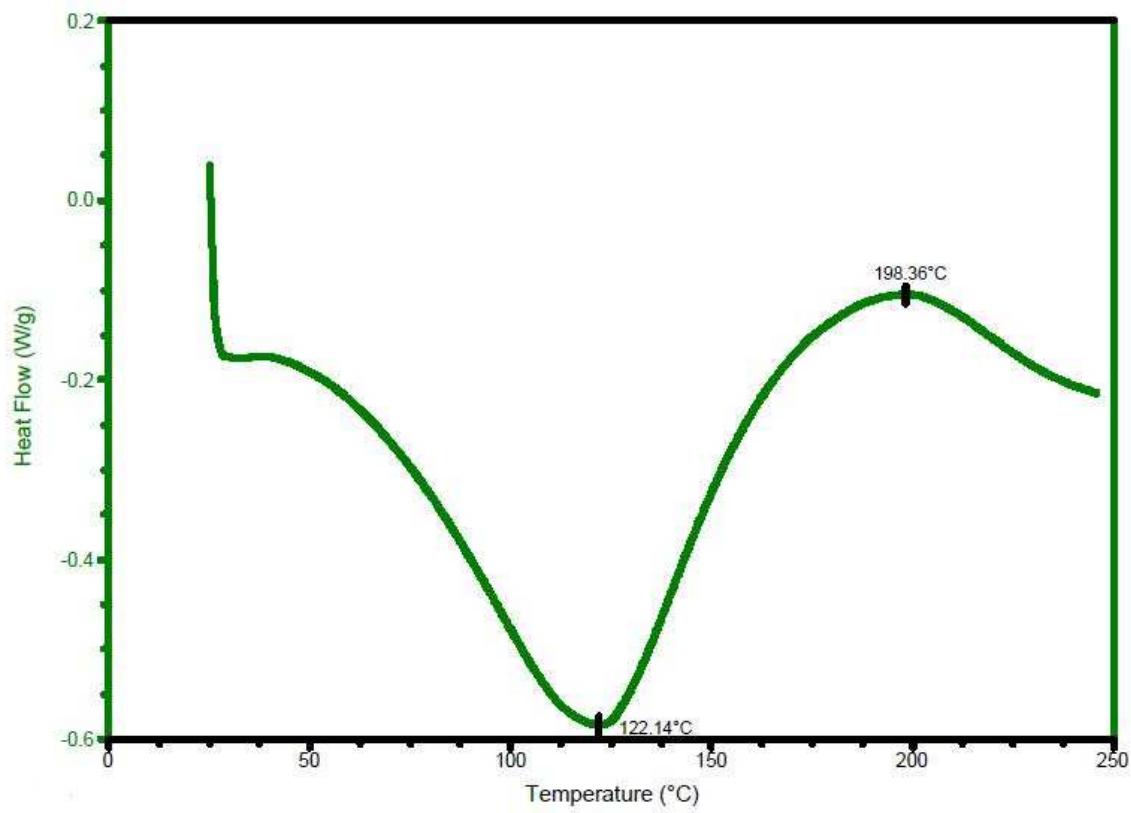


Figure S3. DSC thermogram of AN/DVB/VBC-ED resin.

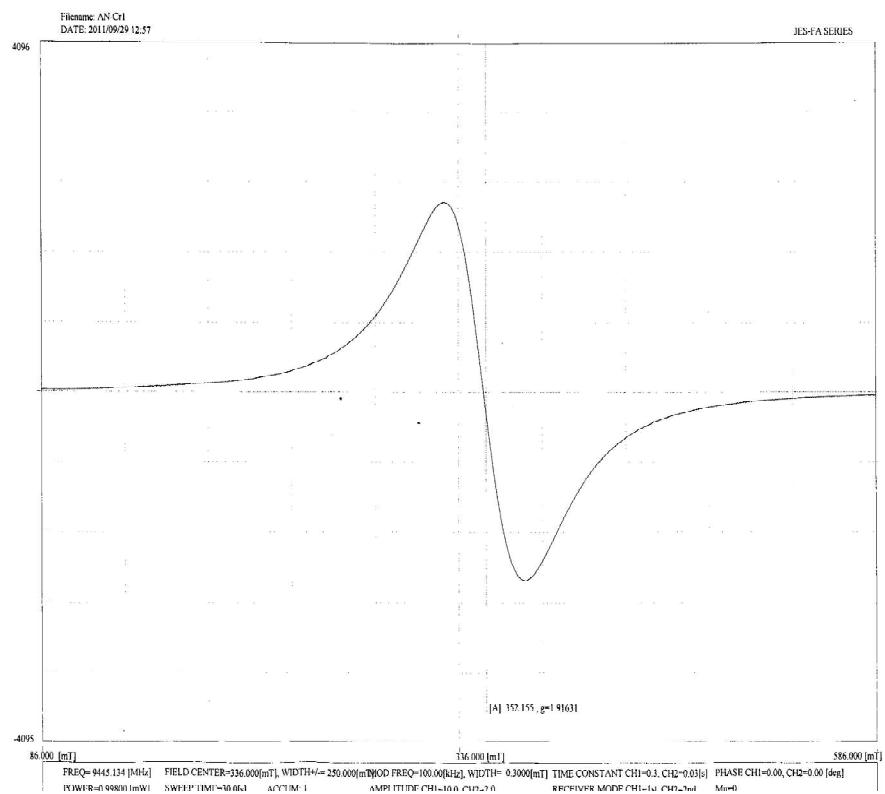


Figure S4. EPR spectra of chromium sorbed AN/DVB/VBC-ED resin

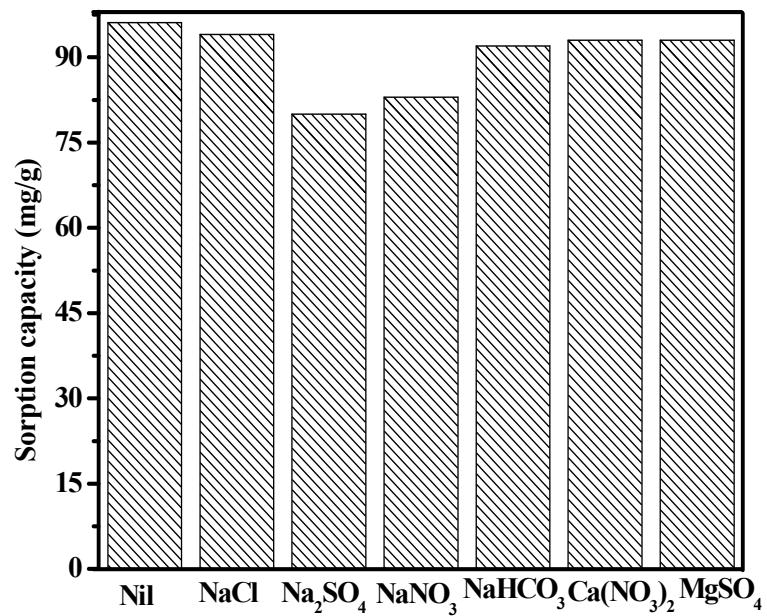
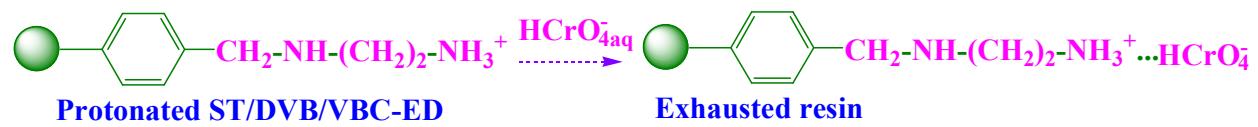
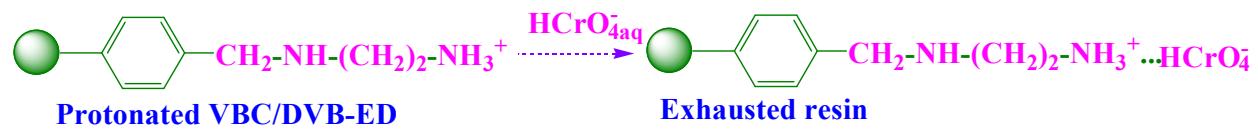


Figure S5. Effect of co-ions on CRC of AN/DVB/VBC-ED resin



Scheme S2. Mechanism of chromium sorption onto synthetic resins.